

Synthesis and chemistry of P-bridged, bent and planar bis(N-heterocyclic) carbenes

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Hiermit versichere ich, dass die vorgelegte Arbeit persönlich, selbstständig und ohne Benutzung anderer als der angegebenen Hilfsmittel angefertigt wurde und alle Quellen kenntlich gemacht wurden.

„It doesn't stop being magic just because you know how it works.“

Terry Pratchett, *The Wee Free Men*

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7.4.10	1,3,5,7-Tetrabutyl-9,10-diethyl-1,3,5,7-tetrahydro-2 <i>H</i> ,6 <i>H</i> -4,8-ethano[1,4]diphosphinino[2,3-d:5,6-d']diimidazole-2,6-ylidene 17b	220
7.4.11	1,3,5,7-Tetrabutyl-9-butyl-1,3,5,7-tetrahydro-2 <i>H</i> ,6 <i>H</i> -4,8-ethano[1,4]diphosphinino[2,3-d:5,6-d']diimidazole-2,6-ylidene 17c	223

7.4.12	[Octacarbonyl(μ -1,3,5,7-tetrabutyl-9-butyl-1,3,5,7-tetrahydro-2 <i>H</i> ,6 <i>H</i> -4,8-ethano[1,4]diphosphinino[2,3-d:5,6-d']diimidazole-2,6-ylidene-2 κ C,6 κ C)diiron(0)] 23b	225
7.4.13	[Tetrachlorido(μ -1,3,5,7-tetrabutyl-1,3,5,7-tetrahydro-2 <i>H</i> ,6 <i>H</i> -4,8-ethano[1,4]diphosphinino[2,3-d:5,6-d']diimidazole-2,6-ylidene-2 κ C,6 κ C, κ P ¹ , κ P ²)tetrakis(η^2 , η^2 -cycloocta-1,5-diene)tetrarhodium(I)] 29a	228
7.4.14	1,3,5,7-Tetrabutyl-9,10-diethyl-1,5-dihydro-4,8-ethano[1,4]diphosphinino[2,3-d:5,6-d']di-2,6-bis(diphenylphosphino)imidazolium bis(trifluoromethanesulfonate) 35a	232
7.4.15	1,3,5,7-Tetrabutyl-9-butyl-1,5-dihydro-4,8-ethano[1,4]diphosphinino[2,3-d:5,6-d']di-2,6-bis(diphenylphosphino)imidazolium bis(trifluoromethanesulfonate) 35c	235
7.4.16	1,3,5,7-Tetrabutyl-9,10-diethyl-1,5-dihydro-4,8-ethano[1,4]diphosphinino[2,3-d:5,6-d']di-2,6-bis(dithiocarboxy)imidazolium 36a	238
7.4.17	1,3,5,7-Tetrabutyl-9,10-diethyl-1,5-dihydro-4,8-ethano[1,4]diphosphinino[2,3-d:5,6-d']di-2,6-bis(dithiocarboxy)imidazolium 36b	241
7.4.18	1,3,5,7-Tetrabutyl-9-butyl-1,5-dihydro-4,8-ethano[1,4]diphosphinino[2,3-d:5,6-d']di-2,6-bis(dithiocarboxy)imidazolium 36c	244
7.4.19	1,3,5,7-Tetrabutyl-4,8-bis(diethylamino)-4,8-dioxo-1,5-dihydro-4,8-[1,4]diphosphinino[2,3-d:5,6-d']di-2,6-bis(trichloroborato)imidazolium 41b	245
7.4.20	1,3,5,7-Tetrabutyl-9,10-diethyl-1,5-dihydro-4,8-ethano[1,4]diphosphinino[2,3-d:5,6-d']di-2,6-bis(trichloroborato)imidazolium 47b	247
7.4.21	(1,3,5,7-Tetrabutyl-1,3,5,7-tetrahydro-2 <i>H</i> ,6 <i>H</i> -4,8-ethano[1,4]diphosphinino[2,3-d:5,6-d']diimidazole-2,6-ylidene-2 κ C,6 κ C,4 κ P)tris(borane) 48a	250
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1 INTRODUCTION

1.1 Phosphorus: From the element to phosphanes

1.1.1 The element phosphorus and phosphanes

Phosphorus is a monoisotopic, mononuclidic element (^{31}P), the 15th element in the periodic table of elements and second element of group 15 (pnictogens).¹ With a concentration of 0.1 % in the earth's bio- and lithosphere it places 13th in the abundance of the chemical elements, but is never found as elemental phosphorus in nature due to its high affinity to oxygen. Consequently, mineral deposits consist of phosphates of various composition, most commonly apatite ($\text{Ca}_5(\text{PO}_4)_3(\text{OH}, \text{F}, \text{Cl})$) and phosphorite ($\text{Ca}_3(\text{PO}_4)_2$). In living organisms phosphorus can be found in hydroxy apatite ($\text{Ca}_5(\text{PO}_4)_3(\text{OH})$) in teeth and bones and as essential element in ribonucleic acids (RNA/DNA) and adenosine phosphates (*e.g.* ATP).¹ Accordingly, the formation and production of elemental phosphorus – going from oxidation state +V to 0 – is very energy consuming. Its discovery and first isolation dates back to 1669, when alchemist Henning Brand obtained a white, chemiluminescent compound after heating the dry residues of urine under exclusion of air. This white phosphorus is the first of five allotropes (four crystalline and one amorphous) and, nowadays, is produced industrially by the reduction of fluorapatite (2.3–4.8 wt. %) with coke in the presence of quartz in an electric arc furnace at 1400–1500 °C, followed by distillation.¹ Among the five modifications at ambient conditions black phosphorus, which is made of a pleated honeycomb structure, is the thermodynamically most stable form while all other allotropes present as metastable. Besides cubic white phosphorus, consisting of distinct tetrahedral P_4 molecules, monoclinic violet phosphorus and triclinic fibrous phosphorus – both made of interlinked tubes – as well as amorphous red phosphorus exist. The different modifications can be converted into each other by adjusting the temperature, pressure and processing time.¹ The vast majority of industrially produced P_4 is transformed into phosphorus pentoxide and, subsequently, into phosphoric acid and phosphates for food additives, detergents and fertiliser. A comparably small amount is converted into phosphorus chlorides (PCl_3 , PCl_5 , POCl_3) which serve as precursor for the synthesis of softeners, flame retardants and insecticides and in even smaller percentages as starting materials in laboratory applications and research.

In its compounds phosphorus can occupy all oxidation states between –III and +V with coordination numbers between one and nine.¹ While nature prefers the stable oxidation state +V (*vide supra*), a large branch of the chemical industry and organic and organometallic chemistry focuses work and research on phosphanes, *i.e.* phosphorus in oxidation state +III (*e.g.* PCl_3 , PR_3 ; R = organic substituent).

Having a free lone pair, phosphanes can undergo complex formation and have been applied in the development of, *e.g.* and majorly, homogenous transition metal catalysts. Their advantages are multifactorial: Their σ -donor and π -acceptor abilities as well as their variable steric bulk, which all have an effect on the catalysts' properties, can be finely – and individually – tuned. Moreover, due to their potential chirality they can be used for asymmetric catalysis in the pharmaceutical industry and last, but not least, ^{31}P NMR spectroscopy is a powerful tool for even *in situ* analysis.² The first tertiary organophosphane was reported as early as 1847;³ the first phosphane transition metal complex was mentioned in 1857 by Hofmann⁴ and since then, phosphanes found numerous applications in, *e.g.*, Wilkinson's catalyst for hydrogenation of alkenes and alkynes,⁵ Grubbs catalysts for olefin metathesis^{6,7} and as chiral ligands like BINAP (2,2'-bis(diphenylphosphanyl)-1,1'-binaphthalene; backbone-chirality),⁸ DIPAMP (bis[(2-methoxyphenyl)phenylphosphanyl]ethane; P-chirality)⁹ and many more¹⁰ in asymmetric catalysis.

The σ -donor ability of phosphanes stems from their lone pair (Figure 1), thus their basicity increases with increased p-orbital contribution to the free electron-pair of the formally sp^3 -hybridised phosphane. Subsequently – according to Bent's rule¹¹ –, the donor ability of tertiary phosphanes follows approximately the series: $\text{P}(t\text{-Bu})_3 > \text{P}(\text{OR})_3 > \text{PR}_3 \approx \text{PPh}_3 > \text{PH}_3 > \text{PF}_3 > \text{P}(\text{OPh})_3$ ¹² which was investigated and confirmed experimentally through, *e.g.*, the aqueous pK_a values of the respective phosphanes¹³ or NMR data of phosphane selenides.^{14–16} The corresponding π -acceptor ability is nowadays attributed to interactions of the transition metal's d-orbitals with the σ^* -orbitals of the P-E (E = C, O, H, F, Cl, ...) bond, *i.e.* more polarised P-E bonds result in lower-lying σ^* -orbitals and stronger π -acceptor ability.²

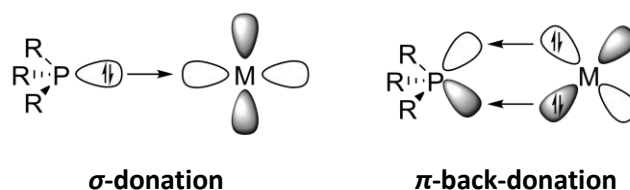


Figure 1. Phosphane and transition metal orbitals involved in the σ -donor ability and π -acceptor ability (R = organic substituent or (bridging) heteroatom E).

Besides these electronic factors in phosphorus metal coordination the steric bulk was found to be of significance in predicting the formation and properties of phosphane metal complexes where the most widely used method is the determination of Tolman's cone angle.^{17,18} Tolman's report from 1977 describes such angles for "simple" phosphanes with values varying between 76° (PH_3) and 212° (PMes_3 , Mes = 2,4,6-trimethylphenyl).¹⁸

To specify the bonding situation of the phosphorus in phosphorus compounds, the $\sigma^n\lambda^m$ notation finds application where σ^n describes the coordination number n (or number n of σ -bonds) and the λ^m -

descriptor refers to the number m of all bonds.¹ To clarify the bonding situation in transition metal complexes containing π -electron ligands that can bind with a contiguous series of atoms (hapticity) the eta (η^n) affix is used where the superscript numerical index n indicates the number of ligating atoms.¹⁹

1.1.2 Caged phosphanes: 1-phosphabarrelenes and 1,4-diphosphabarrelenes

Caged phosphanes display a subclass of phosphanes in which all three vacancies at the central phosphorus atom are linked to carbon or heteroatoms that are part of a cage which usually results in a rigid three-dimensional framework with a large steric hindrance. Linkage via alkyl chains can offer an increased flexibility whereas arene linkage leads to a more constrained cage.²⁰ Verkade in 1960 was the first to mention the exceptional donor abilities of bicyclic organophosphites with constrained P-O angles that well exceeded those of their acyclic counterparts.²¹ Several caged phosphanes with ligand potential were synthesised since then but only since the 1990's their appreciation and application rose.²⁰ Figure 2 gives an overview of selected alkyl- or alkenyl-linked caged phosphanes that have been developed over the last decades and could be applied as ligands in catalysis.

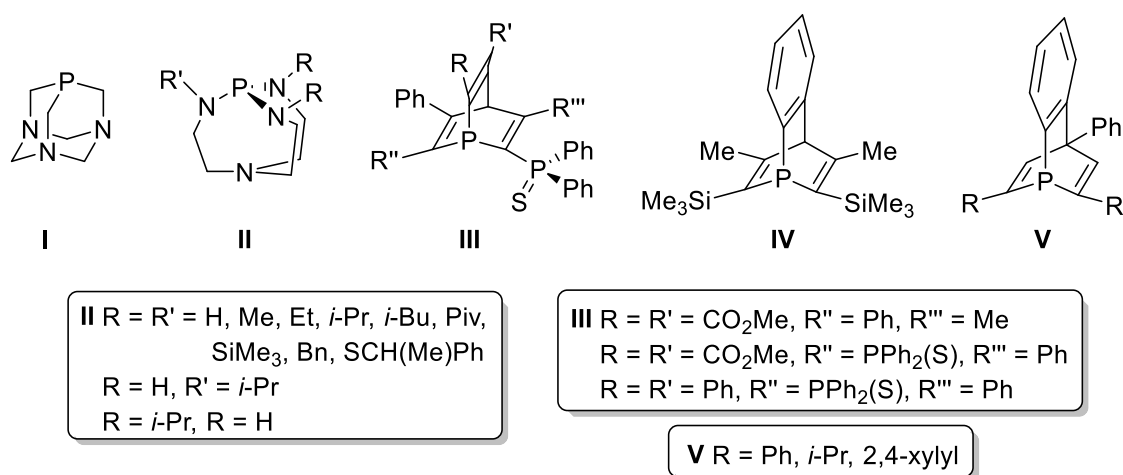


Figure 2. Alkyl- and alkenyl-linked caged phosphanes **I–V**.^{22–28}

1,3,5-Triaza-7-phosphaadamantane (PTA) **I** was reported in 1974²² and is next to the aforementioned phosphites one of the earliest example of caged phosphanes, whose complexes can (co-)catalyse, *e.g.*, regioselective hydrogenations,²⁹ Sonogashira couplings³⁰ and Suzuki-Miyaura arylations.³¹ Proazaphosphatranes^{32,25} **II** were first published in 1989 by Verkade²³ where the caged framework enables a planarisation of the phosphorus environment which leads to increased electron density at and basicity of the phosphorus centre.²⁴ Also known as “Verkade’s bases”, their, through donating interactions of the axial nitrogen atom highly stabilised, protonated forms have pK_a values between 32 and 34.³³ They readily undergo complexation to transition metals and their complexes have found application, *e.g.*, in the amination of aryl halides,³⁴ Stille cross-couplings³⁵ and the one-pot synthesis of various compounds.³⁶ Compounds **III–V** contain 1-phosphabicyclo[2.2.2]octa-2,5,7-triene (1-

phosphabarrelene) frameworks whose motif can also be found in the phosphatriptycenes and 10-hetera-9-phosphatriptycenes displayed in Figure 3 which are caged phosphanes linked via arene annulation.

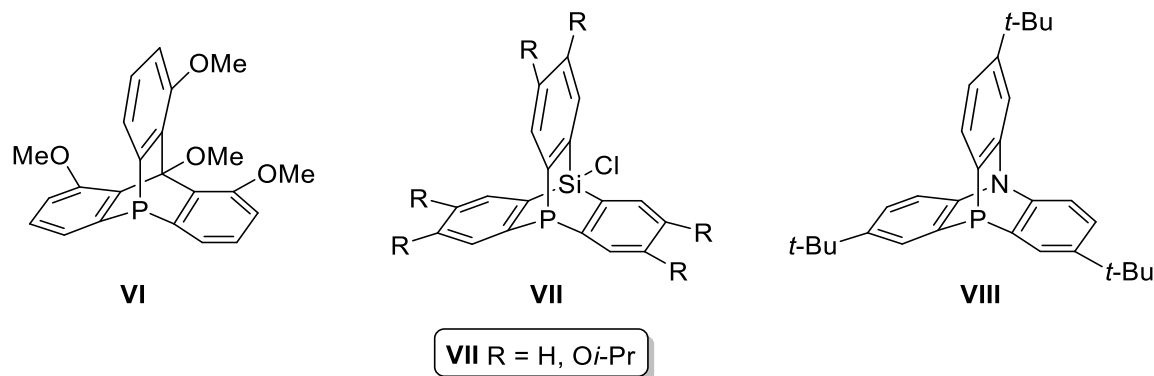
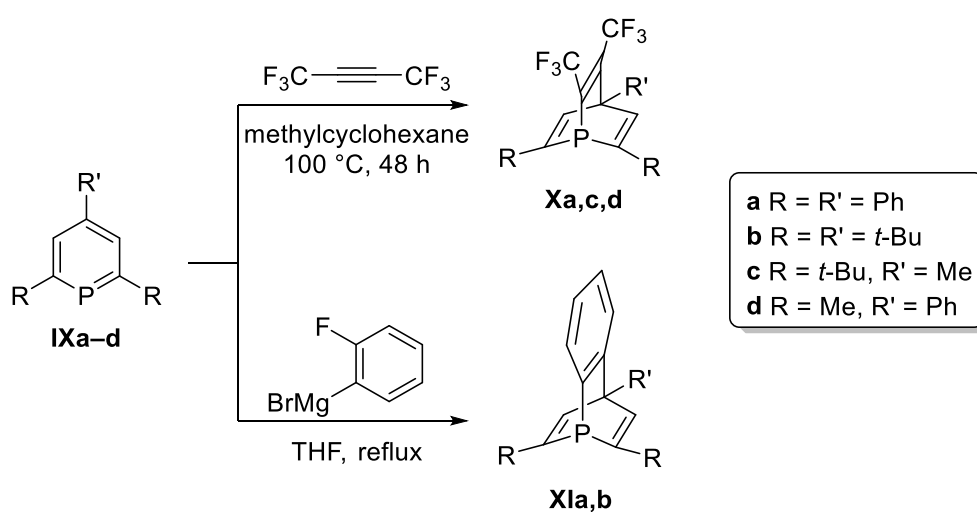


Figure 3. Arene-annulated caged phosphanes **VI–VIII**.^{37–41}

1-Phosphabarrelene **III** was reported in 2005 by Le Floch²⁶; shortly after that **IV** and **V** were described by Le Floch and Mézailles²⁷ and Breit,²⁸ respectively. All of them were employed as mono- or bidentate ligands to transition metals for catalyses.^{26–28} After the report of the phosphatriptycene parent compound in 1974,⁴² **VI–VIII** and derivatives were synthesised several decades later as (precursors for) ligands for transition metal catalysis.^{37–40,43,41} Due to their synthetic availability and functional diversity 1-phosphabarrelenes have become important ligand systems. **III–V** were formed via [4+2]-cycloaddition starting from the corresponding $\sigma^2\lambda^3$ -phosphinine (see chapter 1.1.3) which is the historically most important route as the first described 1-phosphabarrelenes **X** and **XI** (**XIa** = **V**) were obtained in a similar way by Märkl in 1968⁴⁴ and 1971,⁴⁵ respectively (Scheme 1).



Scheme 1. Formation of 1-phosphabarrelenes **X** and **XI** via [4+2]-cycloaddition.^{44,45}

They possess rigid cage structures with good control over the steric hindrance around the bridgehead phosphorus atom and still possibilities for electronic fine-tuning via substitution and annulation. Both Kawashima and Breit put emphasis on the narrow C-P-C angles which result in a, for alkyl- or aryl-substituted phosphanes unusual, constrained geometry and large s-character of the P-lone pair due to the pyramidalisation. The result is a relatively weak σ -donor ability which is also reflected in the NMR data of selenides of **VI**³⁹ and **VII**.⁴⁰

A related class of compounds with an additional coordination site are 1,4-diphosphabicyclo[2.2.2]octa-2,5,7-trienes (1,4-diphosphabarrelenes) that contain two bridgehead phosphorus centres. Despite there being numerous examples of 1-phosphabarrelenes with application in various catalysis reactions, the field of closely related 1,4-diphosphabarrelenes is relatively unexplored and many derivatives belong to the class of 1,6-diphosphatriptycenes due to their trifold annulation to benzenes. The first 1,4-diphosphabarrelene **XII**, synthesised directly from red phosphorus and hexafluoro-2-butyne, was reported by Krespan in 1961 (Figure 4).⁴⁶

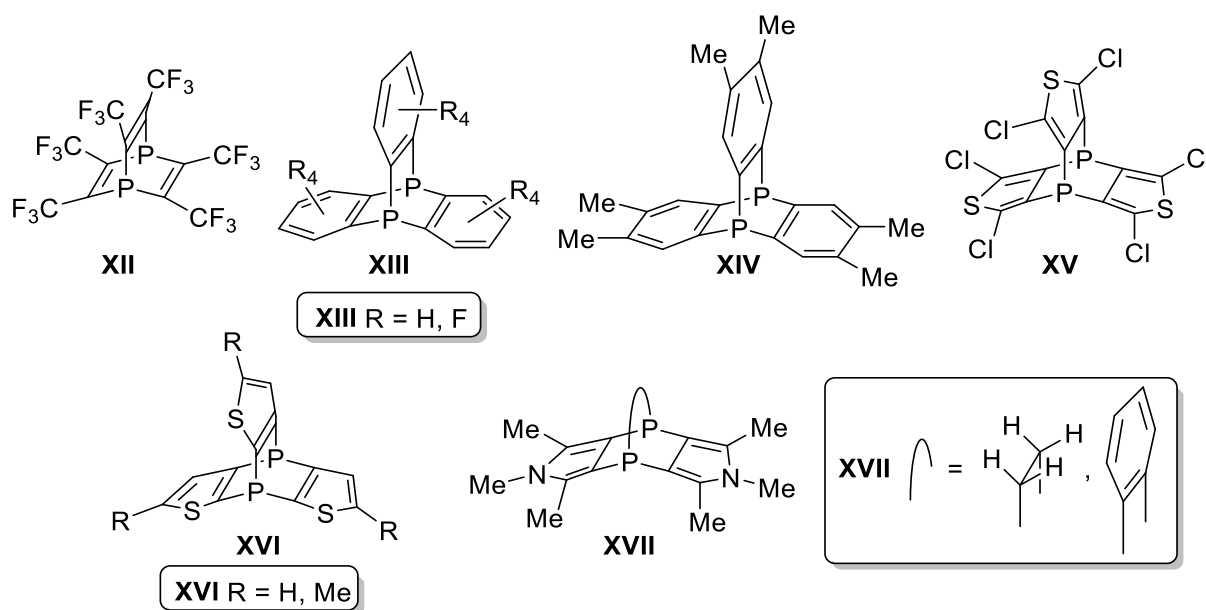
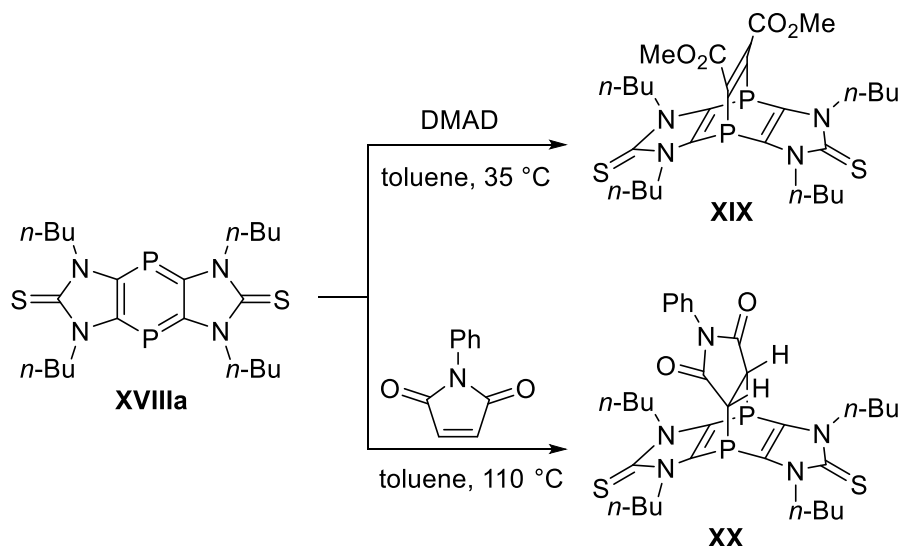


Figure 4. Selected 1,4-diphosphabarrelenes **XII**–**XVII**.⁴⁶

Since then, only a few other derivatives have been synthesised, all of them in annulation to other (hetero-)cycles, namely benzenes (**XIII**⁴⁷ and **XIV**⁴⁸), thiophenes (**XV**⁴⁹ and **XVI**⁵⁰) or pyrroles (**XVII**⁵¹). Except for the most recent example of Dielmann, **XVII**, all syntheses suffered from either multi-step routes and/or low yields and their products were not further investigated. Mazaki made special note of the narrow C-P-C angles of 96.9 ° in **XIV** and historically only one metal complex, of **XVI** (R = Me) to two $\text{W}(\text{CO})_5$ fragments, was reported. Only in 2023, Dielmann described dinuclear Ni(0), Ir(I) and Rh(I) complexes as well Cu_2Cl_2 -bridged chains of **XVII** concluding that, while having a typically strong pyramidalised environment around the phosphorus centres and, subsequently large s-character of the lone

pairs, their 1,4-diphosphabarrelene derivatives are among the strongest donors in their class due to the pyrrole annulation.

The for 1-phosphabarrelenes well-established, facile synthetic route of [4+2]-cycloadditions for the synthesis of 1,4-diphosphabarrelenes was utilised by Streubel after the first isolation of a 1,4-diphosphinines in 2017⁵³ (Scheme 2).



Scheme 2. Synthesis of imidazole-annulated 1,4-diphosphabarrelenes **XIX** and **XX** via [4+2]-cycloaddition of tricyclic 1,4-diphosphinine **XVIII**.⁵²

Imidazole-annulated 1,4-diphosphabarrelenes **XIX** and **XX** could be isolated in excellent yields⁵² and thus, the [4+2]-cycloaddition presented a very good option for the synthesis of 1,4-diphosphabarrelene scaffolds. Since this report from 2018, several derivatives **XXI–XXV**^{54–56} starting from differently annulated 1,4-diphosphinines **XVIIIa–e** (see chapter 1.1.3) were published by Streubel – almost exclusively with electron-deficient 2π-systems, except for one example where the 1,4-diphosphabarrelene formation held as trapping reaction for an *in situ* generated TTF-fused 1,4-diphosphinine (Figure 5).

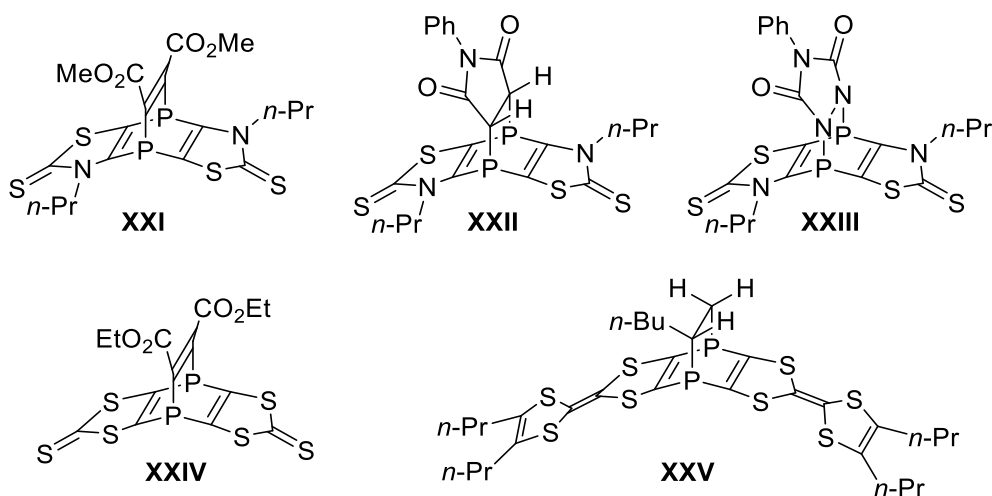
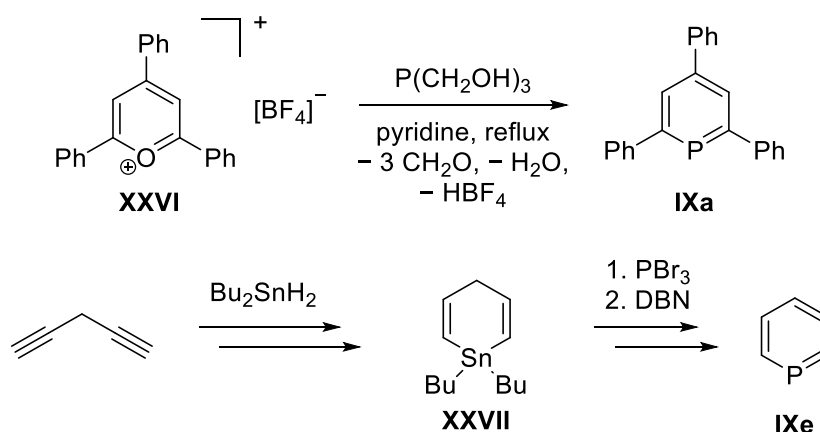


Figure 5. Selected 1,4-diphosphabarrelenes **XXI–XXV**, formed via [4+2]-cycloaddition to a 1,4-diphosphinine.^{54–56}

Notably, **XVIII** did not react at all with more electron-rich alkynes like diphenylethyne.⁵² 1,4-Diphosphabarrelene **XXIII** from the reaction with 4-phenyl-1,2,3-triazoline-3,5-dione showed back-formation of the 1,4-diphosphinine scaffold under irradiation, while this type of reactivity was not observed for any of the other scaffolds.

1.1.3 Low-valent phosphorus in heterocycles: phosphinines and 1,4-diphosphinines

The chemistry of phosphorus-containing heterocycles found its start as early as 1915 with the report on 1-phenylphosphinane.⁵⁹ Despite that, the further development of phosphorus-carbon heterocycles was delayed years into the second half of the 20th century, not least because they behave very different from their well-established nitrogen analogues due to the lower electronegativity of phosphorus and its diagonal relationship to carbon.^{60,61} Nowadays several pieces of literature review and summarise the evolution of phosphorus-containing heterocycles in great detail.^{60–64} After the publication of the first phospholane, namely 1-phenylphospholane in 1916,⁶⁵ the synthesis of 5-phenyldibenzophosphole in 1953⁶⁶ and the publication of the patented McCormack reaction in the same year,⁶⁷ another milestone of phosphorus-heterocyclic chemistry was achieved by Märkl in 1966: the first report on the synthesis of a $\sigma^2\lambda^3$ -phosphinine **IXa** and therefore, a low-coordinate phosphorus centre in a (six-membered) heterocycle.⁵⁷ While this first derivative was formed through an O⁺/P exchange of a suitable pyrilium salt **XXVI** the parent compound **IXe** was reported only a few years later by Ashe and synthesised through a Sn/P exchange reaction of **XXVII** (Scheme 3).⁵⁸



Scheme 3. Synthesis of the first $\sigma^2\lambda^3$ -phosphinine **IXa** and the parent compound **IXe**.^{57,58}

Since then, phosphinines have been investigated thoroughly on a theoretical⁶⁸ and experimental level.^{61–63,69,70,71} As mentioned above despite being the analogue to pyridine, phosphinines show very different behaviour in their chemistry. $\sigma^2\lambda^3$ -Phosphinines display high aromaticity of at least 88 % of that of benzene⁶⁸ because there is a large overlap of the p-orbital of the P-centre and the π -orbital of the carbon ring, with the phosphorus lone pair being co-planar to the planar heterocycle. The frontier

molecular orbital (FMO) distribution differs significantly from that of pyridine and has been calculated and investigated several times since the 1990s^{72,69} (Figure 6, own calculations).

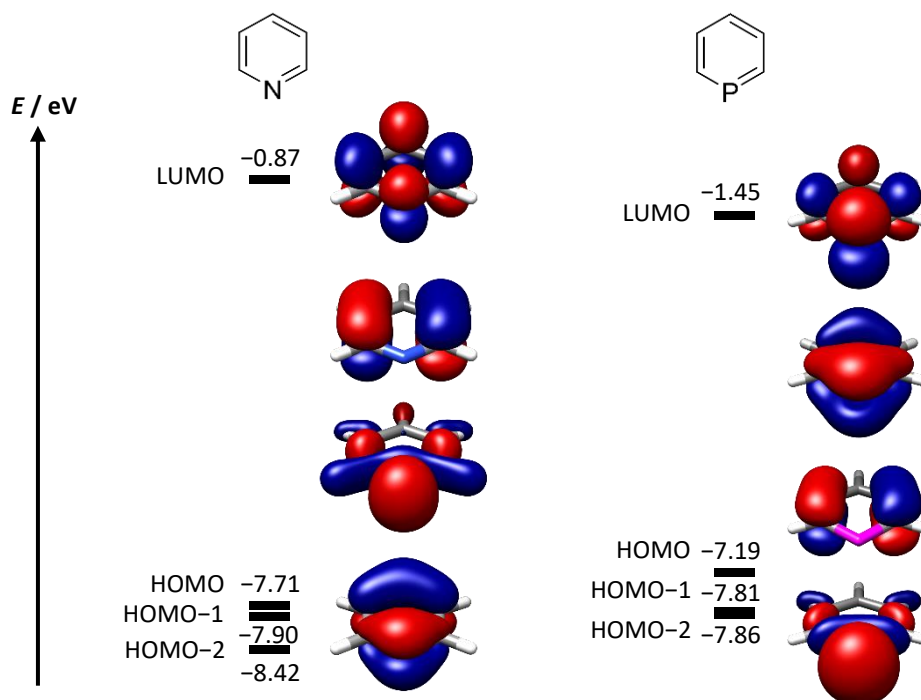


Figure 6. LUMO to HOMO-2 of pyridine and phosphinine at the PW6B95-D4/CPCM_{THF}/def2-QZVP//TPSS-D4/CPCM_{THF}/def2-TZVP level of theory.

While for both heterocycles the LUMO (lowest unoccupied molecular orbital) is of π^* -type, the HOMO (highest occupied molecular orbital) of the parent $\sigma^2\lambda^3$ -phosphinine is of π -type with a smaller HOMO-LUMO gap. The lone pair is more diffuse and constitutes HOMO-2 when in pyridine it corresponds to the HOMO or HOMO-1, depending on the level of theory. This, in combination with the reduced electron density at the heteroatom in comparison to pyridine explains the diminished nucleophilic character and σ -donor ability as well as increased π -acceptor ability. Consequently, most reagents attack the phosphorus atom of $\sigma^2\lambda^3$ -phosphinines. They react with strong nucleophiles at the P-centre generating dihydrophosphinine carbanions which with hard electrophiles react at the α - or γ -carbon atom to neutral dihydrophosphinine derivatives and with soft electrophiles at the phosphorus atom forming $\sigma^4\lambda^5$ -phosphinines.⁷³ When looking at the coordination chemistry, phosphinines can serve as ligands in different coordination modes but η^1 -complexes where the phosphinine acts as weak σ -donor and strong π -acceptor are the most common. Still, various complexes with η^6 -coordination could be synthesised, too, and related 2,2'-bisphosphinine ligands are able to, *e.g.*, stabilise low oxidation state transition metals.^{71,61,74} As seen above (chapter 1.1.2) phosphinines undergo [4+2]-cycloaddition reactions but only with highly activated alkynes, such as electron-deficient derivatives or benzyne.

The compound class of λ^3,λ^3 -diphosphinines results from the introduction of another $\sigma^2\lambda^3$ -phosphorus centre into the six-membered heterocycle. Here, there are three regioisomers to consider: 1,2-

phosphinines, 1,3-diphosphinines and 1,4-diphosphinines. Despite the great potential for coordination chemistry, the field of λ^3, λ^3 -diphosphinines is still much less developed than that of phosphinines. For example, there exists no isolated derivative of 1,2-diphosphinines – only one report on ^{31}P NMR spectroscopic evidence for a $1\lambda^5, 2\lambda^3$ -diphosphinine **XXVIII** by Bickelhaupt from 1991 (Figure 7).⁷⁵ In case of $1\lambda^3, 3\lambda^3$ -diphosphinines the literature is less scarce; the first isolated example **XXIX** was prepared by Zenneck in 1995 via a targeted synthesis as η^6 -ligand to an Fe(0) complex and oxidative release afterwards.⁷⁶ Shortly after that, derivatives **XXX**⁷⁷ and **XXXI**⁷⁸ were reported.

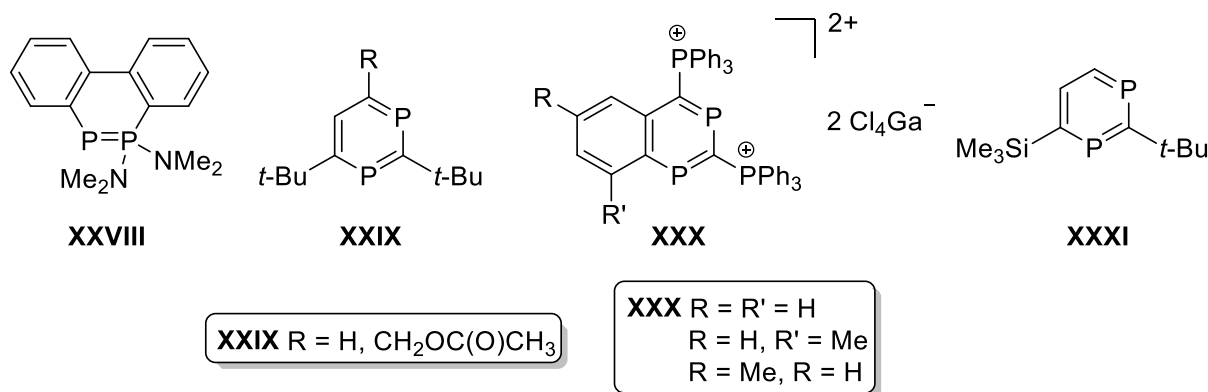
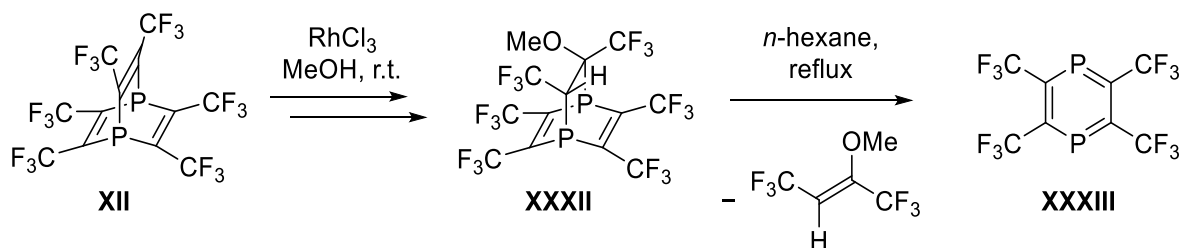


Figure 7. $1\lambda^5, 2\lambda^3$ -diphosphinine **XXVIII**⁷⁵ and selected $1\lambda^3, 3\lambda^3$ -diphosphinines **XXIX–XXXI**.^{76–78}

XXXI was formed through retro-[4+2]-cycloaddition of an 1,2,4-azadiphospha-barrelene which only occurred for the displayed substitution pattern, raising awareness to the electronic and steric influences on the reversibility of [4+2]-cycloaddition of diphosphinines. The same publication also described an η^1 -bound mononuclear $\text{W}(\text{CO})_5$ complex selectively to the sterically less crowded P-centre in **XXXI**.

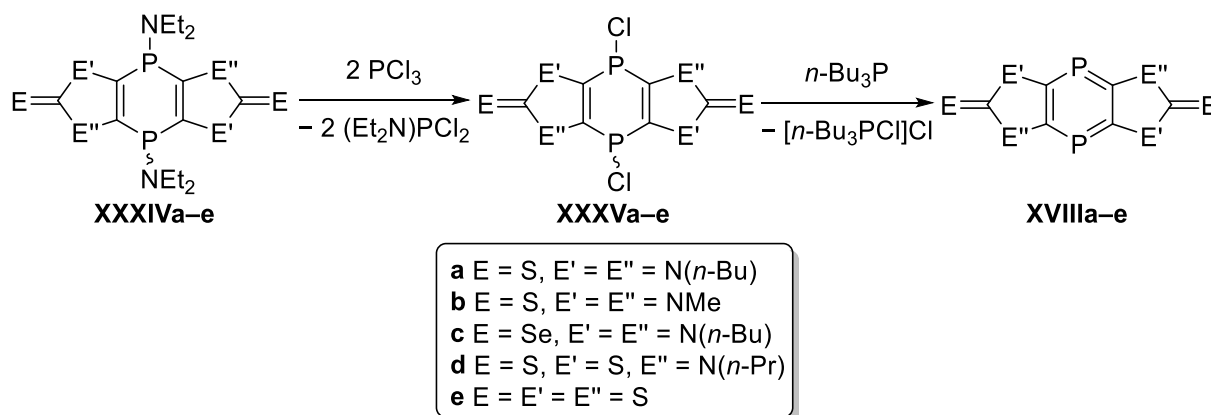
Until 2017, there was only one report on a $1\lambda^3, 4\lambda^3$ -diphosphinine scaffold by Kobayashi from 1976,⁷⁹ who observed evidence for the six-membered heterocycle **XXXIII** (Scheme 4).



Scheme 4. Synthesis of the first $1\lambda^3, 4\lambda^3$ -diphosphinine **XXXIII**.⁷⁹

Similarly to **XXXI**, **XXXIII** was accessed from the thermal retro-[4+2]-cycloaddition of a 1,4-diphospha-barrelene **XXXII**, obtained from the addition of methanol to one of the alkenyl-bridges of Krespan's 1,4-diphospha-barrelene **XII**.⁴⁶ Although **XXXIII** could never be isolated due to its sensitivity to air and moisture, a few years later Kobayashi reported a ^{31}P NMR resonance of 287.1 ppm and some reactions, namely [4+2]-cycloadditions and the formation of a diphosphanorbornadiene and suspected 1,4-dichloro-1,4-dihydro-1,4-diphosphinine from the reaction with tetrachloromethane.⁸⁰ In 2017, Streubel

and co-workers found a new entry point for the synthesis of 1,4-diphosphinines **XVIIIa** and **XVIIIb** from tricyclic 1,4-dihydro-1,4-diphosphinines **XXXIVa,b** via **XXXVa,b** (Scheme 5).⁵³



Scheme 5. Synthesis of the first isolable 1,4-diphosphinines **XVIIIa-e**.^{53,81,82,55}

The stabilisation of the 1,4-diphosphinines **XVIIIa,b** was achieved through annulation to two imidazole-2-thione units in a tricycle. Soon thereafter, stable, differently annulated derivatives **XVIIIc-e** were synthesised and investigated.^{81,82,55} In comparison to the report on Kobayashi's first 1,4-diphosphinine, the new derivatives were relatively air-stable and showed highfield-shifted ³¹P NMR resonances between 76 ppm (**XVIIIb**) and 135 ppm (**XVIId**). Theoretical calculations by Nyulászi⁶⁸ attribute a high aromaticity to the central ring which is largest for imidazole-annulated derivatives **XVIIIa-c**.^{53,82} The FMO diagram of all these 1,4-diphosphinines shows combinations of the FMOs of the two annulated five-membered units and the 1,4-diphosphinine parent compound. They are displayed exemplary for derivative **XVIIIc^{Me}** (*N*-*n*-Bu substituted by *N*-Me) which is of the largest importance for the work described in chapter 3 (Figure 8).

The chemistry of 1,4-diphosphinines and 1,4-dihydro-1,4-diphosphinines with focus on tricyclic derivatives up to date was summarised in 2021.⁸³ Due to their electronic situation the electrophilic sites of the former are at the low-valent P-centres while electrophiles readily attack the thione or selenone functionality, respectively. Thus, upon nucleophilic attack several anionic compounds could be generated and their follow-up reactivity, including reversible redox behaviour, was described.^{82,84} In terms of coordination chemistry, 1,4-diphosphinines are less explored, though in 2019 7-metalla-1,4-diphosphanorbornadienes were reported.⁸⁵ As mentioned above (see chapter 1.1.2) tricyclic 1,4-diphosphinines readily undergo [4+2]-cycloadditions with electron-poor 2π-systems to form 1,4-diphosphabarrelenes that have not been explored in great depth, so far.^{52,54-56}

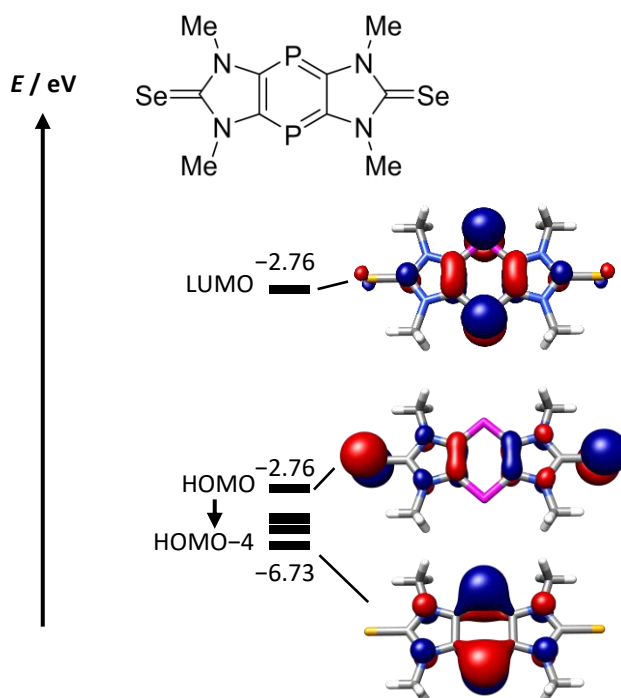


Figure 8. Selected FMOs for model compound **XVIIIc^{Me}** (N-Me instead of N-n-Bu) at the PW6B95-D4/CPCM_{THF}/def2-QZVP//TPSS-D4/CPCM_{THF}/def2-TZVP level of theory

In 2021 Ghadwal reported tricyclic 1,4-diphosphinine-1,4-diide **XXXVI**, accessed via a tricyclisation reaction followed by reduction, that can be converted into dicationic tricyclic 1,4-diphosphinine **XXXVII** (Figure 9).

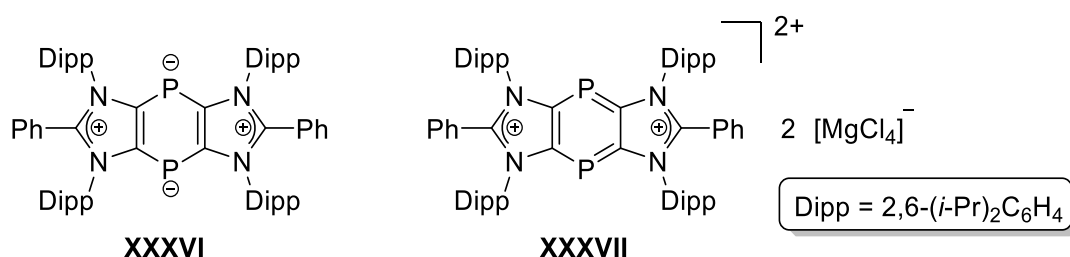


Figure 9. Tricyclic 1,4-diphosphinine-1,4-diide **XXXVI** and 1,4-diphosphinine **XXXVII**.⁸⁶

The dicationic part of **XXXVII** is thoroughly described as fully aromatic 14 π -electron system but exhibits a much more highfield-shifted ³¹P NMR resonance (δ = 16.5 ppm) than Streubel's 1,4-diphosphinines.

1.2 N-heterocyclic carbenes and phosphorus

1.2.1 Mono-, bis- and poly(N-heterocyclic carbenes): properties and application

The first isolable, crystalline N-heterocyclic carbene (NHC), namely 1,3-di(1-adamantyl)-2,3-dihydro-1*H*-imidazol-2-ylidene (**XXXIX**), was published by Arduengo in 1991,⁸⁷ only shortly after the synthesis of the first acyclic carbene (**XXXVIII**) by Bertrand in 1988 (Figure 10); the “true” bonding in **XXXVIII** was discussed for many years.⁸⁸ Carbenes – divalent compounds with only an electron sextet at the carbon centre – had been proposed for a long time already and the exceptional reactivity of short-lived derivatives was discussed by Buchner and Curtius as early as 1885⁸⁹ and Staudinger since 1912.⁹⁰ Carbenes can either have a triplet or singlet ground state, which can be distinguished by their calculated energies, often presented in the form of a singlet-triplet gap. In NHCs the singlet ground state is stabilised by around 80 kcal mol⁻¹ due to the ring structure and, more importantly, the π -donating and σ -accepting properties of at least one nitrogen atom in α -position to the carbene centre (Figure 10).⁹¹

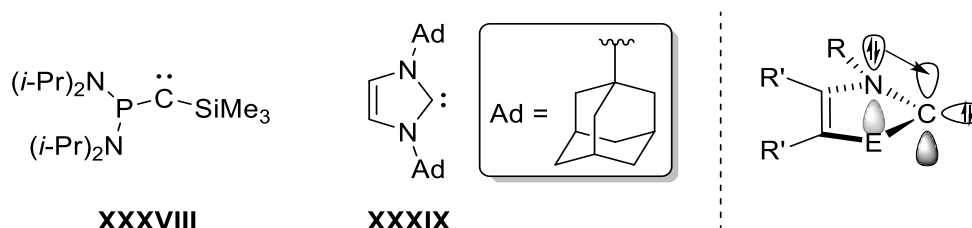


Figure 10. First isolated acyclic carbene **XXXVIII**⁸⁸ and NHC **XXXIX**⁸⁷ and depiction of σ -donation from α -nitrogen atoms in singlet ground state NHCs (R, R' = organic substituent; E = e.g., N, C).

Due to their electronic state NHCs act as good σ -donors and moderate π -acceptors and, hence, since 1991 great progress has been made to develop new NHC scaffolds and find applications for stable NHCs in coordination chemistry and catalysis.^{92,93} In many cases they substituted well-established phosphane ligands due to their superior binding properties. The first transition metal complexes with NHC ligands were reported as early as 1968 by Öfele⁹⁴ and Wanzlick,⁹⁵ but their success story started with their implementation in, *e.g.*, the second-generation Grubbs' catalyst.^{7,96} A large variety of coordination complexes to transition metals⁹⁷ and adducts to main group elements as well as complexes of the latter^{98,99} has been synthesized. The first adducts to main group element compounds – alane and germylene adducts – were published only shortly after the isolation of the first NHC by Arduengo in 1992¹⁰⁰ and 1993,¹⁰¹ respectively. Since then, a plethora of adducts of group 13–16 compounds and transition metal complexes thereof have been isolated, including main group elements in unusual, previously inaccessible oxidation states.^{98,99} The electronic¹⁰² and structural⁹³ features of NHCs can

easily be fine-tuned for the desired employment, *e.g.* in homogenous catalysis,^{103,104} as organocatalysts¹⁰⁵ and in medicinal areas as well as functional and polymeric material science.¹⁰⁶

There are a few main routes for the synthesis of NHCs for *in situ* use or isolation:¹⁰⁷ The deprotonation of azolium salts has been applied since the isolation of the first NHC and often benefits from readily accessible precursors. Furthermore, NHCs can be accessed via the direct reductive desulfurisation of suitable thione precursors or treatment of 2-chloro azolium salts with $\text{Hg}(\text{SiMe}_3)_2$. Lastly, thermally induced α -eliminations from, *e.g.*, carbon dioxide adducts or the products of formal E-H insertion reactions, releasing volatile side-products have been utilised. Besides these, various other synthetic routes have been developed over the years, especially since the first report on abnormal NHCs¹⁰⁸ and remote NHCs that opened pathways to new transition metal complexes.¹⁰⁹

Molecules that contain two or more NHC units are known as bis- or poly(NHCs) accordingly. In comparison to their monocyclic derivatives their chemistry is much younger and, hence, less developed. An example of flexible bis(NHCs), often containing N-bound linkers, has first been reported by Herrmann in 1995 as ligand in a Pd(II) complex **XL**.¹¹⁰ In 2002 Danopoulos published isolated pincer-type bis(NHC) **XLI**,¹¹¹ followed by Smith's *m*-terphenyl-linked example **XLII** (Figure 11).¹¹² Several flexible, *N*-ferrocenyl-linked bis- or tetra(NHCs) have been investigated in the synthesis of transition metal complexes as well.¹¹³

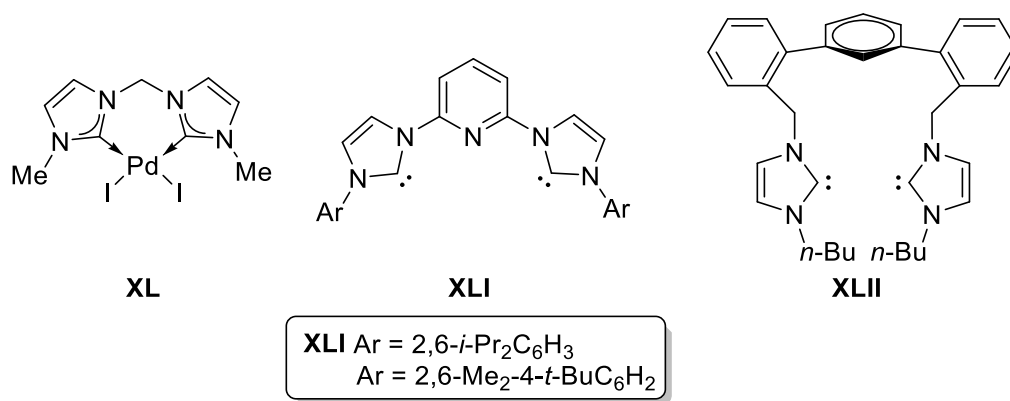


Figure 11. First reported flexible bis(NHC) in a complex **XL**¹¹⁰ and isolable flexible bis(NHCs) **XLI**¹¹¹ and **XLII**.¹¹²

On the other hand, the first rigid, monocyclic bis(NHC) **XLIII** (Figure 12) was published by Bertrand in 1997¹¹⁴ and could be implemented in a one-dimensional, Ag(I) bridged polymer¹¹⁴ as well as homo- and heteronuclear complexes to Rh(I) and Ir(I).¹¹⁵ Annulated, Janus-type bis(NHCs) **XLIV** and **XLV** were reported a decade later by Bielawski¹¹⁶ and Peris,¹¹⁷ respectively, and used in the synthesis of various homodinuclear transition metal complexes to Ag(I), Rh(I), Ir(I), Fe(II) and Ru(II) and organometallic polymers linked by Pt(II) or Pd(II).^{117,118} Since then, great efforts have been made in the development of annulated bis(NHCs) that could provide metal-to-metal separation of different lengths, be implemented in the construction of metallocupramolecular assemblies and serve as ligands in transition

metal catalysis.^{103,119,120} Although not containing directly opposing NHC units, rigid, bent bis(NHCs) that are backbone-fused like in **XLVI**¹²¹ are often also regarded as Janus bis(NHCs) and related Pd(II) complexes have shown modest catalytic activity.¹²² Only recently, Cu(I), Au(I) and Pd(II) complexes of a bent, N-bridged bis(NHC) were reported by Shen and tested in catalytic application as well.¹²³ The formation of main group element adducts to bis(NHCs) is far less reported and concentrated on small, flexible bis(NHCs).¹²⁰

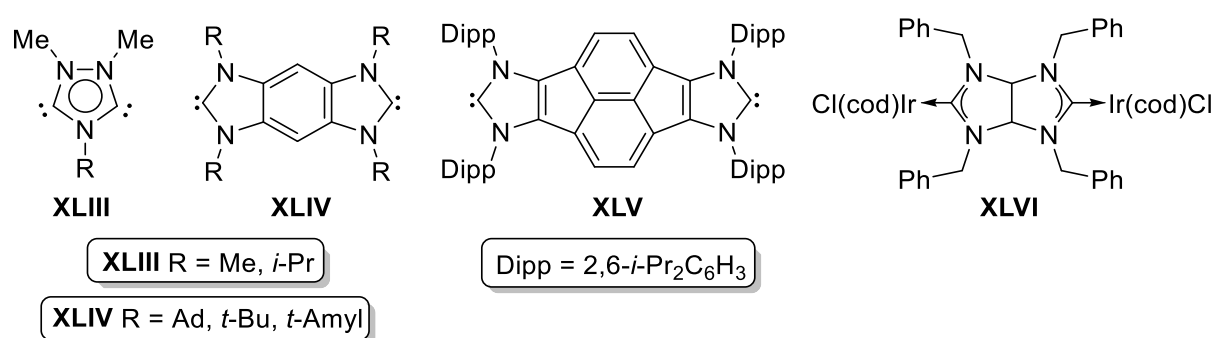


Figure 12. First reported rigid, monocyclic bis(NHC) **XLIII**,¹¹⁴ selected examples of isolable rigid bis(NHCs) **XLIV**¹¹⁶ **XLV**¹¹⁷ and a backbone-fused rigid, bent bis(NHC) in **XLVI**.¹²¹

1.2.2 Phosphorus-containing mono- and bis(N-heterocyclic carbenes)

The first instance of heteroatom introduction in mono(NHCs) through backbone substitution to tune the electronic features of the NHC and provide additional functionalities was reported by Arduengo in 1997 with halogen substitution.¹²⁹ Overall the field remains relatively unexplored, still, but some studies on different backbone-halogen substituted NHCs were published since then¹³⁰ and a few examples of silyl-substituted NHCs^{131,132} and their transition metal complexes¹³² can be found in the literature as well. Especially 1,3-bis(2,6-diisopropylphenyl)imidazole-2-ylidene proved to be suitable for versatile backbone-substitution, including phosphanyl substituted mono(NHCs) such as **XLVII** (Figure 13).¹²⁵

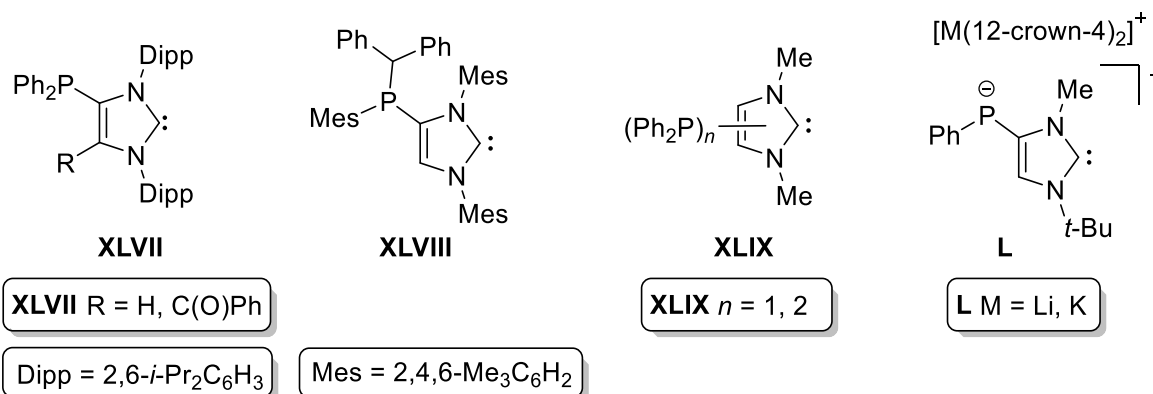


Figure 13. First reported backbone-phosphanylated NHC **XLVIII**¹²⁴ and examples of backbone phosphorus substituted NHCs **XLVII**,¹²⁵ **XLIX**^{126,127} and **L**.¹²⁸

However, the first backbone-phosphanyl substituted mono(NHC) **XLVIII** had been synthesised a few years earlier in 2009 by Gates from the abnormal reaction of a stable NHC with a phosphalkene.¹²⁴ Ruiz reported mono- or disubstituted NHCs **XLIX** in 2015 and 2012, respectively.^{126,127} The bifunctionality of **XLVII–XLIX** towards metal complexes from having both carbene and P(III) centres was explored by Gates,¹³³ Bertrand¹³⁴ and Ruiz^{126,127} using different strategies and transition metals, though in all cases the carbene centre reacted preferably. Furthermore, an anionic P-functional mono(NHC) was reported in 2013 by Streubel as part of the salt **L**.¹²⁸

The literature on heteroatom-bridged bis(NHCs) – especially through direct backbone substitution – is even more scarce although the introduction of additional functional sites bears a lot of potential for metalorganic polymers and supramolecular chemistry. In the field of phosphorus-containing bis(NHCs), derivative **LI** (Figure 14) could be isolated in 2016 but was not investigated in great depth.¹³⁵

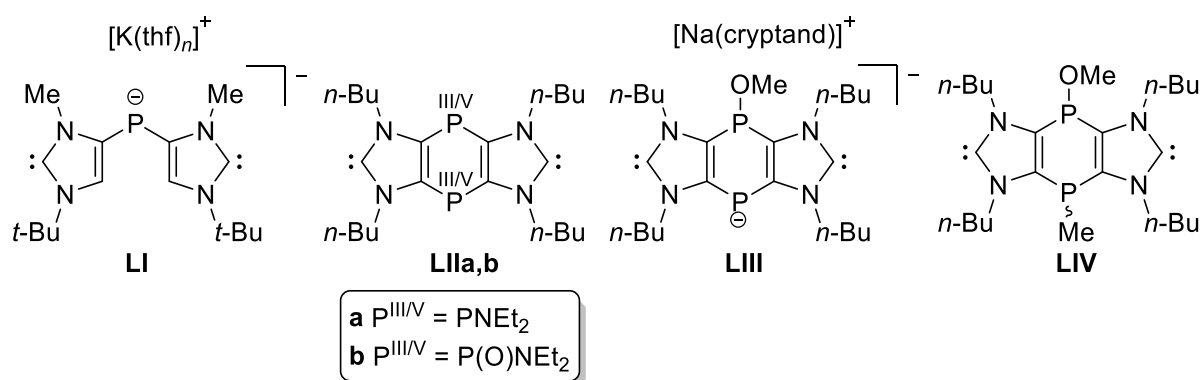
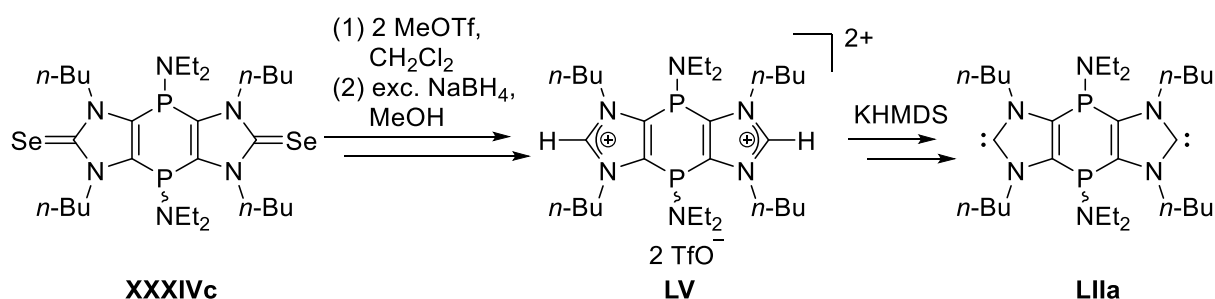


Figure 14. First P-bridged bis(NHC) **LI**¹³⁵ and planar, rigid bis(NHCs) **LII**,¹³⁶ **LIII** and **LIV**.⁸¹

Soon after that, rigid doubly P-bridged bis(NHCs) **LII–LIV** were introduced by Streubel in 2020¹³⁶ and 2021,⁸¹ respectively. While earlier attempts of a reductive desulfurisation of **XXXIVa,b** had failed, **LIIa** was accessed through a reductive deselenisation of **XXXIVc** to yield bis(imidazolium) salt **LV** which could then be deprotonated (Scheme 6).



Scheme 6. Synthesis of rigid, planar bis(NHC) **LIIa**.¹³⁶

On the other hand, the synthesis of **LIIb** had been achieved via an oxidative deselenisation reaction, followed by deprotonation. **LIIa,b** show behaviour analogously to backbone-phosphanyl substituted mono(NHCs) and could be implemented in dinuclear coinage metal complexes (Cu(I), Ag(I) and Au(I))¹³⁶

and complexes to Rh(I) and Ir(I)¹³⁷ (**LVla,b**) without participation of the phosphorus centres (Figure 15). Coordination to the latter in **LV** and **LIIa**, respectively, could only be achieved with BH₃ and was not studied in great detail.¹³⁷ Cyclovoltammetric measurements reveal several strongly solvent-dependent oxidation processes with heavily offset reduction processes and one reduction in the cathodic region for both **LIIa** and **LIIb**.

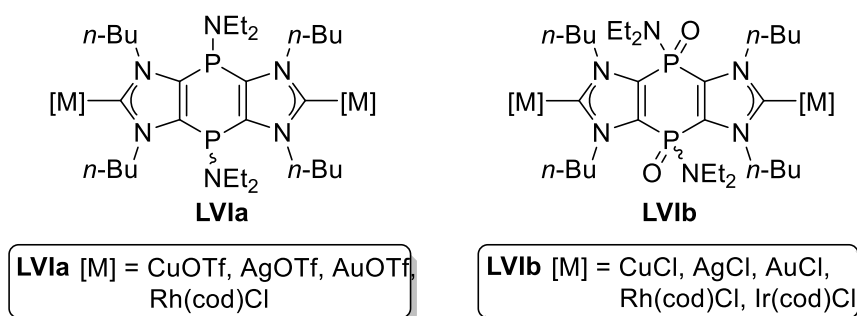
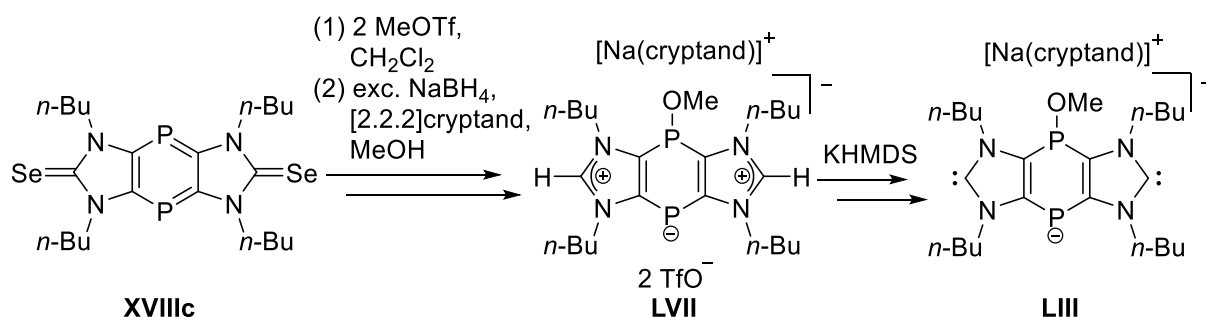


Figure 15. Isolated transition metal complexes **LVI** of bis(NHCs) **LII**.^{136,137}

Anionic bis(NHC) **LIII** was synthesised via a similar reductive deselenisation/deprotonation approach, starting from tricyclic 1,4-diphosphininie **XVIIIc** (Scheme 7).



Scheme 7. Synthesis of anionic, *P*-bridged bis(NHC) **LIII**.⁸¹

Bis(NHC) **LIII** shows similar properties as **LIIa,b** but its coordination behaviour was not investigated experimentally. However, complexation reactions with **LVII** showed that the *P*-methoxy substituted site reacts preferably over the *P*-anionic site.⁸¹ The reduction reaction in Scheme 7 was initially targeted at a 1,4-diphosphinine bis(imidazolium) salt and the corresponding bis(NHC) – which would offer not only low-valent carbon but also phosphorus centres for coordination – but whose synthesis has been elusive, so far.

None of the reported backbone-phosphorus functionalised mono- and bis(NHCs) **XLVII–LIV** were investigated regarding their reactivity towards main group element compounds and adduct formation.

2 OBJECTIVES OF THE THESIS

The PhD project, described in this thesis, focused on the synthesis and properties of rigid, bent P-bridged bis(N-heterocyclic carbenes) and to find entry points to previously not accessible tricyclic, imidazole-based 1,4-diphosphinine bis(NHCs). The following research objectives can be formulated:

1. Synthesis of 7,8-dihydro-1,4-diphosphabarrelenes and their characterisation as caged diphosphanes as well as their subsequent conversion into bent, P-bridged bis(imidazolium) salts and bis(NHCs)
2. Investigations on carbene- vs. phosphorus-centred reactions towards transition metal complexes and main group compounds of the new bent, P-bridged bis(NHCs), also in comparison to already established planar, P-bridged bis(NHCs)
3. Theoretical and experimental studies on the possibility of retro-[4+2]-cycloadditions of the 7,8-dihydro-1,4-diphosphabarrelene scaffolds to access new tricyclic 1,4-diphosphinine derivatives
4. Synthesis of 1,4-diphosphinine bis(imidazolium) scaffolds from planar, *P*-NEt₂ substituted, imidazole-annulated 1,4-dihydro-1,4-diphosphinines and their theoretical and experimental investigations

3 RESULTS AND DISCUSSION

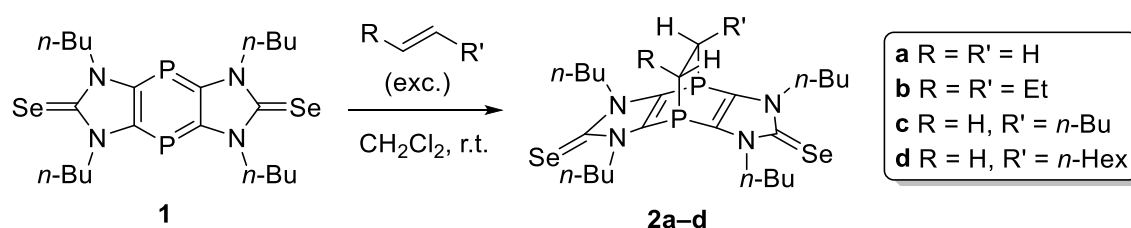
3.1 Rigid, bent bis(NHCs) derived from 7,8-dihydro-1,4-diphosphabarrelenes

As alluded to in the introduction, 1,4-diphosphabarrelenes represent a subclass of caged phosphanes with two geometrically constrained phosphorus centres that can potentially be tuned by substituents and/or annulation to heterocycles. While most 1,4-diphosphabarrelenes feature an unsaturated, often functionalised bridge only one example of a 7,8-dihydro-1,4-diphosphabarrelene were reported by Dielmann.⁵¹ Hence, an extension of this compound class was targeted in this first chapter by using the established [4+2]-cycloaddition of 2π -electron reagents to tricyclic, imidazole-based 1,4-diphosphinines. Here, not only their properties and donor ability were investigated but also their conversion into bent, P-bridged bis(imidazolium) salts and, subsequently, isolable bis(NHCs) as new tetra-topic ligands with two types of donor centres of different Lewis basicity. For all 7,8-dihydro-1,4-diphosphabarrelene scaffolds the possibility of a retro-[4+2]-cycloaddition was explored with theoretical calculations as well as experimentally to potentially access new 1,4-diphosphine scaffolds.

3.1.1 Synthesis and reactions of new 7,8-dihydro-1,4-diphosphabarrelenes

3.1.1.1 Synthesis and characterisation of 7,8-dihydro-1,4-diphosphabarrelene diselones

New 7,8-dihydro-1,4-diphosphabarrelenes **2a–d** were synthesised via [4+2]-cycloaddition of 1,4-diphosphine diselone **1**¹³⁷ (formerly **XVIIIc**) with an approximately 50-fold excess of ethene (**2a**) or five- to tenfold excess of alkyl substituted alkenes (**2b–d**), respectively (Scheme 8). Upon reaction the intense pink-violet solution of **1** turned orange to light red and 7,8-dihydro-1,4-diphosphabarrelenes **2a–d** could be isolated as yellow to orange solids in yields up to 75 %.



Scheme 8. Synthesis of 7,8-dihydro-1,4-diphosphabarrelenes **2a–d** from 1,4-diphosphine diselone **1**.

The ^{31}P NMR spectra of **2a–d** show typically highfield-shifted resonances (Table 1) ranging from –86.3 ppm to –94.7 ppm which compare well to previously published values of nuclei in 1,4-diphosphabarrelene scaffolds.^{137,50,52,54,51}

Table 1. Selected NMR data for compounds **2a–d** in CDCl_3 (**2a**) or CD_2Cl_2 (**2b–d**).

	$\delta(^{31}\text{P})$ / ppm	$^3J_{\text{P,P}}$ / Hz	$\delta(^{77}\text{Se}\{^1\text{H}\})$ / ppm	$\delta(^{13}\text{C}\{^1\text{H}\})$ / ppm	$^1J_{\text{Se,C}}$ / Hz
2a	–94.7	-	26.4	159.1	233
2b	–86.3	-	31.2	159.6	235
2c	–91.4, –87.0	17.4	27.7, 30.5	159.3, 159.7	–*
2d	–91.4, –87.0	17.6	27.7, 30.5	159.3, 159.7	–*

*not observed due to low signal intensity

In case of **2c** and **2d**, where asymmetry is introduced through the terminal alkene, a $^3J_{\text{P,P}}$ -coupling constant of around 17.5 Hz could be determined. Similarly, the corresponding $^{77}\text{Se}\{^1\text{H}\}$ NMR resonances are highfield-shifted to values between 26.4 ppm and 31.2 ppm with two diastereotopic Se nuclei for derivatives **2c** and **2d**. Despite the significant change in the NMR resonance, the $^1J_{\text{Se,C}}$ -coupling constants are around 234 Hz, which is almost unchanged in comparison to **1** ($^1J_{\text{Se,C}} = 236$ Hz). Following the trend, the $^{13}\text{C}\{^1\text{H}\}$ NMR shifts are highfield-shifted to values around 159 ppm ($\delta(^{13}\text{C}\{^1\text{H}\})(\mathbf{1}) = 168.3$ ppm). Both the $^{77}\text{Se}\{^1\text{H}\}$ and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopic data are similar to the ones of planar, tricyclic *P*- NEt_2 -substituted diselone **XXXIVc**, but experience slight highfield shifts due to the only alkyl substituted bridging motif. Going from *n*-butyl to *n*-hexyl substitution in **2c** and **2d**, respectively, does not have any effect on the NMR spectroscopic data of the product or the reaction behaviour.

Single crystals of derivative **2b** could be grown from a dichloromethane solution at –30 °C and studied via single crystal X-ray diffraction (SCXRD) (Figure 16). The structure shows the typical feature of 7,8-dihydro-1,4-diphosphabarrelenes, namely the high degree of pyramidalisation around the phosphorus centres: The C-P-C angles lie between 94.2(3) ° and 95.8(3) ° with an average angle sum of only 285 ° which is smaller than for compact phosphanes like PF_3 or PMe_3 . These values compare very well to previously published imidazole-annulated 1,4-diphosphabarrelenes⁵² but also, *e.g.*, pyrrole-based derivatives.⁵¹ The same applies to the bond lengths which are almost identical to the ones in **XIX**, except for the C23-C24 bond (1.560(10) Å) due to its single bond instead of double bond character. The C-Se bond lengths are unchanged when compared to **1**. The overall folding angle (C2-P1-P2-C13) of the scaffold amounts to 125 °.

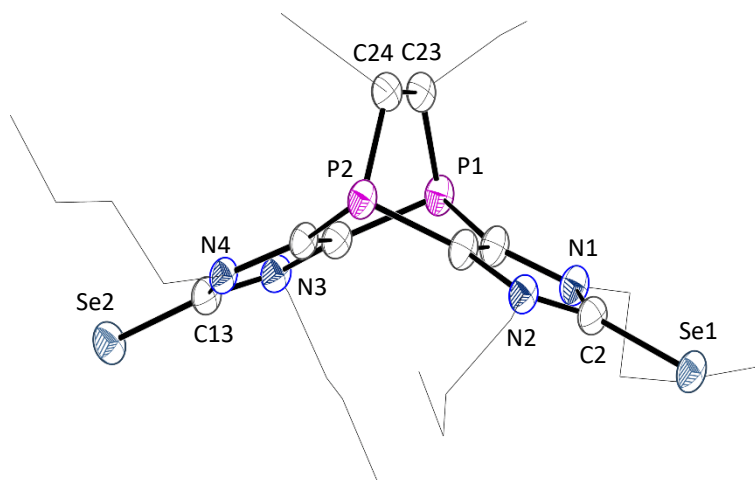
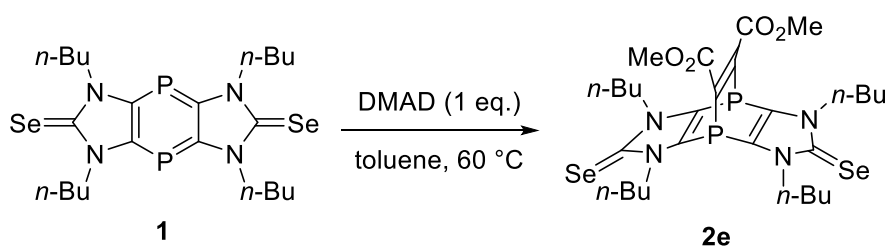


Figure 16. Molecular structure of **2b** in the single crystal. Thermal ellipsoids are set at 50 % probability. Hydrogen atoms were omitted for clarity. *n*-Butyl and ethyl chains are simplified as wires for additional clarity.

3.1.1.2 Retro-[4+2]-cycloaddition and theoretical investigations

In contrast to previous 1,4-diphosphabarrelene scaffolds which were accessed through the [4+2]-cycloaddition with electron-deficient alkynes or cyclic alkenes,^{137,52,54} the formation of **2** could be achieved with non-functionalised alkenes with only alkyl substituents at room temperature. Compounds **2a–c** and the mechanism of their formation were studied through state-of-the-art calculations at the PW6B95-D4/CPCM_{THF}/def2-QZVP//TPSS-D4/CPCM_{THF}/def2-TZVP level of theory (for further information see 5.2.9). As derivative **2d** did not display any different properties and would only suffer from increased computational cost it was not included in the calculations. For all calculations simplified structures (*N*-*n*-Bu substituted by *N*-Me) were used as model compounds, indicated by the “Me”-exponent. The computed structural features align well with the analytically determined ones for **2b**. For comparability the formation of previously reported¹³⁷ 1,4-diphosphabarrelene **2e** from the reaction of **1** with the electron-deficient alkyne DMAD was also examined (Scheme 9).



Scheme 9. Synthesis of previously reported 1,4-diphosphabarrelene **2e** from 1,4-diphosphinine diselone **1** and DMAD.

Mechanistic investigations reveal a concerted mechanism that involves the π^* -type LUMO of the corresponding alkene and the HOMO-4 of the 1,4-diphosphinine **1** (Figure 17) which is largely centred in a π -type orbital around the two P centres with opposing phases.

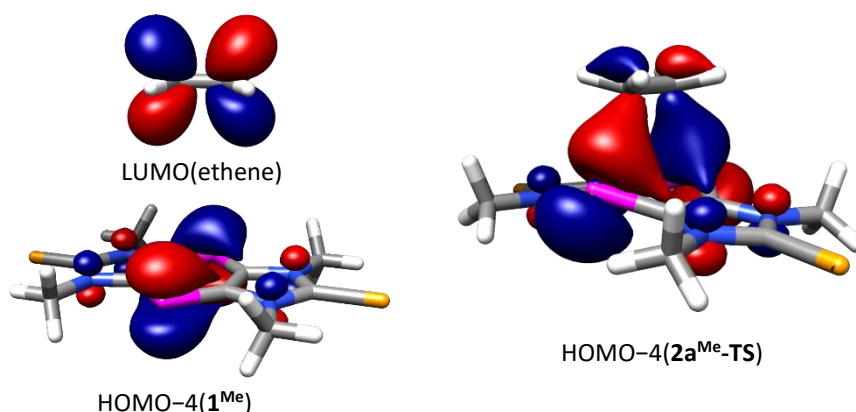


Figure 17. FMOs involved in the concerted step of the [4+2]-cycloaddition reaction to form **2a**^{Me}.

Thus, the feasibility of the [4+2]-cycloaddition should be inversely dependent on the LUMO energy of the alkene or alkyne and dependent on the gap between this LUMO and the HOMO-4 energy of **1** ($E_{\text{HOMO-4}}(\mathbf{1}) = -6.73$ eV). Electron-withdrawing substituents lower the energy of the LUMO which explains why reactions with such substituted alkenes or alkynes tend to occur more readily. Looking at the Gibbs reaction energies of (**2a–c**)^{Me}, the formation of **2a**^{Me} is the one that is clearly exergonic (Figure 18, Table 2) proceeding over the smallest transition state barrier of 21.1 kcal mol^{−1}.

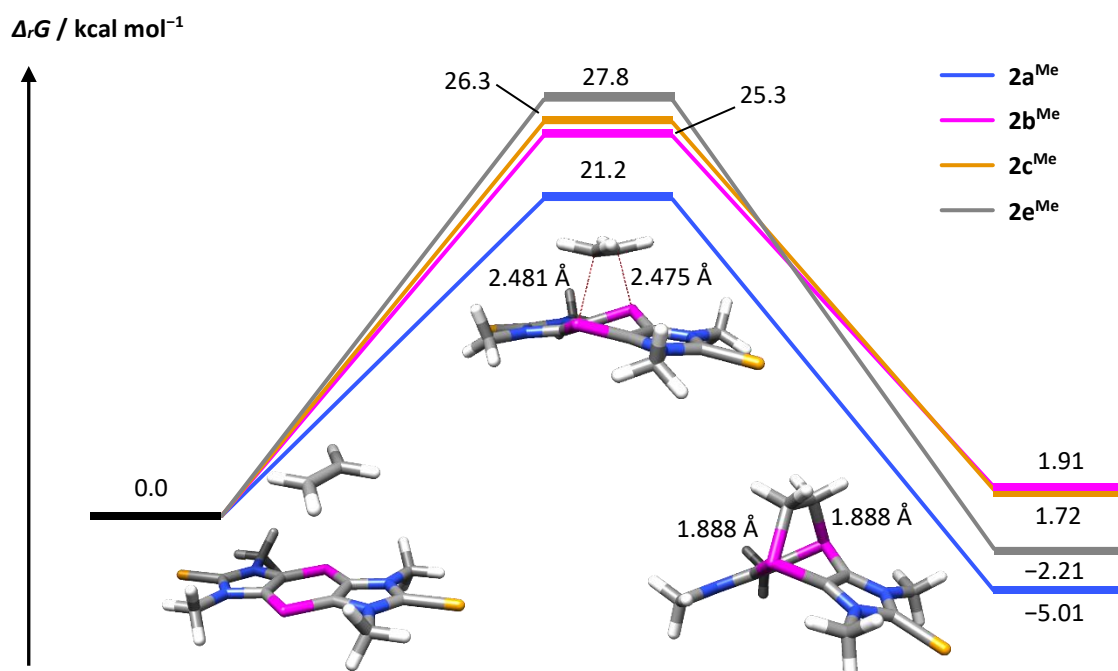


Figure 18. Gibbs reaction energies and transition state barriers for model compounds (**2a–c,e**)^{Me}. Exemplary structures are given for **2a**^{Me}.

The formation of **2b**^{Me} and **2c**^{Me} are approximately thermoneutral as reaction energies fall within the method's error margins, and have slightly higher transition state energies than the aforementioned. Derivative **2e**^{Me} is also formed in a slightly exergonic reaction but has to overcome the highest reaction barrier which is in line with the need to heat the reaction mixture. Taking into account the LUMO

energies of the corresponding alkenes/alkynes as well as the different degree of steric hinderance, the calculated numbers correlate well with observed reaction times (Table 2).

Table 2. Gibbs reaction energies, $LUMO(alkene/alkyne)-(HOMO-4)(1^{Me})$ energies and reaction times for the formation of model compounds $(2a-c)^{Me}$ and $2e^{Me}$.

	$\Delta\Delta_r G^\circ / \text{kcal mol}^{-1}$	$\Delta\Delta_r G^\ddagger / \text{kcal mol}^{-1}$	$E_{LUMO-(HOMO-4)} / \text{eV}$	reaction time
2a^{Me}	-5.01	21.1	6.79	2 h
2b^{Me}	1.91	25.3	7.18	7 d
2c^{Me}	1.72	26.3	7.06	2.5 d
2e^{Me}	-2.21	27.8	4.97	1 h (at 60 °C)

Although having the disadvantage of longer reaction times, the almost thermoneutral reaction energies of $(2a-c)^{Me}$ should allow for reversibility of the reaction in Scheme 8, which could prove advantageous in a potential follow-up chemistry. The possibility was explored by heating a solution of **2c** in toluene in a *J Young*® NMR tube and monitoring the reaction via $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy (Figure 19).

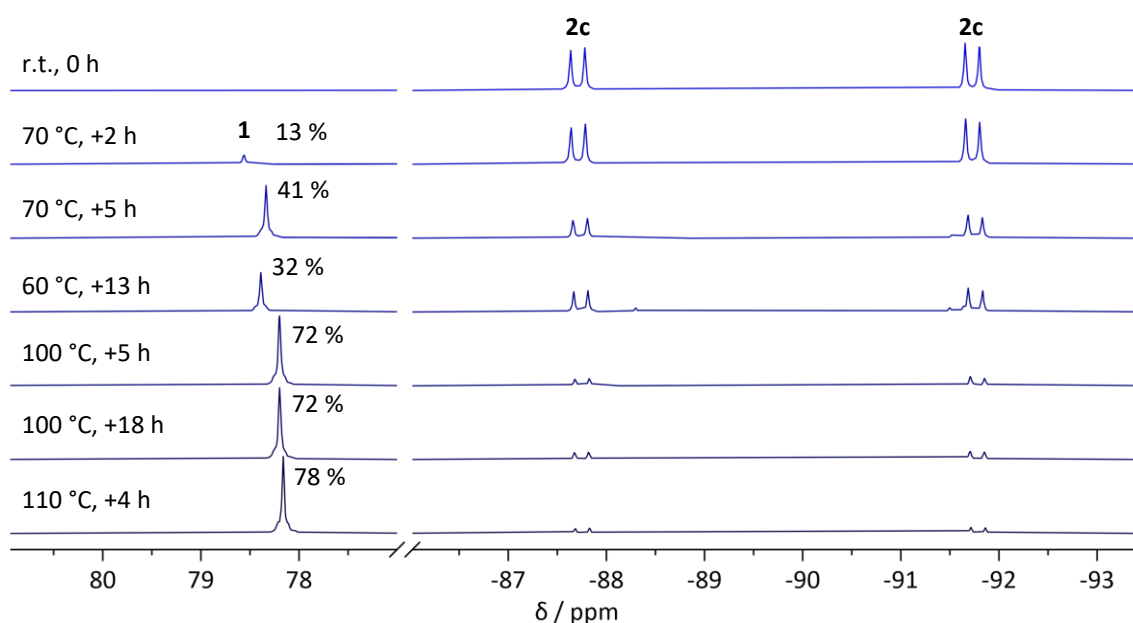
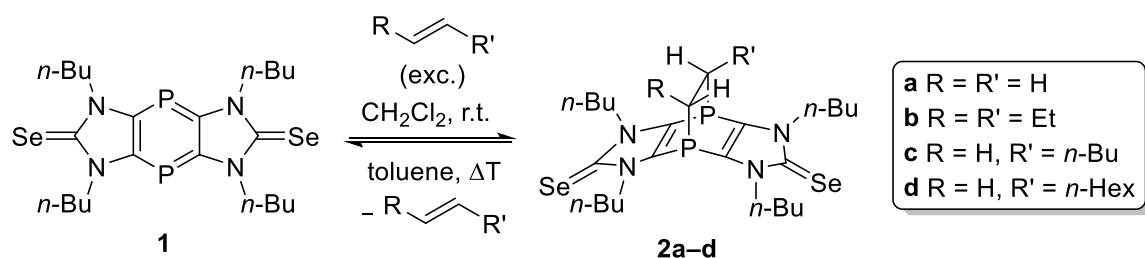


Figure 19. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **2c** in toluene after heating at different temperatures.

During a colour change of the solution from light pink to intense pink-violet signals of **2c** vanished while the resonance for **1** increased in intensity as revealed by the ^{31}P NMR spectra. The retro-[4+2]-cycloaddition occurred faster at higher temperature, stagnated at constant temperature and **2c** formed back when decreasing the temperature, which is in accordance with a strictly controlled temperature dependence. Subsequently, the reaction equation can be rewritten as displayed in Scheme 10.



Scheme 10. Reversible [4+2]-cycloaddition of **1** with alkenes.

Due to the reaction energetics, the reverse reaction already occurs at room temperature to a small degree as evidenced by the pink colour during the reaction work-up of **2a–d**, accommodating for the lower yields than in the synthesis of **2e**,¹³⁷ and the isolated solids turned slightly pink over time when not stored at $\leq 0^\circ\text{C}$.

7,8-Dihydro-1,4-diphosphabarrelenes **2** can be also classified as caged diphosphanes as indicated by the phosphorus centre with high pyramidalisation. Consequently, the P lone pair has a large s-character which could be confirmed by frontier molecular orbital (FMO) analysis (Figure 20) which shows a similar situation for all three derivatives (**2a–c**)^{Me}.

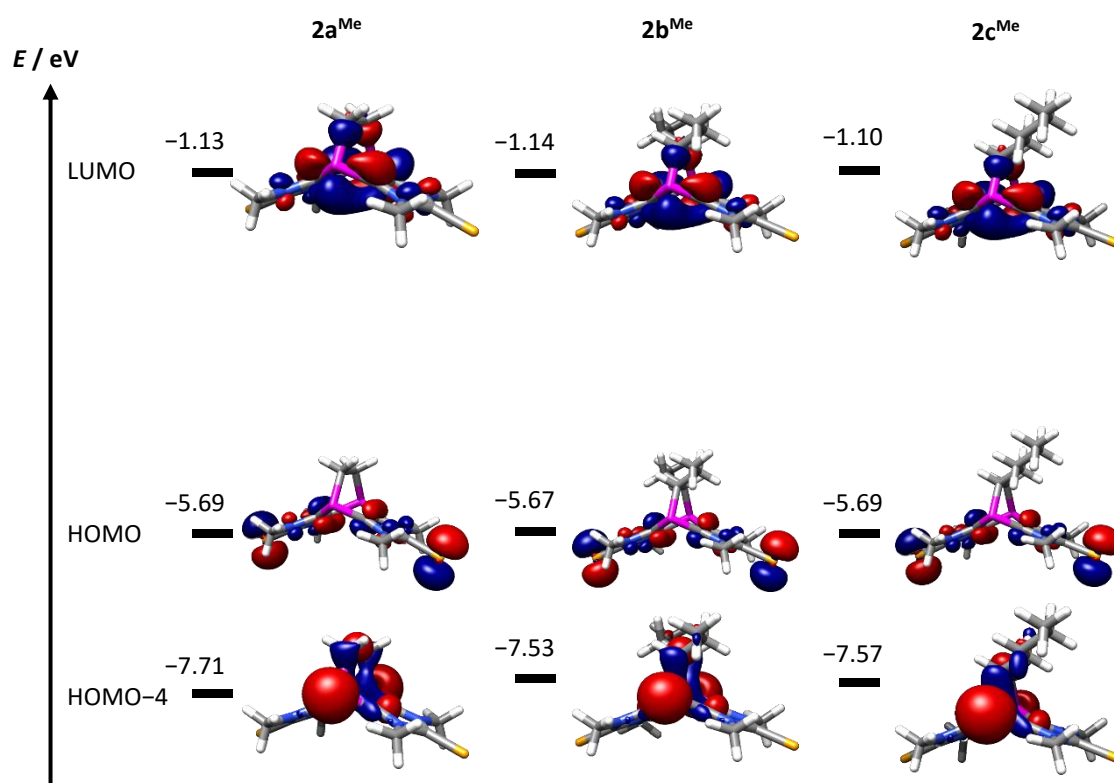


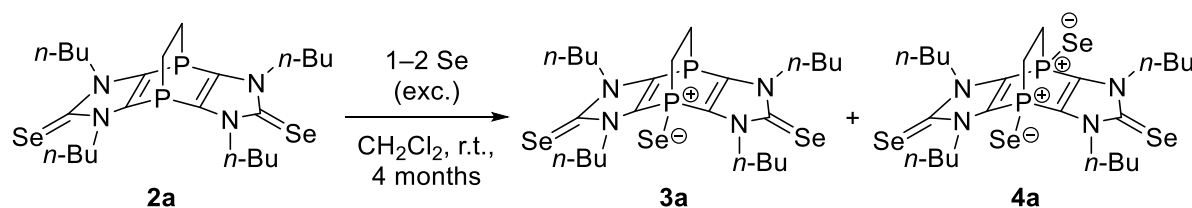
Figure 20. Selected calculated FMOs of compounds (**2a–c**)^{Me}.

The P lone pair has no contribution to the highest occupied molecular orbital (HOMO) which is largely centred at the Se atoms as is usually the case for P-bridged bis(imidazole) diselones. However, the P

lone pairs constitute HOMO-4 which should also be electronically accessible for coordination. The lowest unoccupied molecular orbital (LUMO) of the bent scaffolds is embedded in the central ring around P and therefore less sterically accessible for *e.g.* nucleophilic attacks which explains the relative stability of **2** apart from the already discussed occurring retro-[4+2]-cycloaddition.

3.1.1.3 Experimental investigations on the P-donor ability

As alluded to in the introduction, NMR spectroscopic data of phosphane selenides are used frequently to determine the donor ability of the corresponding phosphanes.^{14–16} Thus, the sterically least hindered and thermally most stable derivative **2a** was reacted with grey selenium (Scheme 11) to access phosphane selenides **3a** and **4a** and characterise the phosphorus lone pairs. Even the first oxidation to **3a** proceeded slowly with only about 63 % conversion after three weeks at room temperature and after four months a mixture of approximately 64 % **3a**, 14 % twofold oxidised **4a** and 22 % structurally related side products could be separated from the remaining selenium and characterised by NMR spectroscopy. Other solvents and heating of the reaction mixture did not have an accelerating effect on the desired reaction and no quantitative conversion could be achieved.



Scheme 11. Reactions of **2a** with elemental selenium yielding a mixture of mono-/di-oxidised products **3a** and **4a**.

3a shows a slightly highfield-shifted $^{31}\text{P}\{^1\text{H}\}$ NMR resonance for the unchanged P nucleus at -101.3 ppm and a significantly downfield-shifted signal in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum for the Se-bound P nucleus ($\delta(^{31}\text{P}\{^1\text{H}\}) = -14.8$ ppm) with a $^1J_{\text{Se,P}}$ -coupling constant of 829 Hz. Phosphane selenides are commonly synthesised and investigated to evaluate the basicity of phosphanes.^{14,16,15} The $^1J_{\text{Se,P}}$ -coupling constant is directly related to the s-character of the former P lone pair as the coupling's main contribution arises from Fermi contact between nuclear magnetic moments and electron spins in s orbitals.¹³⁸ Bent's rule states that the s-character of the lone pair increases with more electron-withdrawing substituents,¹¹ so a phosphane's basicity is heavily influenced by its substitution pattern. Trialkylphosphanes like $\text{P}(\text{n-Bu})_3$ show $^1J_{\text{Se,P}}$ -coupling constants around 680 Hz, while those of triarylphosphanes like PPh_3 lie expectedly higher at 730 Hz.¹⁴ While imidazole substitution increases the coupling constant further,¹⁴ the large $^1J_{\text{Se,P}}$ -coupling in **3a** can certainly be derived from its caged structure that only allows a P lone pair with large s-character and small amounts of π -bonding. Thus, the P-Se bond in Scheme 11 is drawn as single bond with the corresponding formal charges on P and Se. This

depiction is also reflected in the $^{77}\text{Se}\{^1\text{H}\}$ NMR shift of **3a** which can be assigned to a doublet at -454.6 ppm – significantly more highfield-shifted than for common phosphane selenides.¹⁴ The effect is even more pronounced in **4a** which shows a resonance at -22.7 ppm in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, accompanied by a 856 Hz $^1J_{\text{Se,P}}$ -coupling and a doublet $^{77}\text{Se}\{^1\text{H}\}$ resonance at -438.3 ppm. The coupling pattern of the signal in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum is especially interesting as it shows not only the expected singlet with ^{77}Se satellites. Under the singlet signal lies also a doublet of around 7 % of the total signal intensity which accounts for the amount of **4a** that has one NMR active ^{77}Se nucleus bound to one of the ^{31}P nuclei. The former $\text{A}_2\text{XX}'$ spin system becomes an $\text{AA}'\text{XX}'$ spin system with a $^3J_{\text{P,P}}$ -coupling of 49 Hz which fits the doubly oxidised P^{V} species. Subsequently, the satellite signals also constitute doublets with a 49 Hz coupling. This particular signal was simulated with the NMR simulation software *gNMR*¹³⁹ and although an iterative approach was not successful the aforementioned spin system could be confirmed by using the experimentally obtained coupling constants (Figure 21).

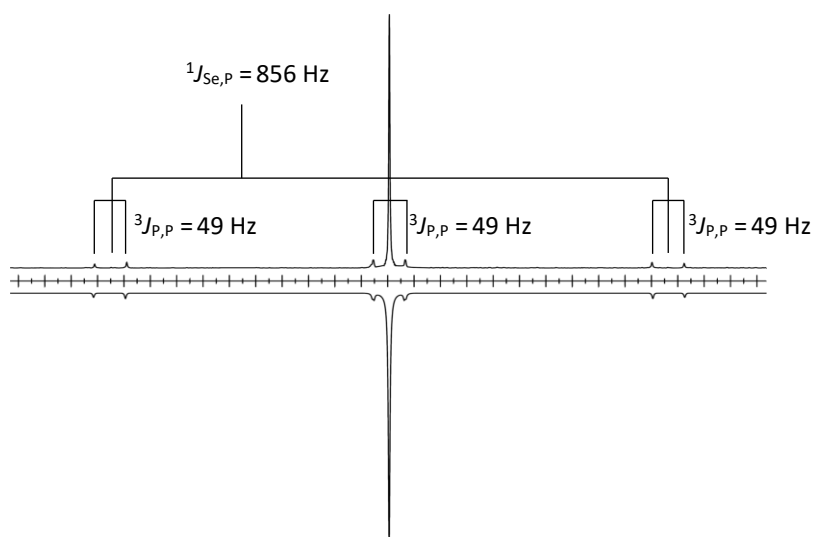
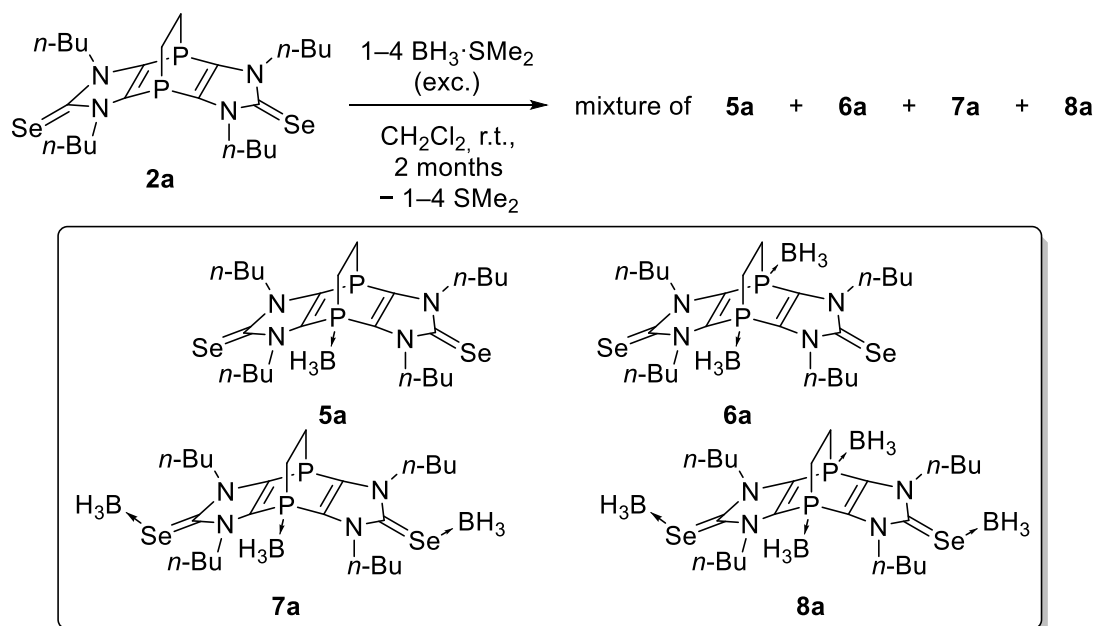


Figure 21. Experimental $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **4a** (top) and simulated spectrum (bottom).

While the presence of these kind of subspectra is known and can be used to gather further information on compounds containing, *e.g.*, ^{13}C and ^{15}N nuclei,¹⁴⁰ in the case of **4a** it again confirms the strong s-orbital character in the lone pair of the P atoms in **2** which is heavily influenced by the bond to an NMR-active nucleus.

Furthermore, the coordination behaviour of **2a** was investigated in the reaction with an excess of circa 11 equivalents of $\text{BH}_3\cdot\text{SMe}_2$ (Scheme 12). The phosphane-borane adduct formation was also used by Streubel and Koner to evaluate the coordination behaviour of planar 1,4-dihydro-1,4-diphosphinine dithiones like **XXXIVa,b** where exclusive coordination to P was observed for the *P*- NEt_2 derivative, while S coordination occurred for *P*-Ph substitution.^{141,142}



Scheme 12. Reaction of **2a** with $\text{BH}_3\cdot\text{SMe}_2$ yielding a mixture of BH_3 adducts **5a–8a**.

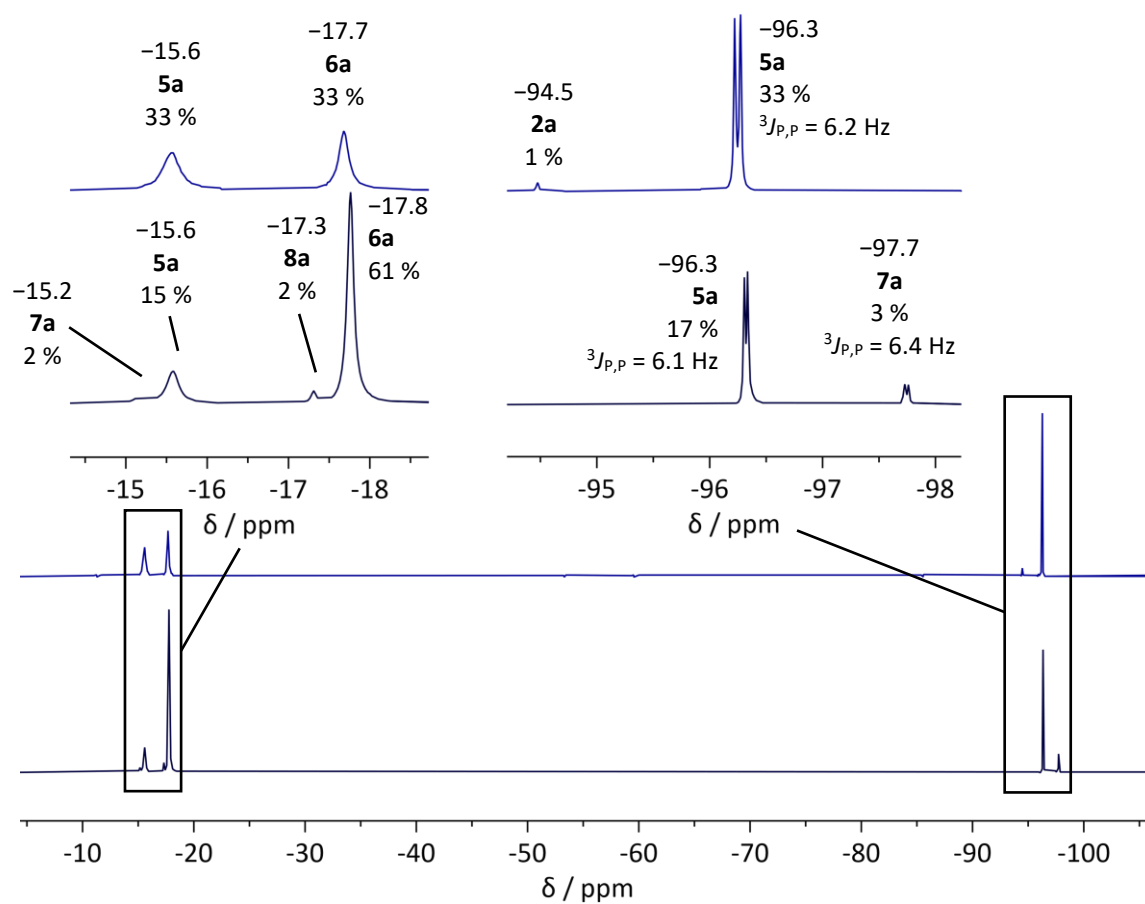


Figure 22. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **2a** with excess $\text{BH}_3\cdot\text{SMe}_2$ in reaction mixture in CH_2Cl_2 after four days (top) and after two months and work-up in CD_2Cl_2 (bottom).

Reaction of **2a** with $\text{BH}_3\cdot\text{SMe}_2$ quickly leads to a mixture of **2a** (1 %), **5a** (66 %) and **6a** (33 %), that is converted to an unchanging mixture of **5a** (32 %), **6a** (61 %), **7a** (5 %) and **8a** (2 %) over a time of two months (Figure 22). The use of fewer equivalents of the reagent prevents the full consumption of **2a** and also leads to partial Se-coordination before full conversion to **6a**, additionally hampering the isolation or characterisation of one of the products. The resonances belonging to the P nuclei that are coordinated to a BH_3 unit experience significant downfield shifts and broadening in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum; the latter due to the not resolved $^1J_{\text{P,B}}$ -coupling to the quadrupolar ^{11}B nucleus ($\text{FWHM}(\mathbf{5a}) = 30\text{--}35\text{ Hz}$, $\text{FWHM}(\mathbf{6a}) = 17\text{--}19\text{ Hz}$). Asymmetric products **5a** and **7a** with diastereotopic P nuclei show an, in comparison to *e.g.* **2c**, reduced $^3J_{\text{P,P}}$ -coupling of 6.2 Hz and 6.4 Hz, respectively, which is in accordance with a reduced electron density in the central ring system upon coordination to BH_3 . The competing P- versus Se-borylation corresponds to the calculated FMOs and the close-lying occupied orbitals, made up mainly by the p-type lone pairs of Se or s-type lone pairs of P, respectively. However, BH_3 , being a relatively small and therefore harder Lewis acid, should have a better overlap with the P orbitals, therefore forming a stronger adduct which accounts for the observed main product **6a**. Calculations performed on planar, tricyclic dithions¹⁴² have shown that related S-BH_3 adducts have a relatively weakly bound BH_3 , which should be even more pronounced for the disilone at hand – especially in presence of the additionally competing SMe_2 . Proof of the constitution of the main product and preferred P-borylation was achieved by SCXRD analysis of single crystals grown from a dichloromethane solution at $-30\text{ }^\circ\text{C}$, which revealed to be made up by **6a** (Figure 23).

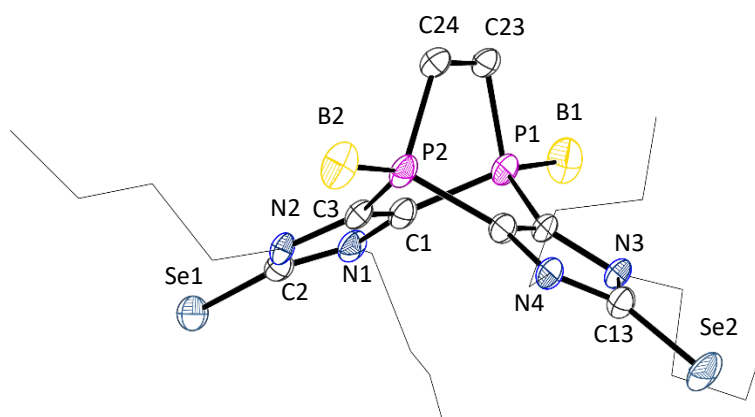
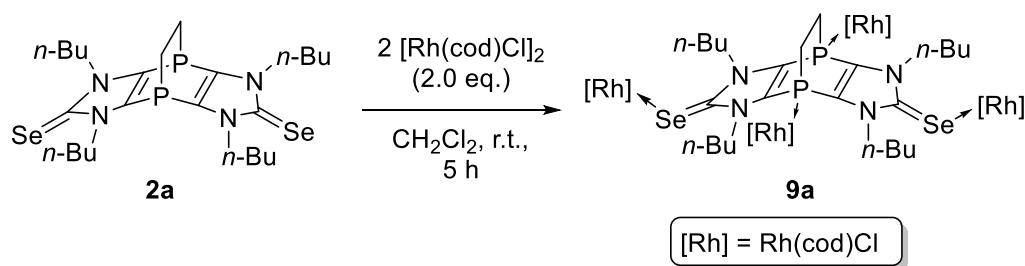


Figure 23. Molecular structure of **6a** in the single crystal. Thermal ellipsoids are set at 50 % probability. Hydrogen atoms and solvent molecules were omitted for clarity. *n*-Butyl chains are simplified as wires for additional clarity.

The additional coordination at the P centres comes with an increased angular sum of 296° on average which is still much smaller than for ideal tetrahedral geometry. With a value of $173.2124(7)^\circ$ the angle between the two P-B bonds is close to a straight angle, and the respective bond lengths are in the range of P-B single bonds, albeit being a little shorter than in BH_3 adducts to *e.g.* PPh_3 ¹⁴³, PMe_3 ¹⁴⁴ or the planar, tricyclic dithion.¹⁴¹ All other structural parameters are almost identical to **2b**.

A final evaluation of 7,8-dihydro-1,4-diphosphabarrelene **2a**'s properties as caged diphosphane in transition metal coordination chemistry was performed by the reaction with $[\text{Rh}(\text{cod})\text{Cl}]_2$ (Scheme 13). Dielmann had shown the synthesis of similar metal complexes with pyrrole-based 7,8-dihydro-1,4-diphosphabarrelenes **XVII**,⁵¹ but metal complexes of imidazole-based 1,4-diphosphabarrelenes have not been reported. The reaction with two equivalents of $[\text{Rh}(\text{cod})\text{Cl}]_2$ in dichloromethane cleanly yields tetranuclear complex **9a**; fewer equivalents do not yield dinuclear, purely Se- or P-coordinated complexes, but mixed complexes with coordination to Se- and P-sites. The emergence of mixed coordination and total coordination to four rhodium fragments is in line with the calculated FMOs (Figure 20) where occupied p-type orbitals at Se and s-type orbitals at P are close in energy.



Scheme 13. Formation of tetranuclear complex **9a** via reaction of **2a** with $[\text{Rh}(\text{cod})\text{Cl}]_2$.

In contrast to the borane used before, the large, electron-rich Rh(I) atom is able to easily coordinate to the Se centres as well. **9a** could be isolated as yellow solid in 73 % yield and fully characterised. The ^{31}P NMR resonance appears significantly highfield-shifted at -21.8 ppm ($\Delta\delta = +72.9$ ppm) with a characteristic $^1J_{\text{Rh,P}}$ -coupling of 167 Hz. Dielmann's related complex shows a similar shift difference of $\Delta\delta = +67.4$ ppm with a smaller $^1J_{\text{Rh,P}}$ -coupling of 151 Hz, which again pronounces the comparably large s-character of the P lone pairs in **2a**. Upon coordination the $^{77}\text{Se}\{^1\text{H}\}$ NMR resonance is shifted to 167.8 ppm with a 21.4 Hz coupling between the ^{103}Rh and ^{77}Se nuclei. The corresponding C-Se nucleus shows a peak at 158.6 ppm in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum, which is almost unchanged in comparison to **2a** but has a significantly decreased coupling constant of only $^1J_{\text{Se,C}} = 209$ Hz due to the decreased electron density in the C-Se bond. The structure of **9a** (Figure 24), determined from SCXRD analysis, confirms the tetranuclear complex of **2a**. Similar to **6a**, the angular sum around P is increased to 290° on average upon coordination to a Rh(I) unit and the two Rh-P bonds form an almost straight angle ($\alpha = 174.0912(2)^\circ$). The lengths of the Rh-P bonds ($d(\text{P1-Rh3}) = 2.2568(16) \text{ \AA}$; $d(\text{P2-Rh4}) = 2.2644(16) \text{ \AA}$) compare well to Dielmann's Rh(I) complex.⁵¹ The additional coordination to the Se centres elongates the Se-C bonds only slightly but induces the overall folding angle of the scaffold to increase to 142° . In comparison to **6a**, the P-C bonds are slightly longer ($d(\text{P1-C39}) = 1.850(8) \text{ \AA}$ vs. $d(\text{P1-C23}) = 1.835(5) \text{ \AA}$ in **6a**, $d(\text{P1-C1}) = 1.813(6) \text{ \AA}$ vs. $d(\text{P1-C1}) = 1.806(5) \text{ \AA}$ in **6a**) and the C-C bonds shorter ($d(\text{C39-C40}) = 1.524(9) \text{ \AA}$ vs. $d(\text{C23-C24}) = 1.538(7) \text{ \AA}$ in **6a**, $d(\text{C1-C3}) = 1.327(8) \text{ \AA}$ vs. $d(\text{C1-}$

C3) = 1.361(7) Å in **6a**); probably due to the increased steric strain of the COD-ligated Rh(I) fragment that widens the immediate phosphorus environment while contracting the connecting C-C bonds.

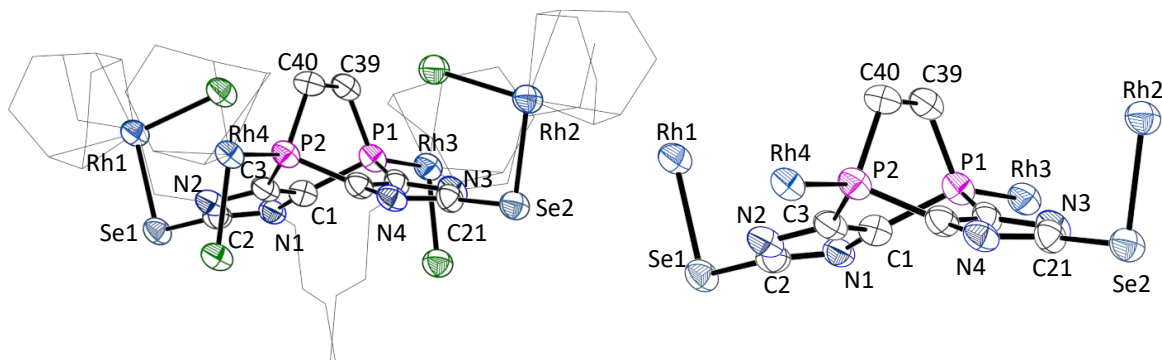
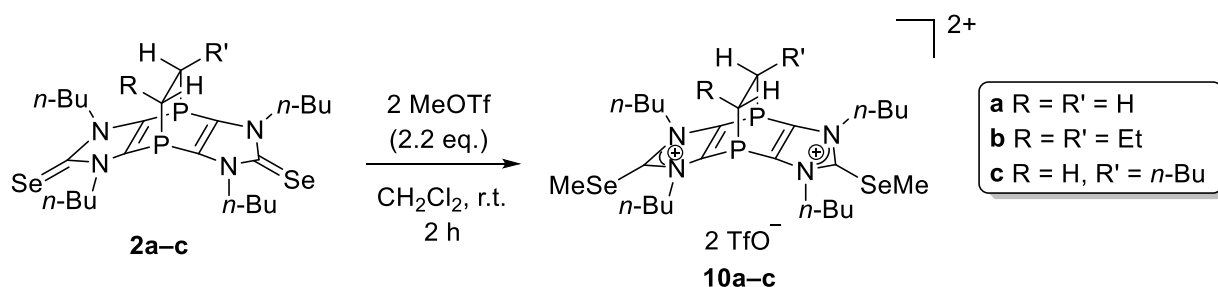


Figure 24. Molecular structure of **9a** in the single crystal (left) and the truncated structure (right). Thermal ellipsoids are set at 50 % probability. Hydrogen atoms and solvent molecules were omitted for clarity. *n*-Butyl chains and COD ligands are simplified as wires (left) or omitted, together with Cl ligands, for additional clarity (right).

3.1.2 Synthesis and reactions of P-bridged rigid, bent bis(imidazolium) salts

3.1.2.1 Synthesis and characterisation of P-bridged, bent bis(imidazolium) salts

The aforementioned FMO situation (Figure 20) not only allows for the formation of metal complexes like **9a** but makes 1,4-diphosphabarrelenes **2** prone for selective methylation at the Se centres and subsequent reductive deselenisation to access new bis(imidazolium) salts. The same approach was successfully applied in the synthesis of planar P-bridged bis(NHCs) before,¹³⁶ and thus was chosen for the bent derivatives as well. **2a–c** were treated with a slight excess of methyl triflate (triflate = trifluoromethane sulfonate) to selectively yield salts **10a–c** without any observed P-methylation (Scheme 14).



Scheme 14. Synthesis of methylated salts **10a–c** from 1,4-diphosphabarrelenes **2**.

10a–c could be isolated as colourless to yellow, sticky solids in good to excellent yields up to 95 %. Upon methylation and salt formation the resonances of the P nuclei shift slightly towards lower field and the P,P-coupling constant in the asymmetric derivative **10c** is slightly reduced in comparison to **2c**. The more significant change is inflicted upon the $^{77}\text{Se}\{^1\text{H}\}$ NMR resonances which are shifted about 75–90 ppm downfield upon change in hybridisation (Table 3). The $^{13}\text{C}\{^1\text{H}\}$ NMR resonances experience a

highfield shift to around 138 ppm and the coupling constant between ^{77}Se and ^{13}C is decreased to 181 Hz which is indicative of the decreased s-orbital involvement in the C-Se bond.

Table 3. Selected NMR data for compounds **10a–c** in CD_2Cl_2 .

	$\delta(^{31}\text{P})$ / ppm	$^3J_{\text{P,P}}$ / Hz	$\delta(^{77}\text{Se}\{^1\text{H}\})$ / ppm	$\delta(^{13}\text{C}\{^1\text{H}\})$ / ppm	$^1J_{\text{Se,C}}$ / Hz
10a	−94.5	−	115.8	138.2	181
10b	−87.0	−	105.8	138.9	181
10c	−91.2, −87.8	16.7	102.8, 103.5	138.3, 138.4	−*

*not observed due to low signal intensity

The structural composition of derivatives **10a** and **10c** could be confirmed via SCXRD analysis but both structures are of low quality and, thus, only **10a** is shown in Figure 25. Although no further structural parameters will be discussed, the methylation increases the N1-C2-N2 angle to 108.0 ° which is a typical value for imidazolium-type structures like the corresponding imidazolium salt to Arduengo's first crystalline carbene⁸⁷ or, *e.g.*, 1,3-dimesitylimidazolium (mesityl = 2,4,6-trimethylphenyl).¹⁴⁵

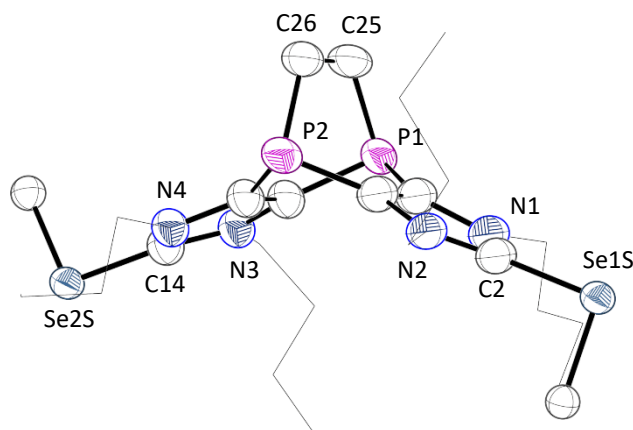
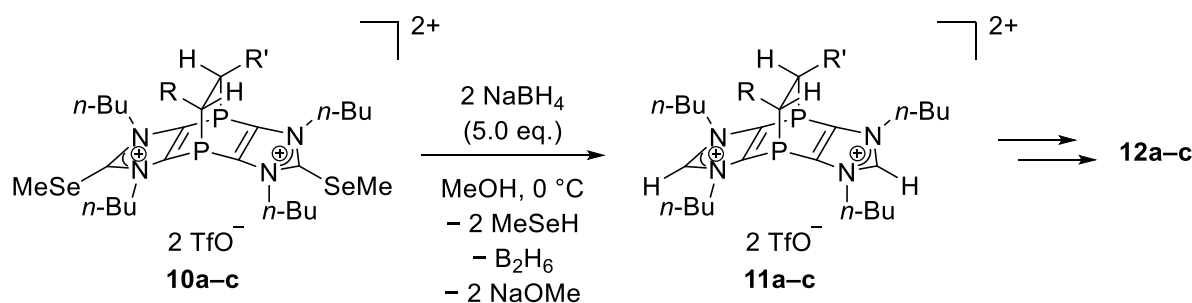


Figure 25. Molecular structure of **10a** in the single crystal. Thermal ellipsoids are set at 50 % probability. Hydrogen atoms and solvent molecules were omitted for clarity. *n*-Butyl chains are simplified as wires for additional clarity.

Compound **10b** could only be isolated containing a small impurity (3 % according to ^{31}P NMR integration) with a ^{31}P NMR resonance of −88.7 ppm and an accompanying proton signal at 8.81 ppm (t , $^4J_{\text{P,P}} = 2.9$ Hz) which fit data expected for the corresponding $\text{C}^2\text{-H}$ imidazolium salt **11b** which will be discussed below. Nevertheless, this already hints towards a strong driving force towards the formation of the imidazolium salts and their inherent stability.

To achieve the synthesis of imidazolium salts **11** that should allow for deprotonation and the formation of bent bis(NHCs) the same protocol that was used for the synthesis of planar, P-bridged bis(imidazolium) salts **LV**¹³⁶ was applied (Scheme 15).



Scheme 15. Synthesis of methylated salts **10a-c** from 7,8-dihydro-1,4-diphospha-barrelenes **2**.

Initial studies on derivative **10c**, which carries the additional information of the $^3J_{P,P}$ -coupling constant, in the reaction with sodium borohydride in methanol show that the desired product **11c** was formed in the reaction solution. This was indicated by a slight highfield shift of the $^{31}\text{P}\{^1\text{H}\}$ NMR signals ($\delta(^{31}\text{P}\{^1\text{H}\}) = -92.9, -90.0$ ppm) and a diminished $^3J_{P,P}$ -coupling constant of 16.0 Hz. However, upon evaporation of the solvent *in vacuo* a new set of signals at -73.7 ppm (d, $^3J_{P,P} = 3$ Hz) and 80.8 ppm (d, $^3J_{P,P} = 3$ Hz) appeared belonging to a decomposition product **12c** that could not be separated from the desired **11c** and remained as main product after an attempted work-up via extraction with dichloromethane (Figure 26).

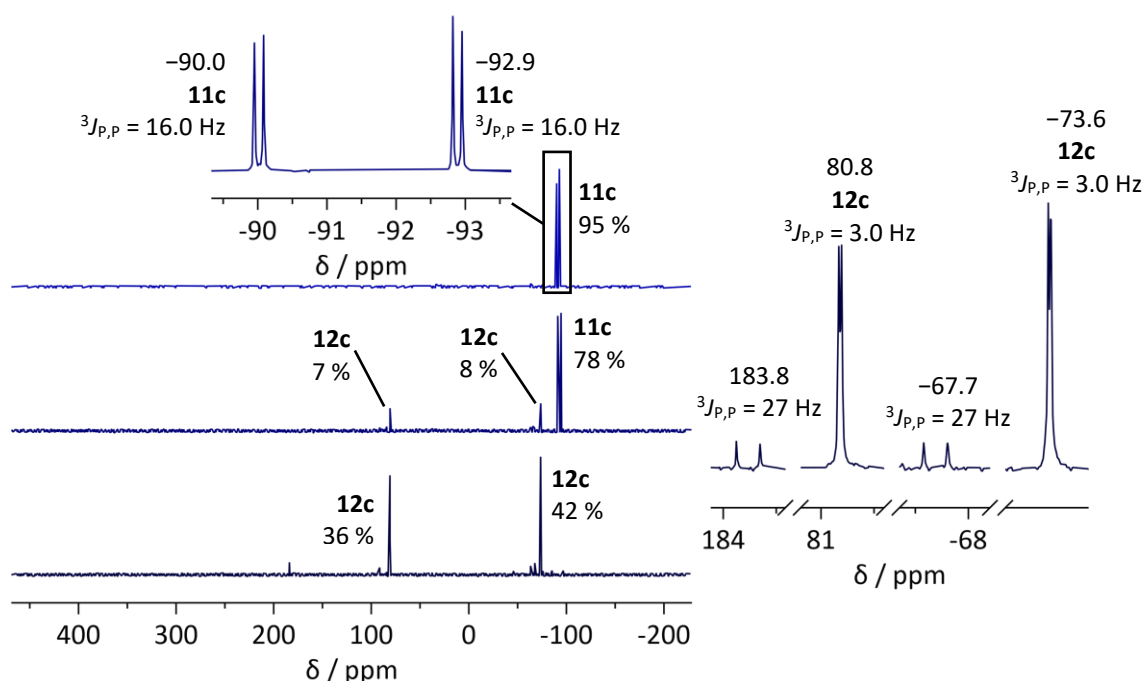
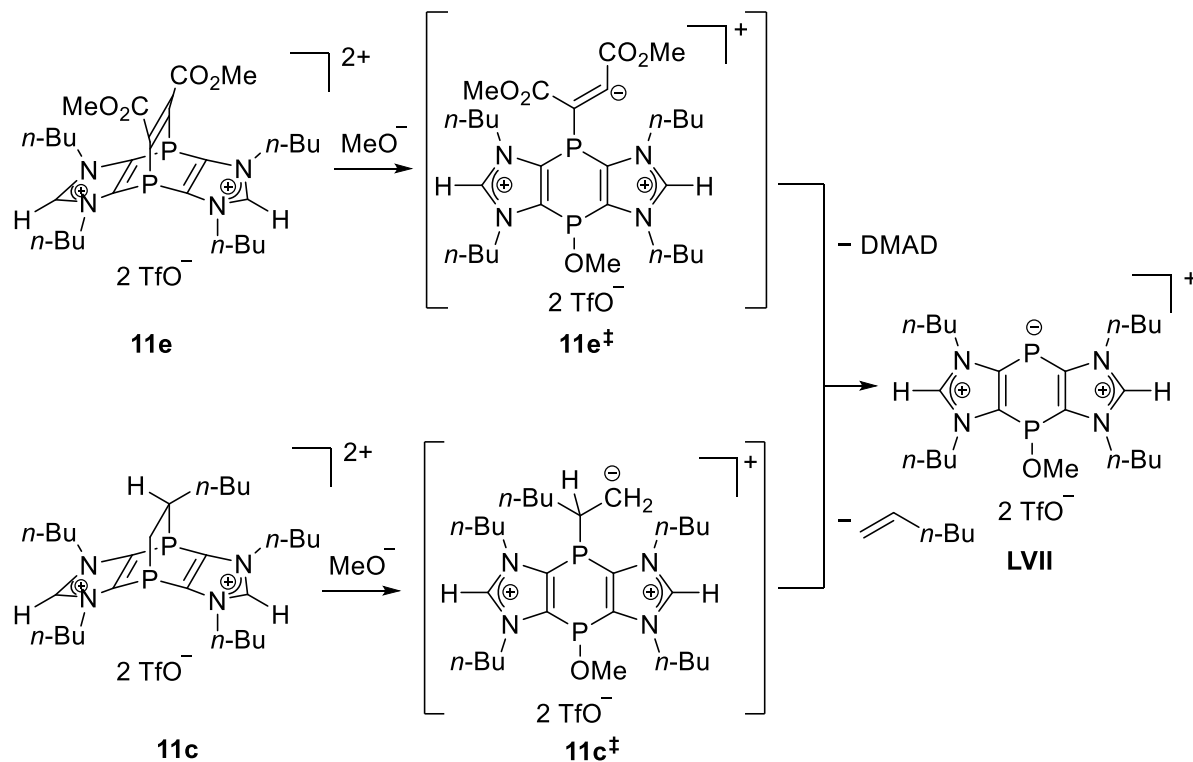


Figure 26. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **10c** with NaBH₄ in reaction mixture in methanol (top, + magnification above), after solvent evaporation in CH₂Cl₂ (middle) and after extraction attempt in CH₂Cl₂ (bottom, + magnification on the right).

A previous attempt on this reaction sequence with derivative **10e** with ten equivalents of NaBH₄ yielded a similar, albeit slightly different outcome.¹³⁷ The bridge was cleaved off via an unidentified

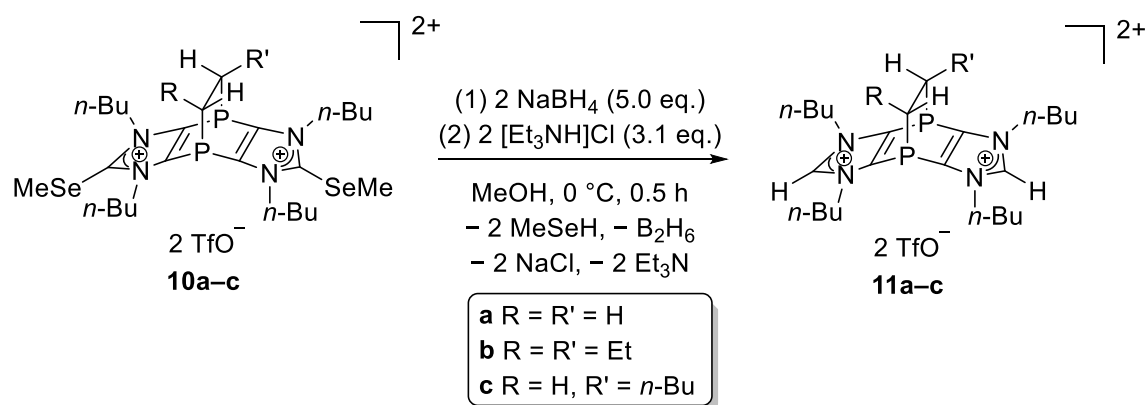
mechanism and the final product with $^{31}\text{P}\{^1\text{H}\}$ NMR resonances at -20.2 and -67.2 ppm ($^3J_{\text{P,P}} = 2.1$ Hz) was confirmed to be planar, P-anionic bis(imidazolium) salt **LVII**. The highfield-shifted $^{31}\text{P}\{^1\text{H}\}$ NMR signal for **12c** ($\delta(^{31}\text{P}\{^1\text{H}\}) = -73.6$ ppm) could also belong to an anionic (or alkyl substituted) phosphorus centre which could only result after a bridge-opening or -removal. Furthermore, the very small $^3J_{\text{P,P}}$ -coupling constant is very typical for a planar, tricyclic scaffold with one anionic phosphorus centre and P,P-coupling constants of that magnitude have never been observed for any 1,4-diphosphabarrelenes. Hence, the most likely reaction mechanism involves a bridge-opening by the strongly nucleophilic methoxide anion which is formed in the reaction mixture from the solvent methanol and NaBH_4 . The belonging signal at 80.8 ppm is untypically downfield-shifted for a 1,4-dihydro-1,4-diphosphinine, close to the resonance of the two-coordinate phosphorus centre in **1** and does not belong to the P-OMe functionality in **LVII**. Assuming the same mechanism of a bridge-opening for the 7,8-dihydro-14-diphosphabarrelenes **11a–c** as for 1,4-diphosphabarrelene **11e**, the first product in all cases is a carbanion **11[±]** that is highly destabilised for derivative **e** (Scheme 16, top). This could result in the elimination of DMAD yielding the observed final product **LVII** with one anionic phosphorus centre. Although the primary carbanion formed in case of **11c** is less destabilised, attempted geometry optimisations in theoretical calculations on the intermediate only yielded **LVII** and 1-hexene indicating that the alkene elimination might be the preferred reaction pathway here, too (Scheme 16, bottom).



Scheme 16. Formation of bridge-opening products from bis(imidazolium) salts **11e** (top) and **11c** (bottom) with the

Taking into account the very similar product formed without the presence of the nucleophile methoxide but a hydride anion in chapter 3.1.3.1, a product that does not contain the methoxy functionality is very probable. The fundamental difference between **11c** and **11e** is that **11c** possesses a saturated bridge which could be deprotonated ($\Delta\Delta G^\circ = -40.8 \text{ kcal mol}^{-1}$) to eventually also yield an anionic phosphorus centre that would fit the $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopic resonance at -73.6 ppm . However, the other phosphorus centre would still be alkyl-substituted which does not explain the downfield-shifted signal of **12c**, so a more complicated reaction sequence with the different reagents in solution, following a nucleophilic attack or deprotonation, can be assumed. Unfortunately, **12c** could not be separated from all side products and proved to decompose to unselective mixtures after some time which prevented the unambiguous identification of it.

Since the decomposition products seem to be the consequence of the presence of the *in situ* formed methoxide, the synthesis was optimised by the addition of a quenching reagent before removing the solvent *in vacuo*. For that, triethylammonium chloride was chosen as it would only yield triethylamine and sodium chloride as side products that should not interact with **10** or **11**, and was added after the gas evolution in the reaction mixture had stopped (Scheme 17).



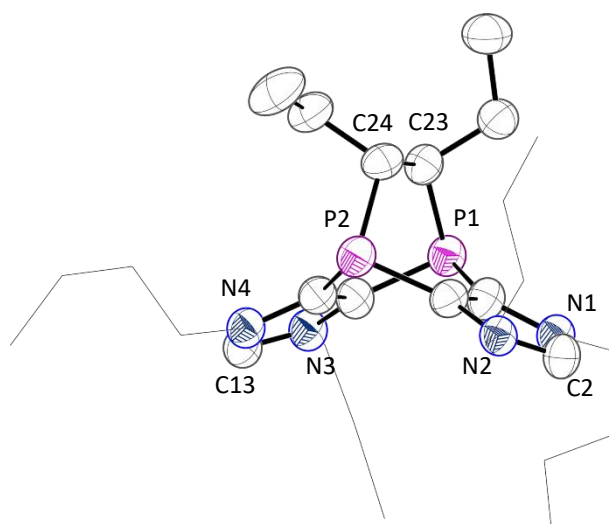
Scheme 17. Optimised synthesis of bis(imidazolium) salts **11a-c** via reduction of **10** using [Et₃NH]Cl as quenching reagent.

Bis(imidazolium) salts **11** could be isolated in good yields after consecutive extraction with tetrahydrofuran and dichloromethane to remove NaCl, NaOMe and residual [Et₃NH]Cl. Similarly to **10** they are present as very sticky, colourless to yellow solids at ambient temperature. In the ^{31}P NMR spectrum the transformation is indicated by a slight highfield shift of the resonance(s) and a decreased $^3J_{\text{P,P}}$ -coupling of 16.0 Hz between the two diastereotopic P nuclei in the asymmetric derivative **11c**. The reduced coupling constant in comparison to **2c** corresponds to the formation of the imidazolium units which act as electron-withdrawing substituents to the central 1,4-diphosphabarrelene. Proof of the reductive deselenisation is given by the resonance signals for the introduced C²-H atoms around 9 ppm, which showed a typical $^4J_{\text{P,H}}$ -coupling of circa 3 Hz (Table 4).^{81,137}

Table 4. Selected NMR data for compounds **11a–c** in CD₂Cl₂.

	$\delta(^{31}\text{P})$ / ppm	$^3J_{\text{P,P}}$ / Hz	$\delta(^1\text{H}(\text{C}^2\text{-H}))$ / ppm	$^4J_{\text{P,H}}$ / Hz	$\delta(^{13}\text{C}\{^1\text{H}\}(\text{C}^2))$ / ppm
11a	−97.4	−	8.93	3.0	138.8
11b	−90.4	−	9.03	2.9	139.6
11c	−94.4, −91.0	16.0	8.88, 9.06	2.9	138.8, 139.4

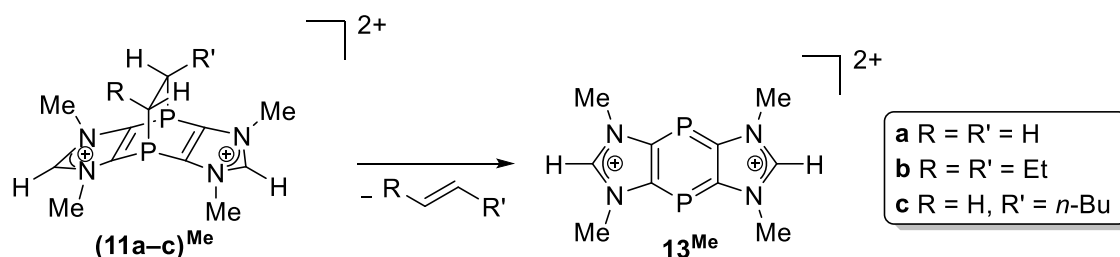
Both derivatives **11a** and **11b** could be crystallised and their structure was confirmed via SCXRD analysis. Unfortunately, **11a** only produced single crystals of poor quality and, hence, only the structure of **11b** is shown (Figure 27) and discussed. Most notably, the N1-C2-N2 angle is increased to almost 110 ° ($\angle(\text{N1-C2-N2}) = 109.7(6)^\circ$) which holds as proof for the formed imidazolium unit. The angle sum around P averages to $\sum \angle(\text{P}) = 282^\circ$ which is similarly constrained in comparison to **2b**, while all other bonds and angles experience no significant change.

**Figure 27.** Molecular structure of **11b** in the single crystal. Thermal ellipsoids are set at 50 % probability. Hydrogen atoms and OTf anions were omitted for clarity. n-Butyl chains are simplified as wires for additional clarity.

Bis(imidazolium) salts **11** show remarkable stability towards oxygen and water and can be stored under air for several days without change in composition. The constrained P environment which – besides the electronic situation of the large s-character lone pair – also prevents full conversion in the oxidation reaction with selenium and the coordination to borane, might prohibit a fast reaction with water and oxygen from the air. The imidazolium units which are known to be stable scaffolds are not heavily influenced by the annulation to the 1,4-diphospha-barrelenes. NICS(1) calculations on the B3LYP-D4/CPCM_{THF}/def2-TZVPPD//TPSS-D4/CPCM_{THF}/def2-TZVP level of theory (for further information see 5.2.9; reference NICS(1)(benzene) = −9.9 ppm, (NICS(1)(1,3-dimethylimidazolium) = −9.4 ppm) confirm aromaticity levels of up to 96 % of benzene or 99 % of 1,3-dimethylimidazolium which could contribute to the inherent stability of **11**.

3.1.2.2 Retro-[4+2]-cycloaddition and theoretical investigations

Furthermore, for **11** a thermal retro-[4+2]-cycloaddition is not feasible under the conditions that were applied to **2** to form back 1,4-diphosphinine **1**, and according to $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR spectra **11a–c** remain unchanged in solution. The prevented back reaction can be understood when looking at the reaction mechanism and the involved FMOs of the reaction in Scheme 18, as was done before for the reaction from **1** to **2**, and vice versa.



Scheme 18. Retro-[4+2]-cycloaddition of **11**^{Me} that was investigated by theoretical calculations.

The reaction mechanism still involves the LUMO of the corresponding alkene but as the 1,4-diphosphinine scaffold changes to bis(imidazolium) salt **13**^{Me} the participating π -type MO at the P centres is now the HOMO (Figure 28).

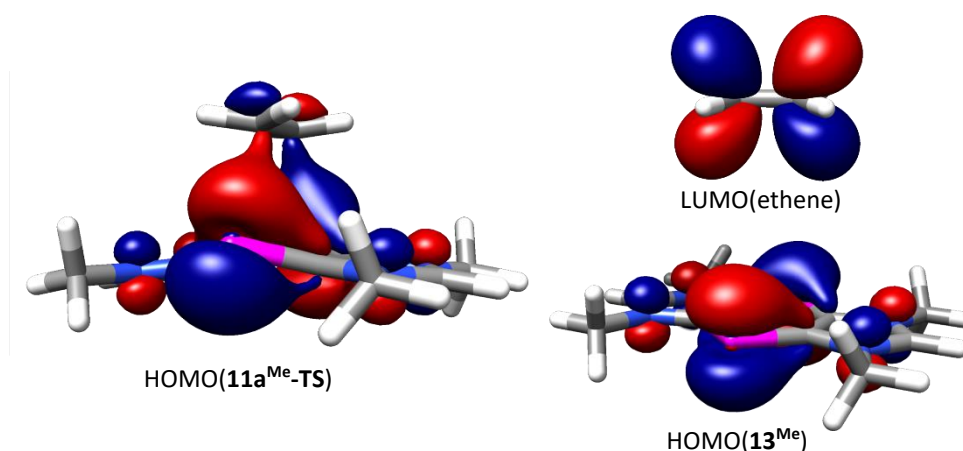
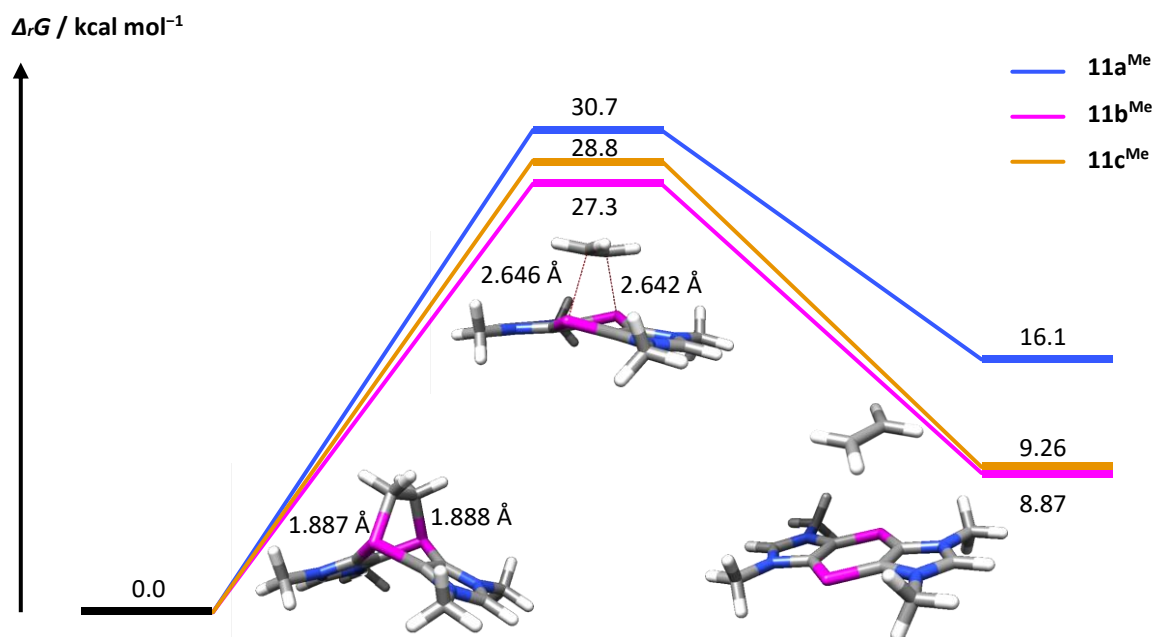


Figure 28. FMOs involved in the concerted step of the retro-[4+2]-cycloaddition reaction to form **13**^{Me} from **11a**^{Me}.

No experimental equivalent to **13**^{Me} could be synthesised so far, although the low-lying HOMO, centred around the two P centres, might enable new and interesting properties that will be further discussed in chapter 3.4. Table 5 and Figure 29 show Gibbs reaction energies, including the reaction barriers, which fall in line with the fact that no retro-[4+2]-cycloaddition was observed for any of the bis(imidazolium) salt derivatives **11a–c**.

Table 5. Gibbs reaction energies and LUMO(alkene/alkyne)–HOMO(**13**^{Me}) energies for the formation of model compounds **13**^{Me} from (**11a–c**)^{Me}.

	$\Delta\Delta_r G^\circ$ / kcal mol ⁻¹	$\Delta\Delta_r G^\ddagger$ / kcal mol ⁻¹	$E_{\text{LUMO-HOMO}}$ / eV
11a ^{Me}	16.1	30.7	8.14
11b ^{Me}	8.87	27.3	8.53
11c ^{Me}	9.26	28.8	8.41

**Figure 29.** Gibbs reaction energies and transition state barriers for the retro-[4+2]-cycloaddition of model compounds (**11a–c**)^{Me}. Exemplary structures are given for **11a**^{Me}.

All reactions are endergonic with up to 16 kcal mol⁻¹ for **11a**^{Me}, which is accompanied by reaction barriers that are higher than for the formation of (**2a–c**)^{Me}. Although elevated temperatures of up to 110 °C should be sufficient to overcome these barriers, there is no driving force. The fact that the involved MO of the 1,4-diphosphinine scaffold is now the HOMO and more easily accessible is enough to drive the hypothetical reaction towards the 1,4-diphosphabarrelenes – despite the relatively large gap between the two interacting MOs of alkene and 1,4-diphosphinine.

To further explore the observed and expected stability as well as reactivity of **11** the FMO situation of (**11a–c**)^{Me} up until those MOs that include the P lone pairs is depicted in Figure 30. First of all, the LUMOs resemble those of (**2a–c**)^{Me} being embedded in the central P ring system which probably contributes to the stability of the scaffold – apart from the observed nucleophilic opening by relatively small and hard nucleophiles like the methoxide anion in protic solvents. Secondly, the HOMO-LUMO gap is significantly larger than for (**2a–c**)^{Me} (e.g. $\Delta E_{L-H}(\mathbf{2a}^{\text{Me}}) = 4.56$ eV vs. $\Delta E_{L-H}(\mathbf{11a}^{\text{Me}}) = 6.24$ eV) which lends additional stability to the bis(imidazolium) salts. The HOMO and HOMO–1 constitute two almost

degenerate MOs: one being a π^* -type orbital across the imidazolium rings and one with large contribution of the P lone pairs. The electronic accessibility of the lone pairs enables the further study of the donor ability of the caged diphosphane after the quite significant change to the outer imidazole rings going from **2** to **11**.

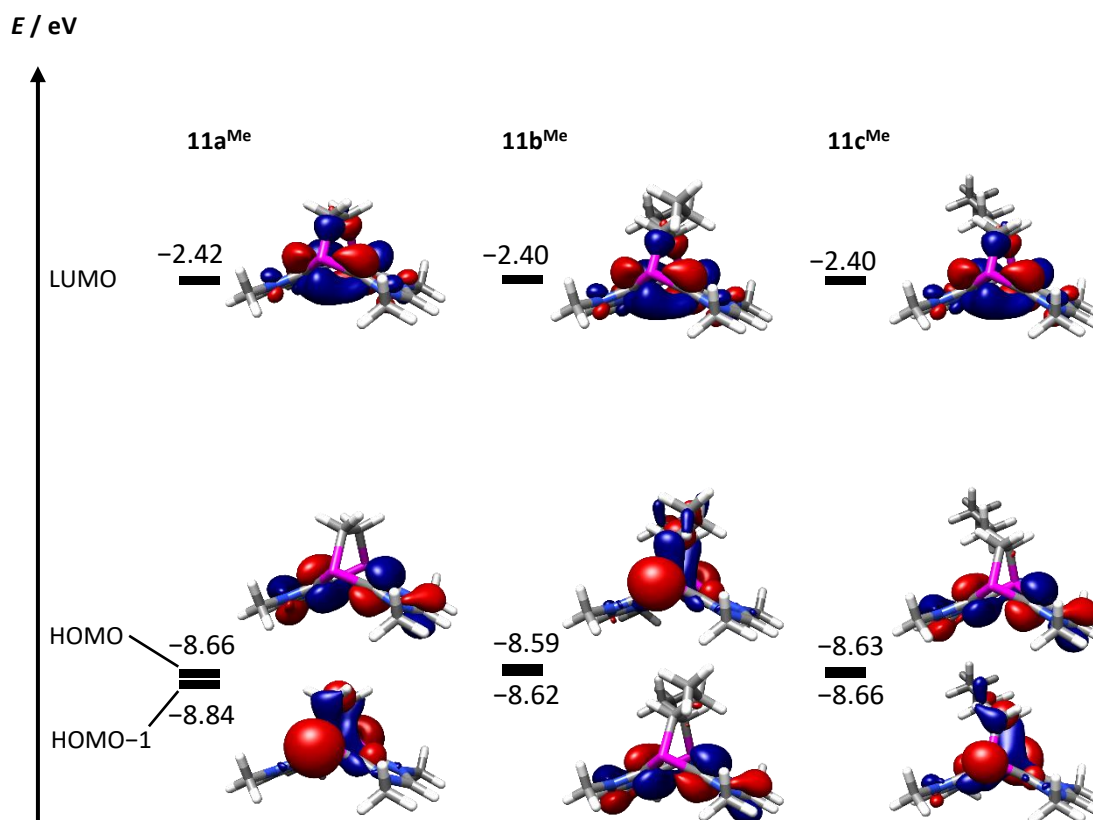
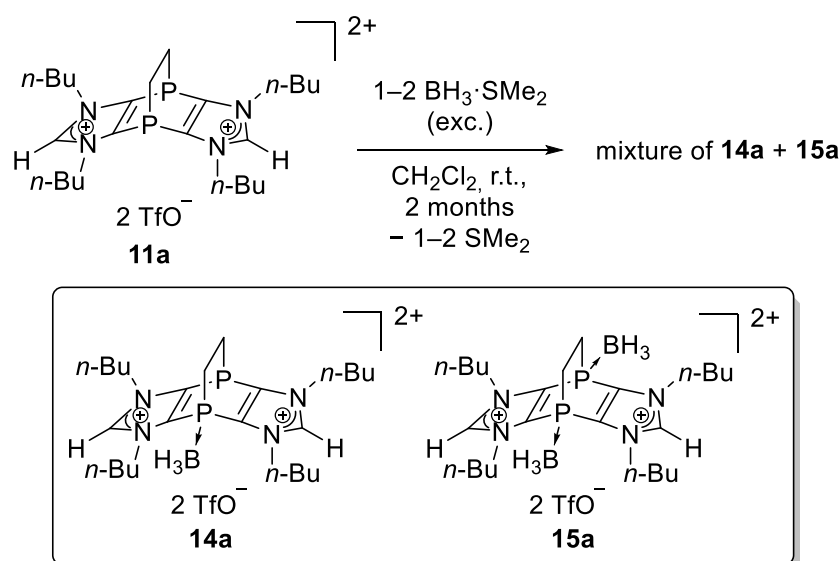


Figure 30. Selected calculated FMOs of compounds (**11a–c**)^{Me}.

3.1.2.3 Experimental investigation on the P-donor ability

Again, derivative **11a** was chosen to perform experiments exploring the donor and coordination ability of the bent bis(imidazolium) salts as it possesses the least steric hindrance around the P centres. Analogously to the investigation of **2a**, **11a** was submitted to an excess of the borane dimethylsulfide adduct to achieve the synthesis of twofold P-borane adduct **15a** (Scheme 19). $^{31}\text{P}\{^1\text{H}\}$ NMR monitoring of the reaction mixture showed that after four days the reaction solution contained 61 % of **14a**, together with only around 2 % of **15a** and 36 % starting material **11a**. The amounts in solution did not change over the course of two months, even after heating and addition of more $\text{BH}_3\cdot\text{SMe}_2$. Nevertheless, the final mixture with slightly different ratios after removal of the solvent *in vacuo* and washing with *n*-pentane was characterised via NMR spectroscopy.



Scheme 19. Reaction of **11a** with $\text{BH}_3 \cdot \text{SMe}_2$ yielding a mixture of BH_3 adducts **14a** and **15a**.

The ^{31}P NMR spectrum revealed 26 % starting material **11a** at -97.6 ppm and 68 % of the mono- BH_3 adduct **14a** at -98.0 and -13.3 ppm. As for **5a** and **7a** the mono-coordination comes with a slight high-field shift for the trivalent P centre and a significant downfield shift for the coordinated P centre. Furthermore, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the respective highfield signal is resolved with a $^3J_{\text{P,P}}$ -coupling of 5.8 Hz which is slightly smaller than for **5a** or **7a**, thus being in line with the trend observed going from **2c** to **11c**. The di-coordinated product **15a** is formed with only approximately 3 % showing a resonance at -14.7 ppm in the ^{31}P NMR spectrum. This is in strong contrast to the formation of the two-fold P-coordinated product **6a** in the reaction with the diselone **2a**, which made up the majority of the reaction mixture. The annulation of the central 1,4-diphosphabarrelene to two imidazolium units withdraws so much electron density that the donor ability of the largely s-type character lone pairs is decreased even further, hampering the quantitative formation of **14a** as well as significant formation of **15a** and thus, favouring the used dimethylsulfide adduct. Interestingly, borane adducts of planar, *P*- NEt_2 substituted bis(imidazolium) salts **LV** via the same route are easily formed quantitatively. In contrast to **11**, the lone pairs at P have a higher p-orbital contribution and an additional interaction with the flexible *P*- NEt_2 unit might be possible to enhance the feasibility of the coordination to BH_3 . The formation of **14a** as main product could also be confirmed via analysis of a single crystal grown from the reaction mixture in dichloromethane (Figure 31). The angular sum around the P that carries the borane adds up to 295° which is almost identical to the one in twofold BH_3 adduct **6a** – the same holds true for the P-B bond. The other P centre remains in an unchanged, constrained environment with an angular sum of 283° , while the imidazolium unit stays intact as well ($\angle(\text{N1-C7-N2}) = 110.0(5)^\circ$).

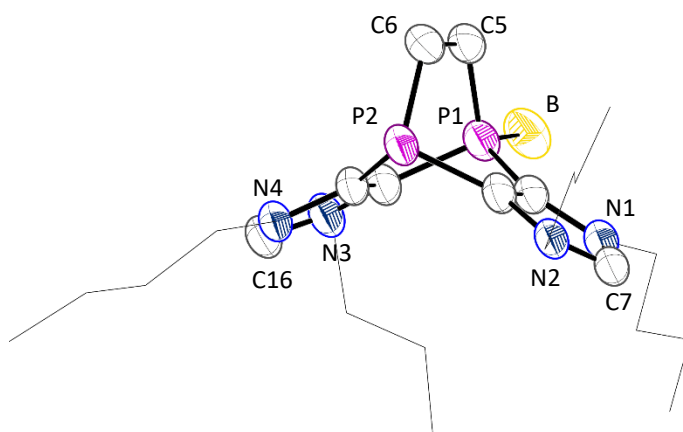
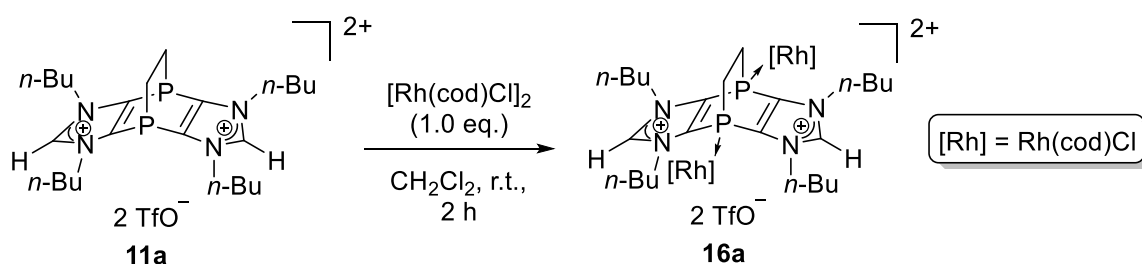


Figure 31. Molecular structure of **14a** in the single crystal. Thermal ellipsoids are set at 50 % probability. Hydrogen atoms and OTf anions were omitted for clarity. *n*-Butyl chains are simplified as wires for additional clarity.

Although the reaction with the borane dimethylsulfide adduct already revealed the bis(imidazolium) salt **11a** to be a worse P-donor than the respective diselone **2a**, **11a** was furthermore reacted with $[\text{Rh}(\text{cod})\text{Cl}]_2$ which had proven before to coordinate more easily to the diphosphane. Saturating both P centres with transition metal fragments also hold the possibility of hetero-tetratopic coordination if the corresponding bis(NHCs) could be formed in a later step, which made the reaction shown below particularly interesting (Scheme 20).



Scheme 20. Reaction of **11a** with $[\text{Rh}(\text{cod})\text{Cl}]_2$ yielding dinuclear complex **16a**.

As expected, the electron-rich rhodium fragments coordinate much better to the P centres in **11a** and the reaction is complete after only two hours. The product **16a** could be isolated as yellow solid and fully characterised. While the ^{31}P NMR spectrum shows a simple doublet with broad resonances at -24.7 ppm with a $^1J_{\text{Rh,P}}$ -coupling of approximately 168 Hz, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum in CD_2Cl_2 shows a more complicated multiplet of two overlaying doublets of doublets. After simulating the multiplet signal with *gNMR*¹³⁹ (Figure 32) it could be confirmed that the observed pattern stems from in total four different Rh,P-coupling constants ($2 \times ^1J_{\text{Rh,P}}$; $2 \times ^4J_{\text{Rh,P}}$) as the coupling to the two P centres is slightly different on each side. The proton coupled spectrum does not resolve the coupling and thus, only reports an average Rh,P-coupling.

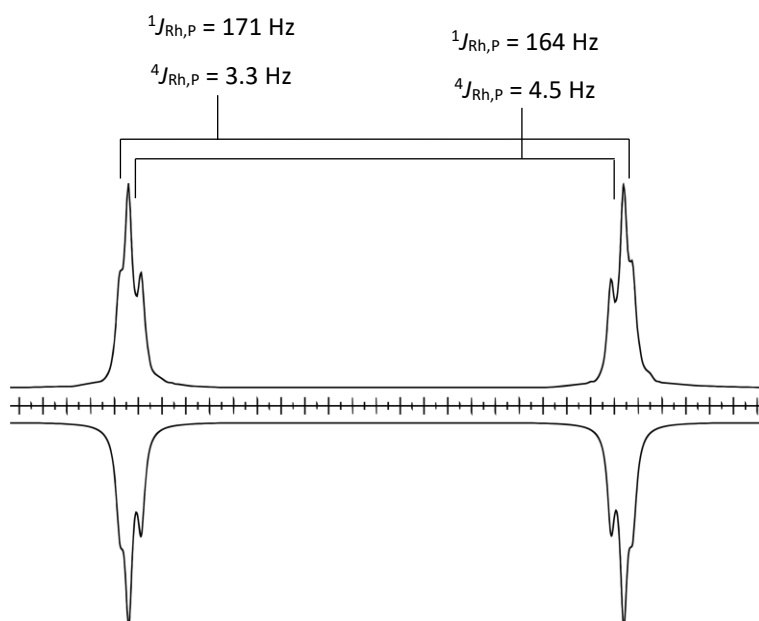


Figure 32. Experimental $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **16a** (top) and simulated spectrum (bottom).

The $\Delta\delta$ of 72.7 ppm as well as the Rh,P-coupling are almost identical to the values obtained for the tetranuclear complex **9a**. The resonance for the C^2 -H protons in the ^1H NMR spectrum is slightly highfield-shifted to 8.55 ppm with a slightly increased $^4J_{\text{P,H}}$ -coupling of 3.3 Hz. Fortunately, **16a** could also be analysed via SCXRD which confirmed the dinuclear complex and resulted in the structure depicted in Figure 33.

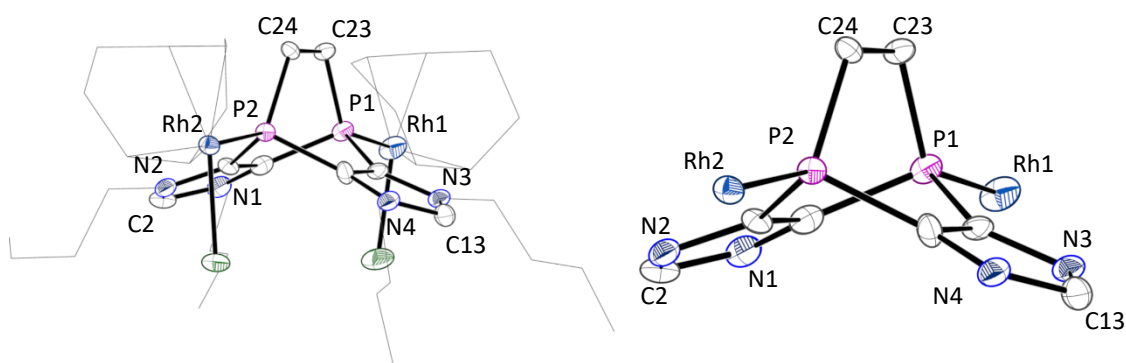


Figure 33. Molecular structure of **16a** in the single crystal. Thermal ellipsoids are set at 50 % probability. Hydrogen atoms, solvent molecules and OTf anions were omitted for clarity. *n*-Butyl chains and COD ligands are simplified as wires (left) or omitted, together with Cl ligands, for additional clarity (right).

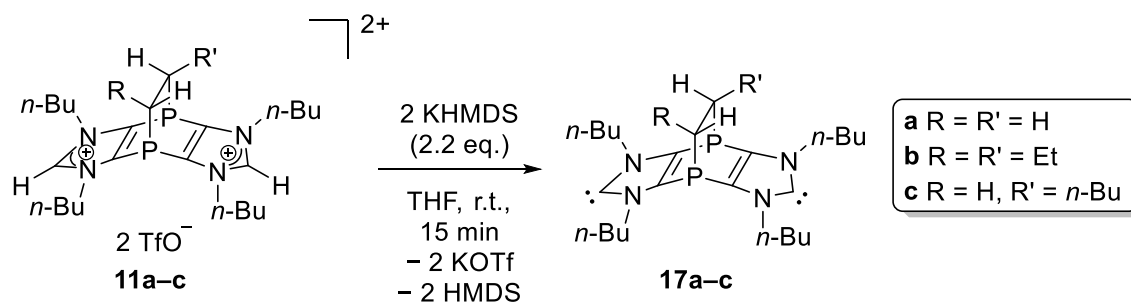
The angular sum around the P centres averages to 292° , which is similarly increased as in mono- BH_3 adduct **14a** and tetranuclear Rh(I) complex **9a**. In contrast to **6a** and **9a**, the two opposing Rh-P bonds deviate by about 16° ($\angle(\text{Rh1-P1})\text{--}(\text{Rh2-P2}) = 15.7882(12)^\circ$) and the overall folding angle is widened to 130° upon the increase in steric bulk through the rhodium fragments. As for **14a**, the imidazolium units remain unaltered and are not influenced by the manipulation at the central 1,4-diphosphabarrelene ($\angle(\text{N1-C2-N2}) = 110.3(9)^\circ$).

16a suffers from an, in comparison to **11a**, relatively low solubility in dichloromethane and tetrahydrofuran. However, dissolving **16a** in deuterated acetonitrile yielded a slightly better signal-to-noise ratio for the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, but also a significant amount (26 %) of mononuclear Rh(I) complex. Removing the solvent *in vacuo* and redissolving in deuterated dichloromethane reinstated the NMR spectrum of pure **16a**, thus confirming that the bis(imidazolium) salt is a poor donor and is partially replaced by acetonitrile when providing the latter in excess.

3.1.3 Synthesis and first investigations of rigid, bent bis(NHCs)

3.1.3.1 Synthesis and characterisation of rigid, bent bis(NHCs)

After the successful synthesis of bis(imidazolium) salts **11**, their deprotonation to yield rigid, bent bis(NHCs), which – due to their unique structure – potentially carry new properties when compared to previously reported planar P-bridged bis(NHCs), was targeted.^{136,81,137} Potassium hexamethyldisilazide (KHMDs) had proven to be a suitable base for the deprotonation of P-bridged bis(imidazolium) salts as it is a strong, but only weakly nucleophilic base and thus, was employed in the synthesis of bis(NHCs) **17a–c** as well (Scheme 21).



Scheme 21. Deprotonation of **11** with KHMDs yielding bis(NHCs) **17**.

In contrast to planar bis(NHCs) **LII–LIV**, the deprotonation reaction could be performed at ambient temperature under immediate slight darkening of the solution and visible formation of partially insoluble potassium triflate. In all cases the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum showed a clean conversion after only 15 minutes in a fast and selective reaction, which is shown below at the example of **17c** (Figure 34, top). The formation of **17c** as deprotonation product is indicated by a slight downfield shift of the two doublets as well as an increased $^3J_{\text{P,P}}$ -coupling of over 19 Hz. Potassium *tert*-butoxide as similarly strong and weakly nucleophilic base performs the reaction equally well, while sodium hydride yields a less selective reaction outcome (Figure 34, bottom). The main side product **18c** with about 23 % is characterised by two doublet resonances at –76.1 and 61.6 ppm with a $^3J_{\text{P,P}}$ -coupling of 4.3 Hz. The shift and coupling are similar to **12c**, side product in the reduction reaction of **10c**, also including a small, strong

nucleophile like the hydride in this case, and, thus, a similar structure can be assumed. An either nucleophilic bridge-opening or deprotonation in the bridge, followed by bridge-opening, could account for an anionic phosphorus centre with a $^{31}\text{P}\{^1\text{H}\}$ NMR shift of -76.1 ppm. As for the 7,8-dihydro-1,4-diphosphabarrelene scaffold the formation of imidazol-2-ylidene units from the imidazolium salts slightly increases the $^3J_{\text{P,P}}$ -coupling constant in the central ring. Despite the unclear nature of the phosphorus centre belonging to the downfield- $^{31}\text{P}\{^1\text{H}\}$ NMR resonance, the imidazolium units should also exhibit a more pronounced electron-withdrawing effect on the central ring which could explain the highfield shift of almost 20 ppm in **18c** compared to **12c**. In conclusion, smaller, more nucleophilic bases are unfitting for the deprotonation of **11**.

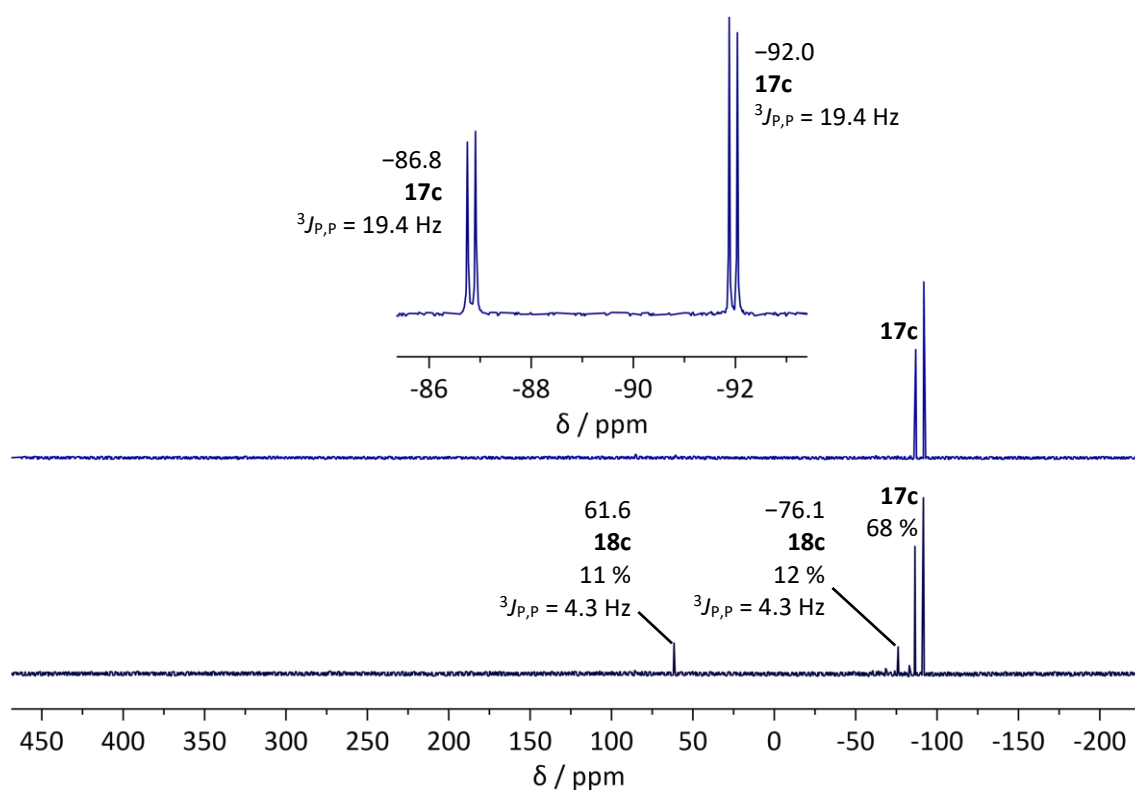


Figure 34. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the reaction solution of **11c** with KHMDS in THF (top) and with NaH in THF (bottom).

Bis(NHC) **17a** could be isolated as a beige solid after extracting the reaction mixture with toluene and washing with *n*-pentane at low temperature after solvent evaporation *in vacuo*. In cases of **17b** and **17c**, which carry alkyl substituents at the carbon bridge that increase the solubility, orange, sticky to oily solids could be isolated, that still contained traces of grease and HMDS (hexamethyldisilazane), that remained even after hours of drying at 0.005 mbar. All bis(NHCs) were characterised by suitable methods according to their purity.

NMR spectroscopic data (Table 6) show a slight downfield shift of the ^{31}P NMR resonances in comparison to the salts **10** and **11** and almost identical values as diselones **2**. Additionally, asymmetric derivative **17c** is characterised by an increased $^3J_{\text{P,P}}$ -coupling that could later be used to distinguish between salt-like structures like **11c** and NHC-like structures like **17c**. Notably, all derivatives show C^2 -resonances in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum that appear around 220 ppm and, for **17c**, a $^3J_{\text{P,C}}$ -coupling of circa 3 Hz can be assigned. The values are very well in accordance with previously reported P-bridged bis(NHCs)^{136,81} and, *e.g.*, Arduengo's *N*-mesityl-substituted mono(NHC)(= IMes).¹⁴⁶ The C^2 -resonances of Ruiz' mono- or di- C-PPh_2 -substituted mono(NHCs) appear only slightly more highfield-shifted at 204 and 208 ppm, respectively.

Table 6. Selected NMR data for compounds **17a–c** in THF- d_8 (**17a**) or C_6D_6 (**17b,c**).

	$\delta(^{31}\text{P})$ / ppm	$^3J_{\text{P,P}}$ / Hz	$\delta(^{13}\text{C}\{^1\text{H}\})(\text{C}^2)$ / ppm	$^3J_{\text{P,C}}$ / Hz
17a	−94.8	−	220.2	−*
17b	−86.2	−	218.4	−*
17c	−92.0, −86.4	19.7	219.9, 220.5	2.7, 3.0

*not observed due to low signal intensity

Fortunately, the structures of **17b** and **17c** could be confirmed via SCXRD analysis (Figure 35) and **17b**'s is of sufficient quality to discuss structural parameters.

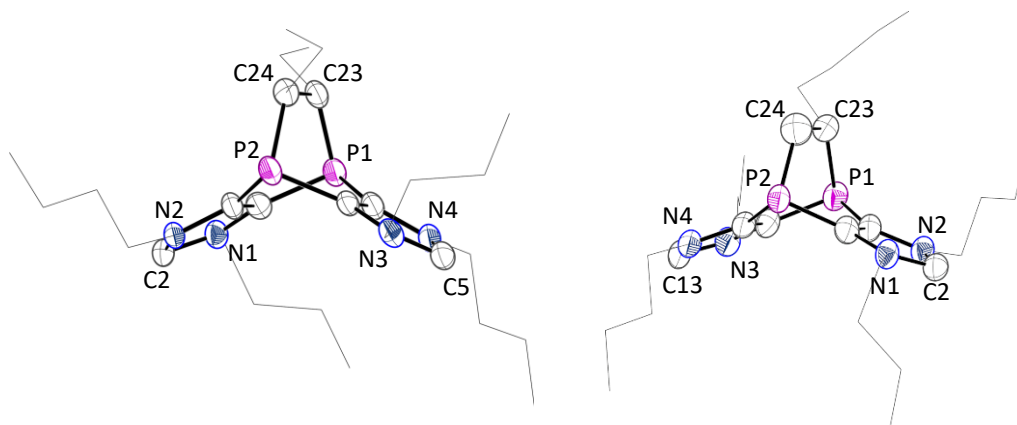


Figure 35. Molecular structure of **17b** (left) and **17c** (right) in the single crystal. Thermal ellipsoids are set at 50 % probability. Hydrogen atoms were omitted for clarity. *n*-Butyl and ethyl chains are simplified as wires for additional clarity.

The two P centres in **17b** are equally constrained as in **2b** with an average angle sum of 286 ° and the overall folding angle is similar, as well ($\angle(\text{C2-P1-P2-C15}) \approx 123^\circ$). The crucial difference can be found in the imidazole-2-ylidene angle which is now decreased to less than 103 ° which is the expected change going from the imidazolium salt to the NHC ($\angle(\text{N1-C2-N2}) = 102.7(4)^\circ$). None of the other bond

lengths and angles experience a significant change – confirming the rigidity of the scaffold over the course of reactions from diselone to bis(NHC).

In contrast to planar, P-bridged bis(NHCs) **LII**, **17a** does not show any redox processes in cyclovoltammetric studies performed in THF which was the only suitable solvent as bis(NHCs) **17** decompose in dichloromethane and acetonitrile. This is reasonable, as calculations at the PW6B95-D4/CPCM_{THF}/def2-QZVP//TPSS-D4/CPCM_{THF}/def2-TZVP level of theory assign the main contribution of the LUMO to HOMO–1 around the P–N bond of **LII** (see chapter 3.3.1.1) which is replaced by the 7,8-dihydro-1,4-diphosphabarrelene unit in **17a**.

All bis(NHCs) **17a–c** change their colour irreversibly at ambient temperature when stored under inert gas, going from beige or orange, respectively, to seemingly black in colour within 24 hours and thus, have to be stored at temperatures below 0 °C. Possible explanations for the observed behaviour will be discussed in chapter 3.1.3.3.

3.1.3.2 Theoretical investigations on the P-donor ability

There are several non-experimental ways to assess the properties of the new bis(NHCs) and the influence of the P-substitution in the backbone as well as its unique scaffold. First, the analysis of the ⁷⁷Se NMR characteristics of the corresponding selone is a well-established mean to determine the σ -donor and π -acceptor ability of the NHC.^{147,148} As alluded to above, the value of the ¹J_{Se,C}-coupling constant is directly related to the s-character of the interacting lone pair; selones with a larger ¹J_{Se,C}-coupling correspond to NHCs with lower σ -donor ability. On the other hand, the ⁷⁷Se NMR resonance shifts towards lower field with increasing degree of C–Se double-bond character which correlates to more π -acidic NHCs. The corresponding ⁷⁷Se{¹H} NMR shifts to **17a–c** can be found at around 30 ppm (Table 1) which means an analogous π -acidity to planar, P-bridged bis(NHCs),^{136,81} but also IMes which has found numerous synthetic applications in coordination to metal complexes and main group element adducts. The ¹J_{Se,C}-coupling of around 230 Hz is similar to these NHCs as well, predestining **17** to react in similar ways. When comparing to the *N*-*n*-butyl-substituted mono(NHC) and the related imidazole selone, respectively, the influence of the backbone phosphanylation becomes clear as the π -acidity increases according to the ⁷⁷Se NMR shift ($\delta(^{77}\text{Se})(1,3\text{-dibutyl-1,3-dihydro-2H-imidazole-2-selone}) = -12$ ppm).

Theoretical calculations can give additional insight into the new bis(NHCs) **17** (Figure 36). Analysis of the FMO situation of exemplary **17b^{Me}** reveals that the LUMO remains unchanged in comparison to the other 1,4-diphosphabarrelene scaffolds **2–11** and is still embedded in the central ring system. As expected, the HOMO has significant contribution from orbitals located at the low-valent C². Surprisingly, it is followed by a series of close-lying MOs that show large contributions from either the lone

pairs at the carbene centres (HOMO to HOMO-2), the P centres (HOMO-5) or a mixture of the two (HOMO-3 and HOMO-4). The value of the HOMO-LUMO gap lies between those for **2**^{Me} and **11**^{Me} (e.g. $\Delta E_{L-H}(\mathbf{17a}^{\text{Me}}) = 5.47$ eV). This electronic set-up could allow for homo- and heterotopic coordination to up to four coordination partners, depending on the steric and electronic nature as well as stoichiometry of the substrate, that will be explored in the following chapters.

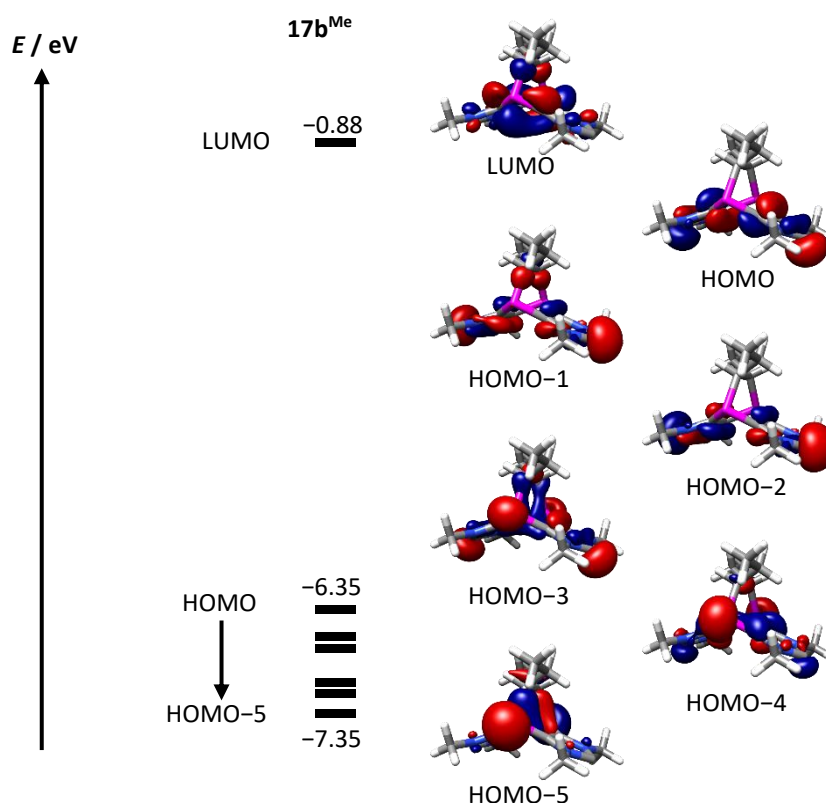
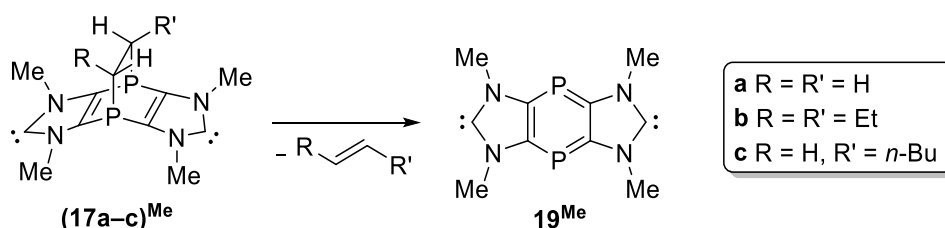


Figure 36. Selected calculated FMOs of compound **17b**^{Me}.

3.1.3.3 Investigation on the possibility of a retro-[4+2]-cycloaddition

The similarities between 1,4-diphosphabarrelene diselones **2** and bis(NHCs) **17** in ³¹P NMR shifts, FMO situation and HOMO-LUMO gap suggested that a similar retro-[4+2]-cycloaddition reactivity might be possible. Further indication was given by the aforementioned colour change of all bis(NHCs) **17a–c** which is a phenomenon that was also observed for **2** where a selective, thermal retro-[4+2]-cycloaddition was feasible. For a first comparison, the reaction according to Scheme 22 was calculated to obtain reaction energies and barriers (Figure 37).



Scheme 22. Retro-[4+2]-cycloaddition of 17^{Me} that was investigated by theoretical calculations.

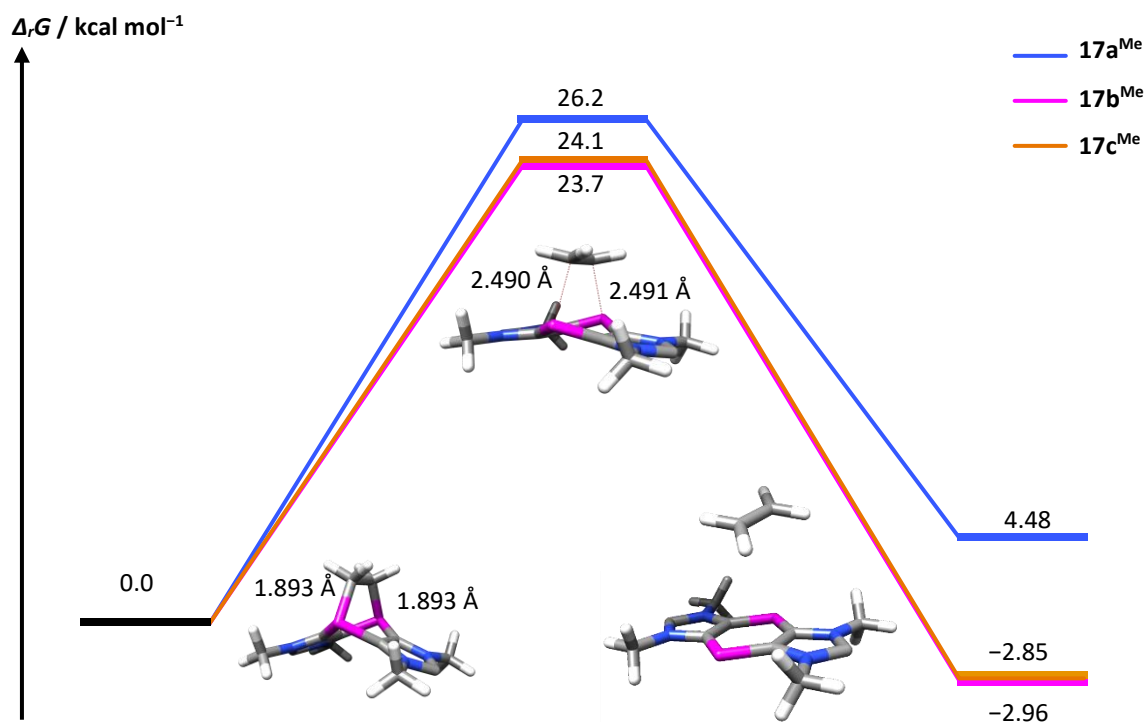


Figure 37. Gibbs reaction energies and transition state barriers for the retro-[4+2]-cycloaddition of model compounds $(17a-c)^{Me}$. Exemplary structures are given for $17a^{Me}$.

The energy diagram looks analogously to the one for diselones 2^{Me} : The 1,4-diphospha-barrelene scaffold is slightly favoured for derivative $17a^{Me}$, while the retro-[4+2]-cycloaddition is preferred for the heavier derivatives $17b^{Me}$ and $17c^{Me}$. Reaction barriers are of values that can be overcome thermally. The crucial difference between the reactions of 2^{Me} and 17^{Me} is found in the 1,4-diphosphinine scaffold. As for the bis(imidazolium) salts 11^{Me} and 13^{Me} , respectively, the bonding interaction in the [4+2]-cycloaddition happens between the LUMO of the alkene and the HOMO of the 1,4-diphosphinine bis(NHC) 19^{Me} – not the HOMO-4 like for 2^{Me} (Figure 38).

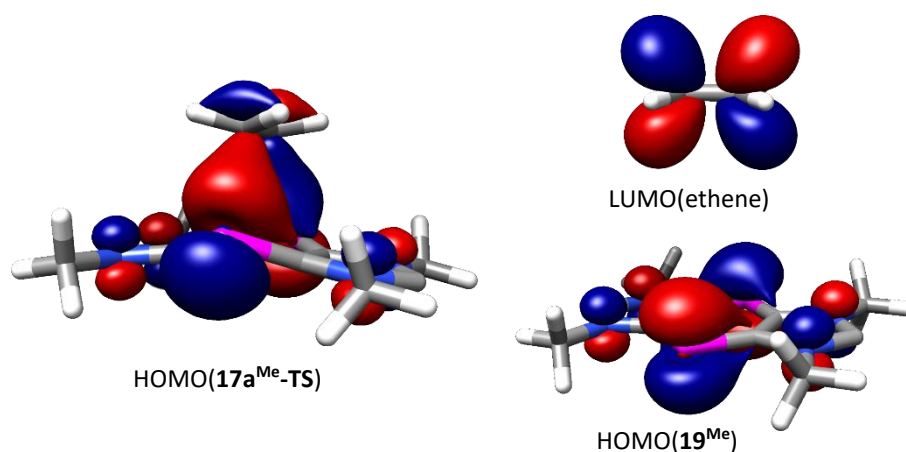


Figure 38. FMOs involved in the concerted step of the retro-[4+2]-cycloaddition reaction to form **19^{Me}** from **17a^{Me}**.

The 1,4-diphosphinine bis(NHC) **19** that would result from the retro-[4+2]-cycloaddition of **17** constitutes a particularly interesting scaffold as it could potentially react as a tetratopic ligand, having both low-valent P and carbene centres. This potential can be validated when looking at a series of FMOs (Figure 39): The LUMO is largely centred in p-type orbitals at the P atoms, as is the case for 1,4-diphosphinine diselone **1** as well, but following the above-described HOMO ($\Delta E_{L-H}(\mathbf{19}^{\text{Me}}) = 3.90$ eV) is a series of MOs with large contributions from the carbene-C atom, completing an electronic set-up that should allow reactions on the P- and carbene centres.

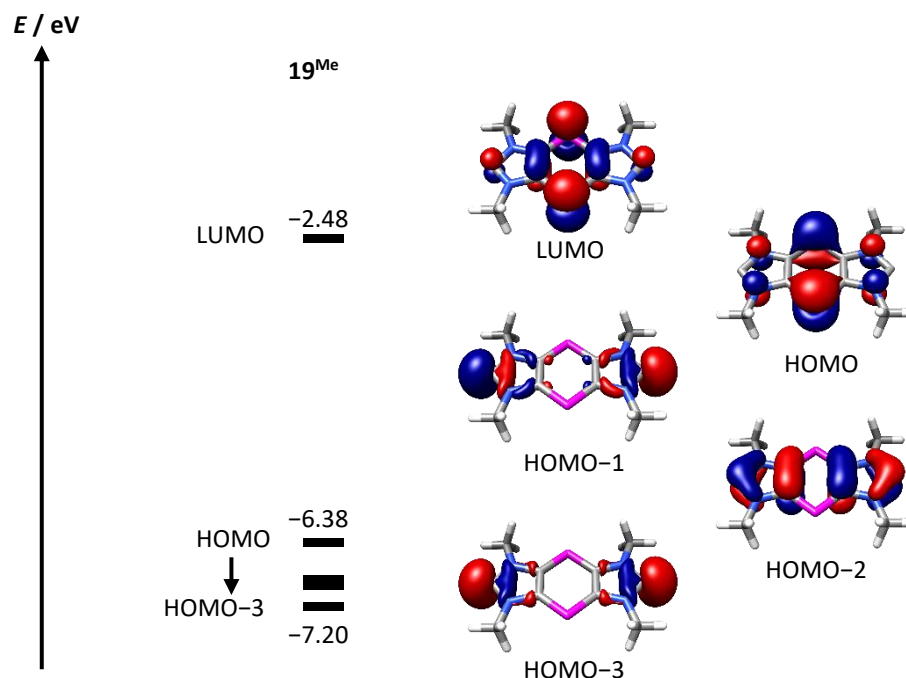
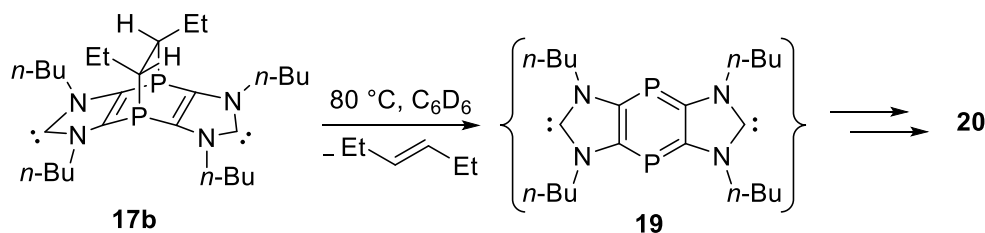


Figure 39. Selected calculated FMOs of compound **19^{Me}**.

According to Figure 37 access to the desired compound **19** should be easiest via the retro-[4+2]-cycloaddition of **17b**. Thus, the reaction displayed in Scheme 23 was carried out in a *J Young*[®] NMR tube

and monitored via $^{31}\text{P}\{\text{H}\}$ NMR spectroscopy (Figure 40). **17b** was heated to 80 °C in deuterated benzene to be able to monitor the ^1H NMR spectra as well (Figure 41) to track the formation of 3-hexene.



Scheme 23. Retro-[4+2]-cycloaddition of **17b** transiently yielding 1,4-diphosphinine bis(NHC) **19**.

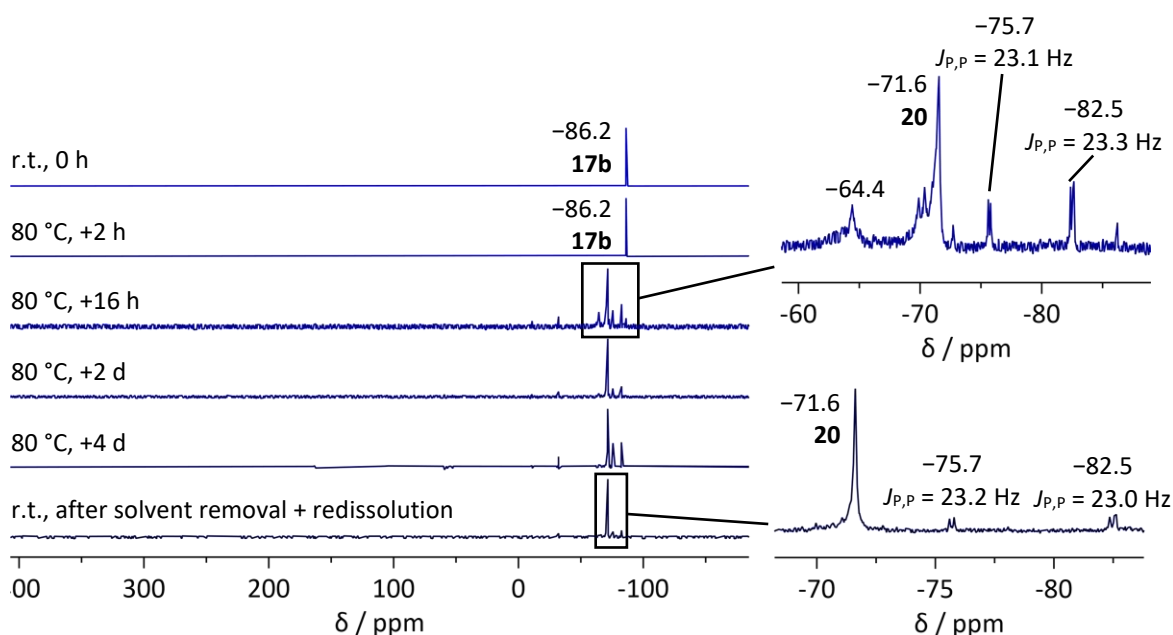


Figure 40. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the of heating a solution of **17b** in C_6D_6 . Important parts of the spectra are magnified for the second heating step (+16 h, top right) and the redissolved mixture (bottom right).

After heating for only two hours the former brown-orange solution had turned a dark brown colour and small amounts of precipitate had formed. Despite the visible change the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum remained unchanged; the ^1H NMR spectrum, however, showed first traces of 3-hexene, identified by the CH-resonance at 5.43 ppm. Over the course of heating for several days, this resonance increased in intensity, accompanied by the corresponding CH_2 and CH_3 resonances at 1.96 and 0.94 ppm, respectively, which is a first indication on a retro-[4+2]-cycloaddition occurring. As expected, after removal of the solvent and redissolving of the sample these signals vanished from the ^1H NMR spectrum.

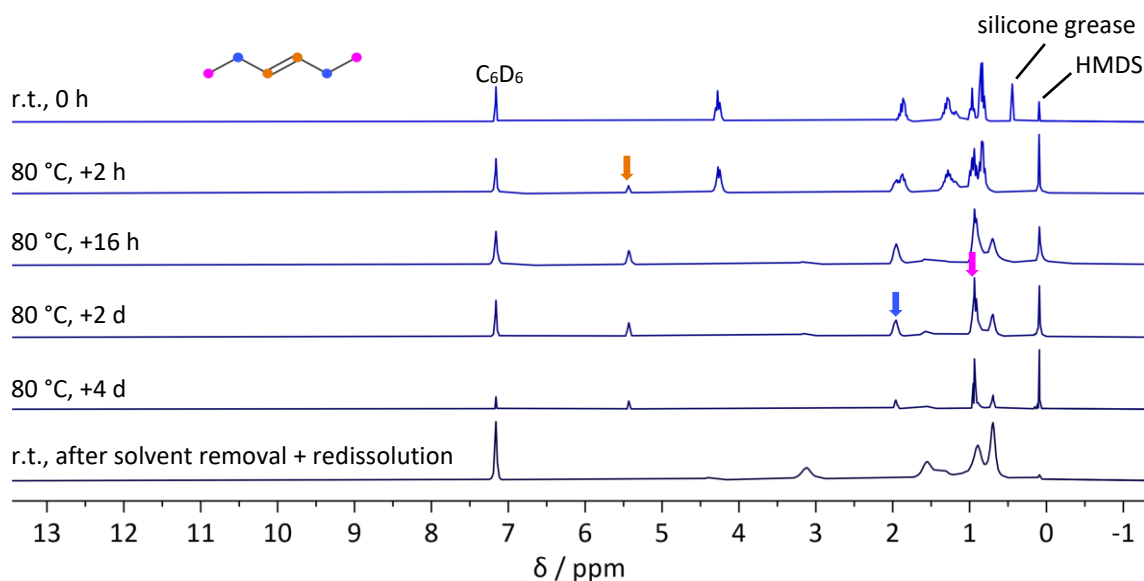


Figure 41. ^1H NMR spectra of the of heating a solution of **17b** in C_6D_6 . The emergences of ^1H NMR resonances for 3-hexene are marked with coloured arrows at the point where the signal can clearly be identified.

After heating overnight for the first time, the solution had turned into a black suspension and **17b** was almost completely consumed according to the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. The formed main products were characterised by broad signals at -64.4 and -71.6 ppm, respectively; a minor product was identified via two doublets at -75.7 and -82.5 ppm ($J_{\text{P,P}} = 23$ Hz). The resonance at -71.6 ppm could be assigned to the main product **20** of the invariable reaction mixture after four days, which was NMR spectroscopically characterised as such after drying and redissolving in deuterated benzene. 2D-NMR experiments (^1H - $^{31}\text{P}\{^1\text{H}\}$ -HMBC, ^1H - ^1H -COSY, ^1H - $^{13}\text{C}\{^1\text{H}\}$ -HSQC and -HMBC) confirm the four prominent broad multiplets at 0.69, 0.90, 1.56 and 3.13 ppm in the ^1H NMR spectrum belonging to the observed main signal in the ^{31}P NMR spectrum. Interestingly, these signals, which can be assigned to the four methylene and methyl groups of each *n*-butyl chain, are all significantly highfield-shifted in comparison to *e.g.* 1,4-diphosphinine diselone **1**, especially the one for the N-CH_2 -protons. The corresponding equally broadened resonances in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum can be found at 13.8, 20.0, 30.2 and 46.2 and do not follow the same trend. Furthermore, a signal group at 150.0 ppm which vanishes in the DEPT 135 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum, belongs to **20** confirming the integrity of the central ring. No signal for the (former) carbene-C atom could be found due to the low resolution and broad resonances.

The ^{31}P NMR resonance clearly indicates that the final product is not the desired 1,4-diphosphinine bis(NHC) **19** whose ^{31}P NMR shift is expected to be far more downfield. The FMO situation displayed in Figure 39 suggests that **19** can easily react intermolecularly – especially at elevated temperatures – to possibly form oligomeric structures that would explain the broad signal groups in all NMR spectra. An NHC adduct to the phosphorus centre in a 1,4-diphosphinine ring could also account for highfield-shifted NMR resonance as both P-anionic as well as P-alkyl substituted phosphorus nuclei

in the imidazole-annulated systems have been shown to have resonance at around -70 ppm in the ^{31}P NMR spectrum.⁸⁴ A theoretical study on oligomers of different size and connectivity (Figure 42) identified cyclic oligomers to be the most likely candidates in the mixture of **20**.

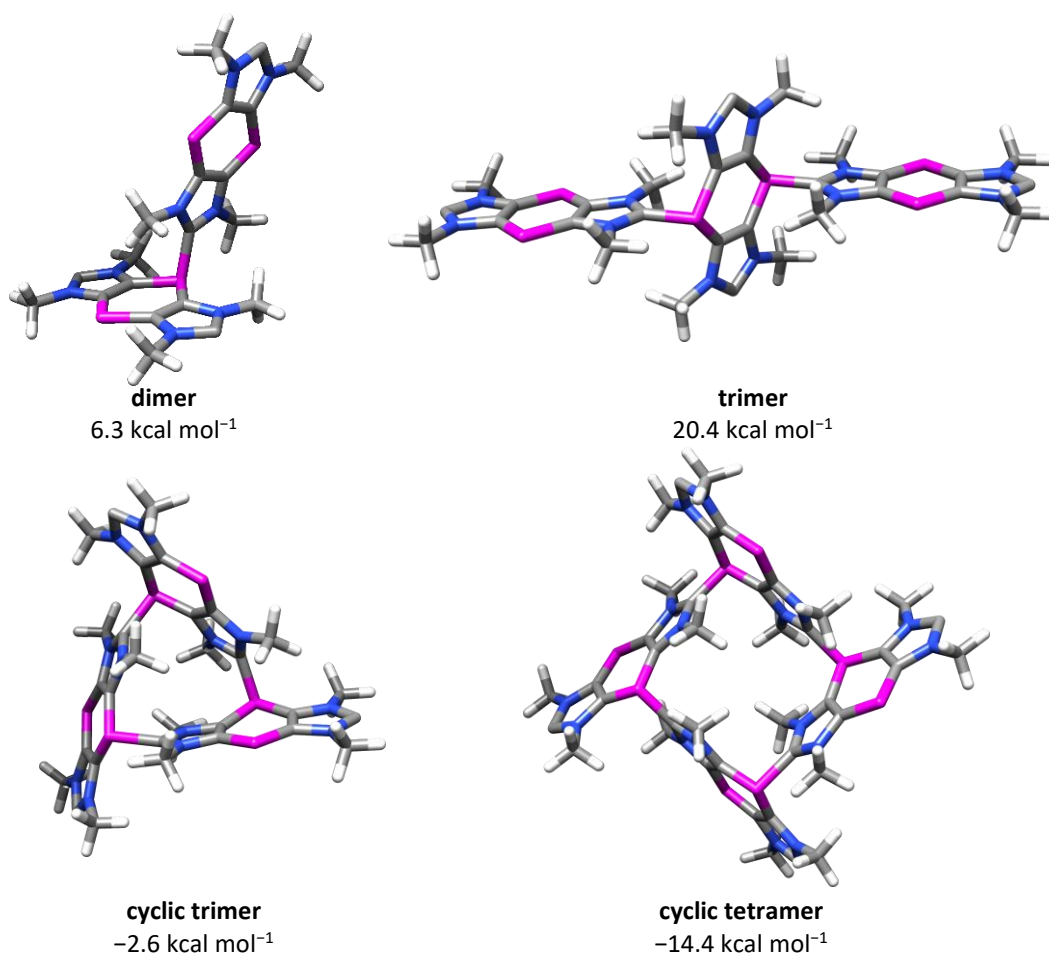
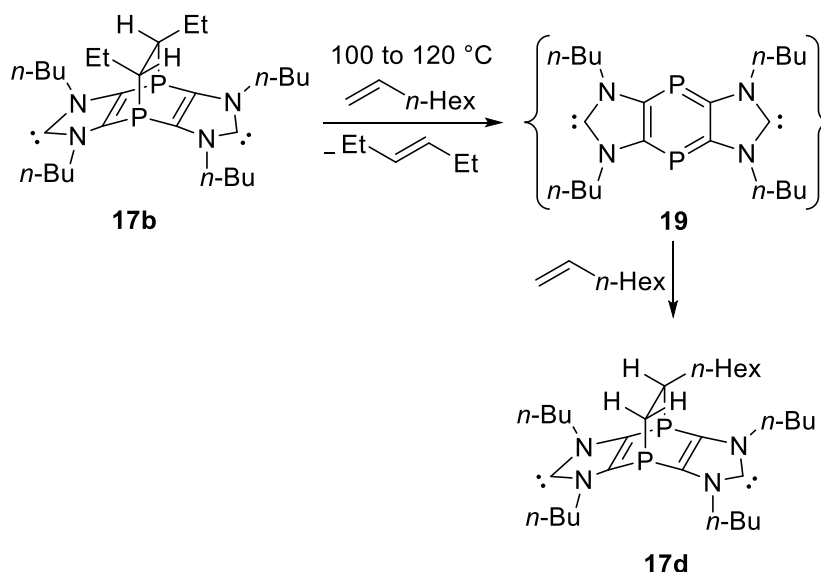


Figure 42. Calculated oligomeric structures contained in the mixture of **20** with their relative energies in comparison to the respective number of separate molecules of **19** in solution.

For three connected molecules of **19**^{Me} the open form is $20.4 \text{ kcal mol}^{-1}$ less stable than three separate molecules in solution while the cyclic trimer is slightly favoured. For four moieties the cyclic structure is clearly energetically preferred over single molecules in solution and it can be assumed that the trend continues for larger cyclomers. Interestingly, the HOMO-LUMO gap for the open forms decreases significantly to 1.57 eV for the dimer and only 0.42 eV for the trimer indicating an increasing electron delocalisation. The HOMO-LUMO gaps of the cyclic trimer and tetramer are 2.83 and 3.28 eV , respectively. Thus, to accommodate for the black colour of the formed solid and taking into account the high reaction temperature, open forms of the oligomers might also form in the solution of **19**. The newly formed P-C bond length in the cyclic tetramer was calculated to be $1.87 \text{ \AA}$ which is slightly longer than the corresponding bond length for the *P*-phenyl substituted derivative of **XXXIVc**. In accordance with this, the N-C-N in the P-bound imidazole unit is 106.5° and thus, only showing moderate imidazolium

character. The calculated angle for the carbene unit is expectedly smaller with 102.4° . The HOMO to HOMO-3 are four almost degenerate MOs that are centred in p-type orbitals on the two-coordinate phosphorus centres, followed by carbene-centred MOs. The LUMO and close-lying unoccupied MOs constitute π^* -type orbitals at the newly formed P-C bonds which suggests the preferred formation of larger oligomers as long as phosphorus centres are only two-coordinate. The *n*-butyl substitution in the solutions of the actual experiment increase the steric strain of the systems and will probably alter the preferred outcome to larger cyclomers or open oligomers. Still, the significant highfield shift of the CH_2 and CH_3 groups' resonances could be an effect of significant steric crowding upon oligomer formation in solution.

Although **19** could not be isolated due to its fleeting nature, proof of its formation could be achieved via a trapping reaction with 1-octene (Scheme 24), using 1-octene not only as reagent but also as high-boiling solvent to guarantee a large excess. While more slowly at lower temperatures, at 120°C **17b** was completely consumed within two hours yielding the asymmetric bis(NHC) **17d** (Figure 43).



Scheme 24. Formation of bis(NHC) **17d** from bis(NHC) **17b** via retro-[4+2]-cycloaddition, followed by [4+2]-cycloaddition in 1-octene.

As for **2c** and **2d** the values of the ^{31}P NMR resonances as well as the $^3J_{\text{P,P}}$ -coupling between the two diastereotopic P centres are almost identical for **17c** and **17d**, proving the formation of the new asymmetric derivative which could only have happened through the transient formation of 1,4-diphosphinine bis(NHC) **19**.

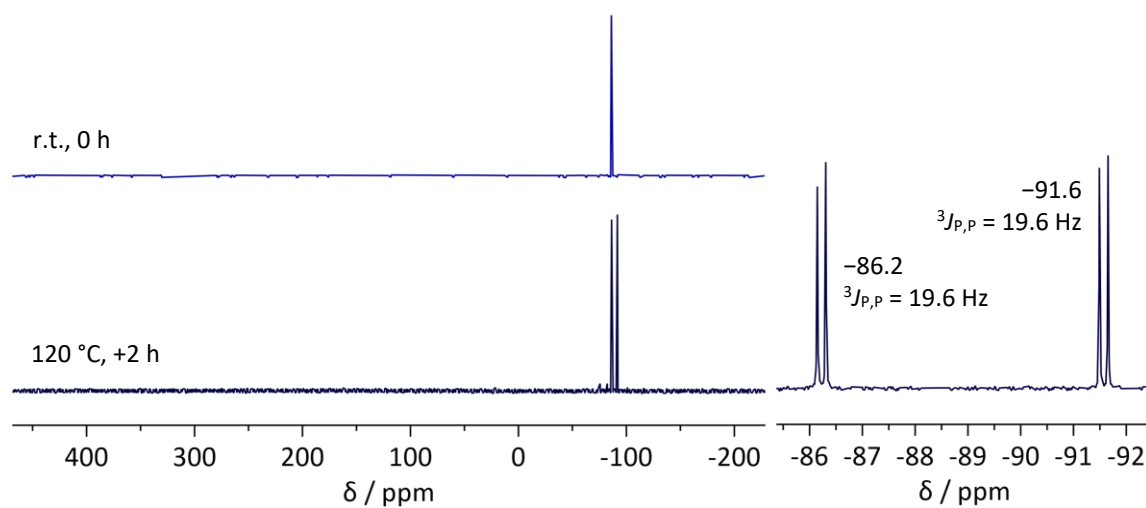


Figure 43. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the of heating a solution of **17b** in 1-octene. Magnification of the product signals on the right.

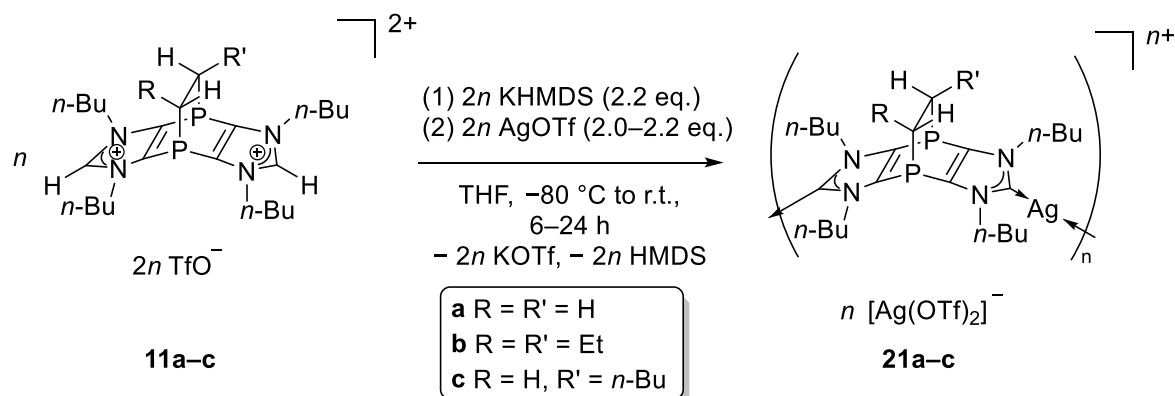
3.2 Transition metal complexes of new P-bridged, bent bis(NHCs)

Transition metal complexes of mono- and bis(NHCs) have thoroughly been investigated and found extensive application in catalysis and bis(NHCs) could also be implemented in metallo-supramolecular assemblies. While dinuclear transition metal complexes of planar, P-bridged bis(NHCs) could be synthesised,^{136,137} the quest for coordination to both the carbene and phosphorus centres in these tetra-topic bis(NHCs) still stands. Thus, the new bent, P-bridged bis(NHCs) described in chapter 3.1 were studied regarding their reactivity towards various equivalents of transition metal complexes from groups 8, 9 and 11 and compared to known mono- and bis(NHCs). The formed transition metal complexes were investigated with respect to potential oligomer formation and their thermal retro-[4+2]-cycloadditions to accomplish the formation of 1,4-diphosphinine bis(NHC) transition metal complexes and proof of the latter.

3.2.1 Synthesis of dinuclear Ag(I) complexes

To achieve a first comparison of the newly formed bis(NHCs) **17** with previously published (backbone-phosphanylated) NHCs the synthesis of dinuclear coinage metal complexes was targeted. The reaction of the corresponding imidazolium salt with the coinage metal(I) oxide constitutes a convenient, high-yielding route that has been successfully employed for Cu(I) and Ag(I) complexes **LVI**.¹³⁶ However, **11a–c** did not show any reaction with Cu₂O or Ag₂O, irrespective of the used equivalents, the solvent and the reaction temperature which further underlines the aforementioned stability of the bis(imidazolium) scaffold **11**. The use of Ag₂O in the synthesis of NHC Ag(I) complexes is most often used for imidazolium halides and calculations on the mechanism have, thus, been performed with silver iodide.¹⁴⁹ These studies showed that the most likely reaction mechanism constitutes a series of single deprotonation and metalation steps where the second deprotonation step is heavily assisted by another imidazolium unit. Consequently, the kinetics are significantly slowed when having bis- or poly(imidazolium) salts and the exchange of the coordinating halide by a weakly coordinating triflate could also affect the first deprotonation step. Nevertheless, the fact that the reaction worked for **LV** attributes a remarkable stability to bis(imidazolium salts) **11** as there seems to be no driving force for the deprotonation with Ag₂O. The desired dinuclear Ag(I) complexes **21a–c** could be synthesised from the reaction of the *in situ* generated bis(NHCs) with silver triflate in THF in which complexes **21a–c** precipitate out of solution almost quantitatively (Scheme 25). The observed precipitation could indicate the formation of oligomeric or polymeric Ag(I) complexes which are the consequence of the typical structural motif of NHC Ag(I) complexes with weakly coordinating anions.¹⁵⁰ In fact, the first NHC Ag(I) complex containing an O-bound triflate was only published in 2015¹⁵¹ while in most cases Ag(I) halides are bound to the NHC unit or bridging motifs with separate triflate anions are observed.¹⁵²

Thus, **21** are not depicted in their monomeric form – as was done for **LVla** – but as shown in Scheme 25.



Scheme 25. Formation of dinuclear Ag(I) complexes **21a–c** from *in situ* generated bis(NHCs) **17**.

21a–c proved to be insoluble in all common organic solvents except acetonitrile. Thus, the complexes could be isolated after extraction with acetonitrile, to remove small amounts of elemental silver, probably formed due to the light sensitivity of the slight excess of AgOTf,¹⁵³ and washing with THF and *n*-pentane as dark brown solids in moderate yields. Derivative **21a** could only be isolated in 87 % purity with impurities belonging to **11a** and a mixed imidazolium/Ag(I) complex, even with larger excess of KHMDS and longer reaction times for the *in situ* generation of **17a**. NMR spectra for characterisation were recorded in deuterated acetonitrile and show broad ³¹P NMR resonances and slightly broadened ¹H and ¹³C{¹H} NMR signals (Table 7). Due to the signal broadening no ³J_{P,H}-coupling constant for asymmetric **21c** could be determined. All resonances for **21a–c** are downfield-shifted in comparison to **17a–c** and their C²-¹³C{¹H} NMR signals are highfield-shifted to around 185 ppm. While the latter is in good agreement with complexes of **LII**,¹³⁶ their ³¹P NMR resonances appear slightly highfield-shifted in comparison to the free bis(NHCs).

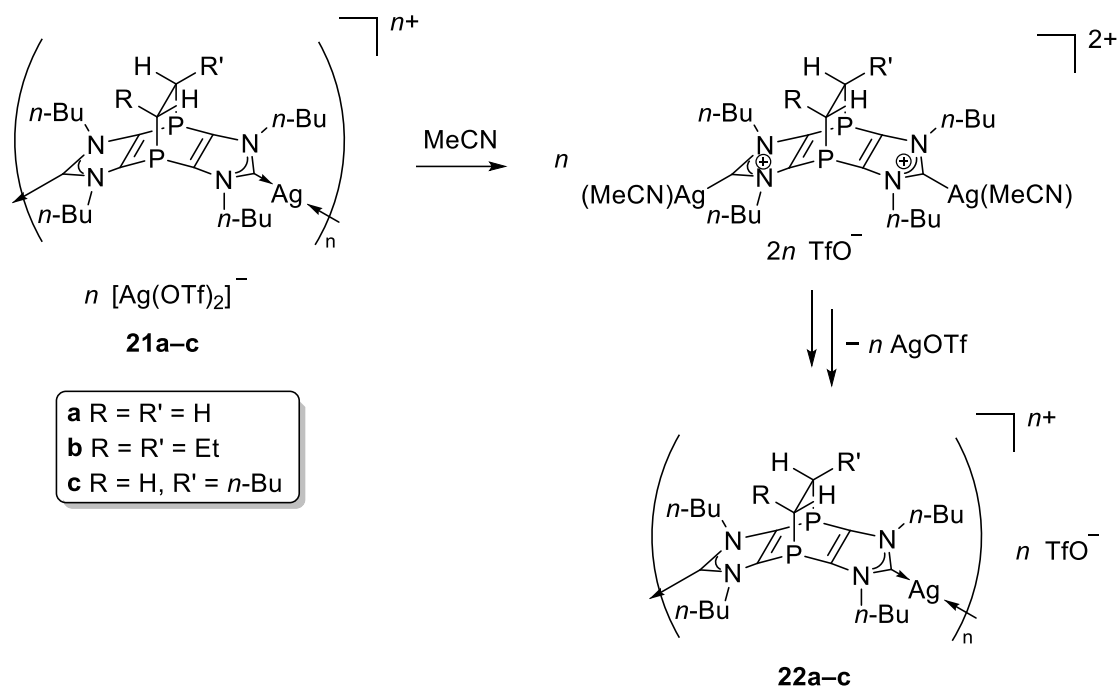
Table 7. Selected NMR data for compounds **21a–c** in CD₃CN.

	$\delta(^{31}\text{P}) / \text{ppm}$	FWHM / Hz	$\delta(^{13}\text{C}\{^1\text{H}\})(\text{C}^2) / \text{ppm}$
21a	–88.9	44	184.7
21b	–79.6	86	186.0
21c	–86.8, –81.7	50	185.0*

*only one signal observed due to signal broadening

The NMR signals of **21** could not be further resolved as the complexes precipitated out of the acetonitrile solution over time at ambient temperature and quickly at lower temperatures. While on the one hand acetonitrile seems to be the only solvent to deoligomerise and dissolve the formed solids **21**, on

the other hand, acetonitrile is known to facilitate the decomposition of NHC Ag(I) complexes to yield Ag(I) bridged dimers¹⁵⁴ and was also used in the formation of one-dimensional Ag(I) bridged polymers of the first monocyclic bis(NHC) **XLIII**.¹¹⁴ Hence, the observed insolubility of **21a–c** can possibly be explained by the formation of dimers or oligomers **22a–c** according to Scheme 26. This is additionally supported by (high-resolution) mass spectrometry in acetonitrile solutions which shows acetonitrile hanging on to the dinuclear, dicationic Ag(I) complexes as well as Ag(MeCN)₂ fragments. Dimers and small oligomers of the bent scaffolds could also explain the broadened signals in the ³¹P NMR spectra.



Scheme 26. Possible formation of Ag(I) bridged oligomers **22a–c** in MeCN solution.

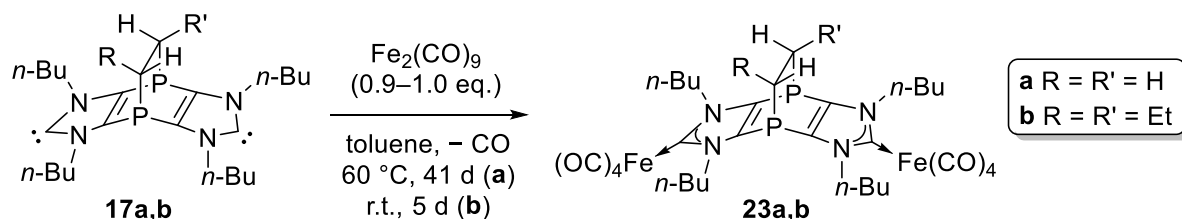
The reaction of **17a–c** – isolated or generated *in situ* – with coinage metal(I) chlorides like anhydrous CuCl, AuCl·SMe₂ or AuCl·PEt₃ always led to the formation of insoluble solids; transmetalation attempts with **21a–c** and a CuCl or AuCl source failed in the same way, even in acetonitrile. Similarly to **LIIa**, no tetranuclear complexes could be obtained, either. This is reasonable when taking into account the weak σ -donating properties of the phosphorus centres, the relatively high-lying LUMO for π -back-donation and the often heterogenous reaction conditions due to the poor solubility of the initially formed complex **21**. However, unselective transmetalation reactions were observed with Fe(CO)₅ as well as [Rh(cod)Cl]₂ (see chapters 3.2.2 and 3.2.3, respectively) but no tetracoordination was achieved.

Ag(I) complexes **21a–c** do not show thermal retro-[4+2]-cycloaddition behaviour but upon heating decompose under the visible formation of elemental silver (“silver mirror” on the glass wall) and further insoluble products. Furthermore, a cyclic voltammetric study on **21c** (see 7.3.1) in acetonitrile

showed a stripping oxidation of Ag(I) on the electrode – characterised by a high current and steep increase – which is very typical for Ag(I) salts in acetonitrile.¹⁵⁵ This additionally supports the tendency of **21** to form oligomers where two NHC units are coordinated to one silver centre.

3.2.2 Synthesis and reactions of dinuclear Fe(0) complexes

Coinage metal complexes like **21** had been synthesised before with P-bridged bis(NHCs) **LII** but the behaviour towards other transition metal complexes is less investigated. Thus, Fe(CO)₄ complexes **23** were targeted to not only further examine the new bis(NHCs) but also the possibility of tri- or tetra-coordination that had not been achieved before. Other NHC Fe(CO)₄ complexes have also been shown to catalyse the reduction of benzaldehydes and acetophenone.¹⁵⁶ As mentioned above, a simple transmetalation approach with the obtained Ag(I) complexes **21** and Fe(CO)₅ or Fe₂(CO)₉ did only yield unselective reaction mixtures – most probably caused by the heterogenous reaction conditions and side reactions of the soluble metal fragments. However, the synthesis of dinuclear complexes **23** could be achieved via the direct reaction of the bis(NHC) with Fe₂(CO)₉ (Scheme 27).



Scheme 27. Formation of dinuclear Fe(0) complexes **23a,b** from bis(NHCs) **17**.

Only the two symmetric derivatives **23a** and **23b** were synthesised as **23a** poses the most promising candidate for tetracoordination due to the decreased steric bulk around the bridge while **23b** proved to be preferable for retro-[4+2]-cycloaddition experiments (*vide supra*).

³¹P{¹H} NMR monitoring of the reaction of **17a** showed a significant amount of **23a** after three days (65 %) but also the formation of another resonance at –92.0 ppm. Over time, the latter vanished and only the desired product peak remained when stirring the reaction mixture at 60 °C (Figure 44). For **17b** on the other hand, the ³¹P{¹H} NMR spectrum after one day revealed a complicated mixture of various A,B spin systems that include coordination to one or two phosphorus centres as indicated by downfield-shifted signals between 27 and 42 ppm. After three more days at ambient temperature the ³¹P{¹H} NMR spectrum showed clean conversion to **23b** (Figure 45).

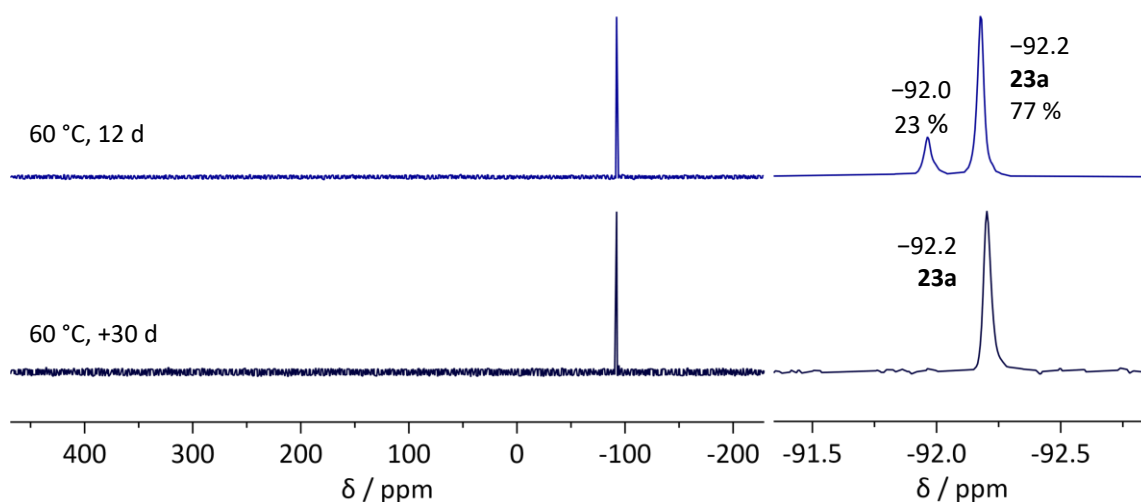


Figure 44. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the reaction mixture of **17a** and $\text{Fe}_2(\text{CO})_9$ in toluene. Magnification of the product signals on the right.

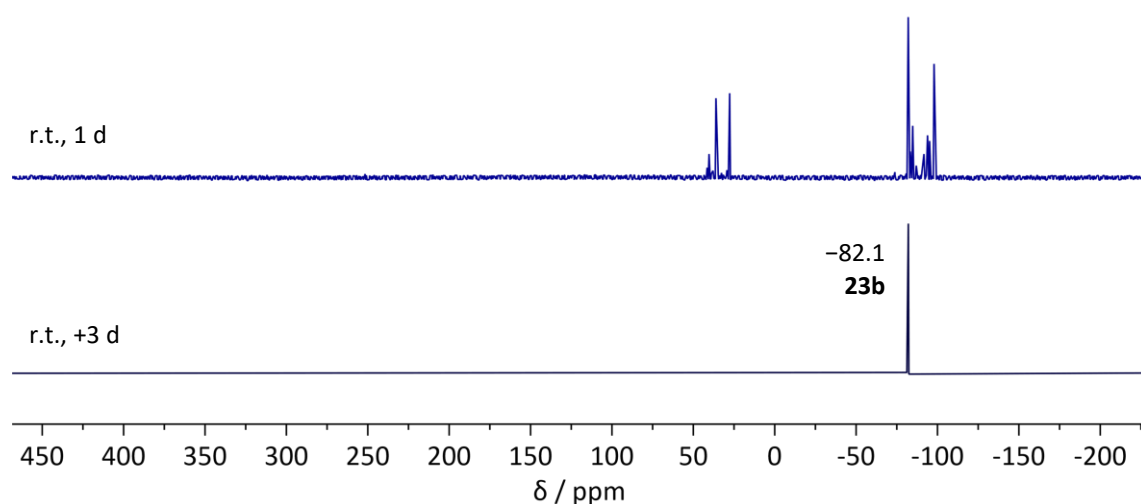


Figure 45. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the reaction mixture of **17b** and $\text{Fe}_2(\text{CO})_9$ in toluene.

These two observations demonstrate a reaction mechanism that initially involves coordination to the phosphorus centres which afterwards is resolved in favour of the coordination to the carbene centres as all downfield-signals vanish. The intermediate that is clearly observed for **23a** could belong to a dimer or oligomer that either converts to the dinuclear complex or precipitates out of solution due to increased insolubility with polymer formation. The fact that the reactions produce a significant amount of an insoluble solid supports this hypothesis.

Both **23a** and **23b** could be isolated as orange solids after extraction with toluene in very moderate yields of about 40 % which further underlines the possibility of oligomer formation. Their ^{31}P NMR resonance appear downfield-shifted in comparison to **17a,b** but not as much as those of $\text{Ag}(\text{I})$ complexes **21** (Table 8). Both the values for resonances of the C^2 -carbon nuclei and the CO ligands in the

$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum appear in the expected regions and compare well with reported values for, *e.g.*, $\text{Fe}(\text{CO})_4$ complexes of IMes.¹⁵⁶

Table 8. Selected NMR and IR data for compounds **23a,b** in C_6D_6 .

	$\delta(^{31}\text{P})$ / ppm	$\delta(^{13}\text{C}\{^1\text{H}\})(\text{C}^2)$ / ppm	$\delta(^{13}\text{C}\{^1\text{H}\})(\text{CO})$ / ppm	$\tilde{\nu}(\nu(\text{CO}))$ / cm^{-1}
23a	−92.2	187.1	218.6	2037 (s), 1909 (vs)
23b	−82.2	187.8	218.7	2037 (s), 1907 (vs)

Similarly, the two detectable IR bands for the CO ligands, where the stronger one shows a shoulder, are very close to the ones of the *N*-mesityl substituted derivative ($\tilde{\nu} = 2035, 1949, 1915 \text{ cm}^{-1}$) which correlates well with previous observations and the idea that the carbene centres in bis(NHCs) **17** electronically resemble the one in IMes.

Derivative **23b** could be analysed via SCXRD (Figure 46) and confirmed the dinuclear Fe(0) complex. The structural parameters of the bis(NHC) scaffold, especially the bond lengths, do not deviate significantly in comparison to the free bis(NHC) **17b**. The average angle sum also still amounts to around 286° and the overall folding angle ($\angle(\text{C}2-\text{P}1-\text{P}2-\text{C}17)$) to approximately 124° . The angles in the imidazolium units lie much closer to those in a free NHC than in the imidazolium units ($\angle(\text{N}1-\text{C}2-\text{N}2) = 104.2(12)^\circ$, $\angle(\text{N}3-\text{C}17-\text{N}4) = 103.3(11)^\circ$). While both Fe-C bonds are of identical length ($d(\text{Fe}1-\text{C}2) = 1.995(15) \text{ \AA}$, $d(\text{Fe}2-\text{C}17) = 1.995(14) \text{ \AA}$), the NHC unit acts as equatorial ligand on one side ($\angle(\text{C}2-\text{Fe}1-\text{C}9) = 126.9(7)^\circ$) and as approximately axial ligand on the other ($\angle(\text{C}17-\text{Fe}2-\text{C}23) = 167.7(6)^\circ$) in the respective distorted trigonal bipyramid. All values correlate well with known NHC $\text{Fe}(\text{CO})_4$ complexes.¹⁵⁶

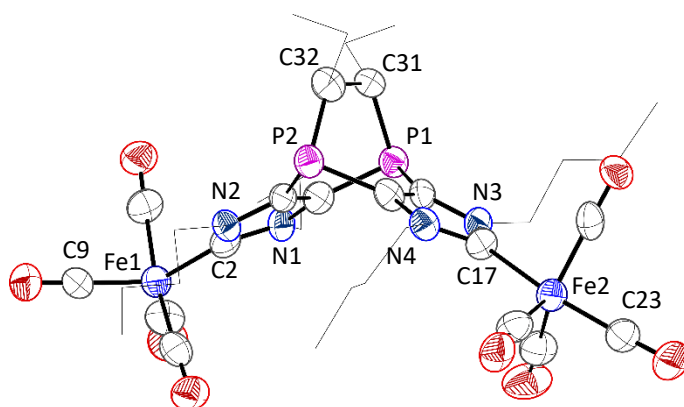


Figure 46. Molecular structure of **23b** in the single crystal. Thermal ellipsoids are set at 50 % probability. Hydrogen atoms were omitted for clarity. *n*-Butyl and ethyl chains are simplified as wires for additional clarity.

Theoretical calculations on the FMOs of **23b**^{Me} show an energetically similar situation to **17b**^{Me} with an unchanged LUMO (Figure 47). The HOMO and the following three molecular orbitals have their

largest contribution at the $\text{Fe}(\text{CO})_4$ fragments, followed by two π^* -type orbitals and only the HOMO-6 constitutes the two phosphorus lone pairs.

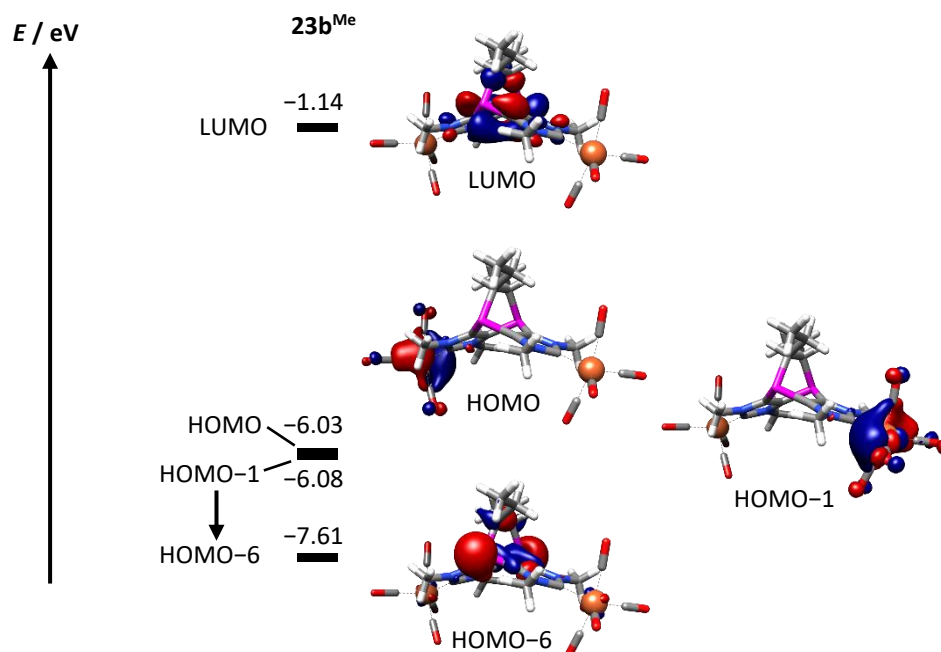
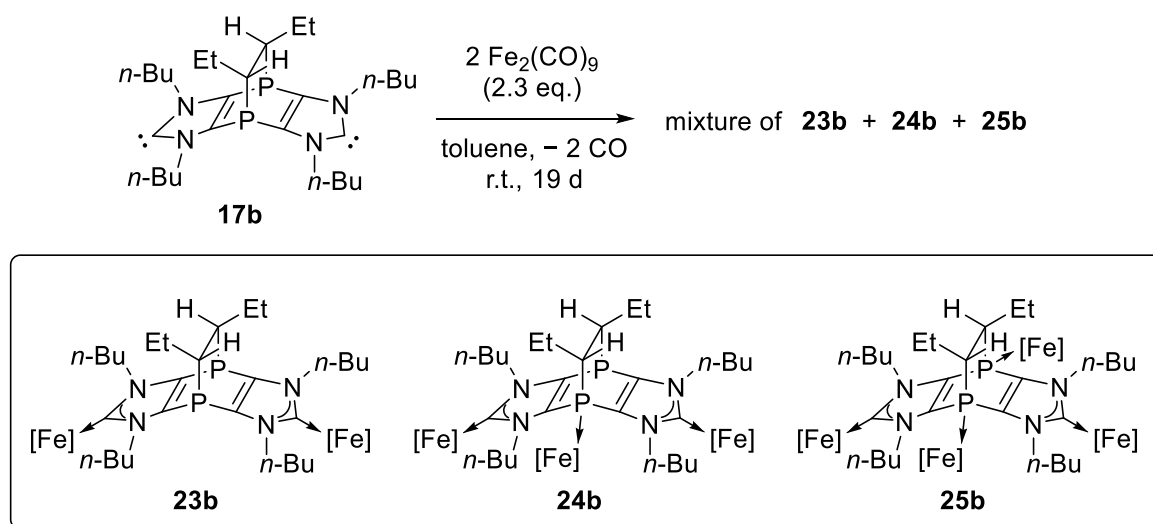


Figure 47. Selected calculated FMOs of compound **23b^{Me}**.

For the sterically least hindered derivatives **2a** and **11a** P-coordination was achieved with a very similar FMO – and especially phosphorus lone pair – situation of **2^{Me}** (Figure 20) or **11^{Me}** (Figure 30). Because of that and the initial $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum in the formation of **23b** (Figure 45) which showed tri- and tetracoordination, **17a** and **17b** as well as **23a** and **23b**, respectively, were submitted to excesses of $\text{Fe}_2(\text{CO})_9$ or $\text{Fe}(\text{CO})_5$ in toluene at ambient temperature. In no case a quantitative formation of a tri- or tetranuclear complex could be observed through $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopic monitoring. The outcome of the reaction of **17b** with $\text{Fe}_2(\text{CO})_9$ according to Scheme 28 is displayed in Figure 48. The trinuclear $\text{Fe}(0)$ complex **24b** forms up to an amount of 42 % in the reaction mixture and shows typical NMR spectroscopic features: The $\text{Fe}(0)$ coordinated phosphorus centre's signal experiences a significant downfield shift to 41.5 ppm while the other one's is slightly highfield-shifted. Both show a reduced $^3J_{\text{P,P}}$ -coupling constant of around 9 Hz due to the decreased electron density in the central ring system upon coordination. The tetraordinated complex **25b** is only formed in around 2 % and its resonance appears slightly highfield-shifted in comparison to **24b** as has been observed for the, *e.g.*, BH_3 coordination above (see chapter 3.1.1.3). The amounts of formation do not change over time or upon addition of more $\text{Fe}(0)$ reagent.



Scheme 28. Attempted formation of tri- and tetranuclear Fe(0) complexes **24b** and **25b** from bis(NHCs) **17b**.

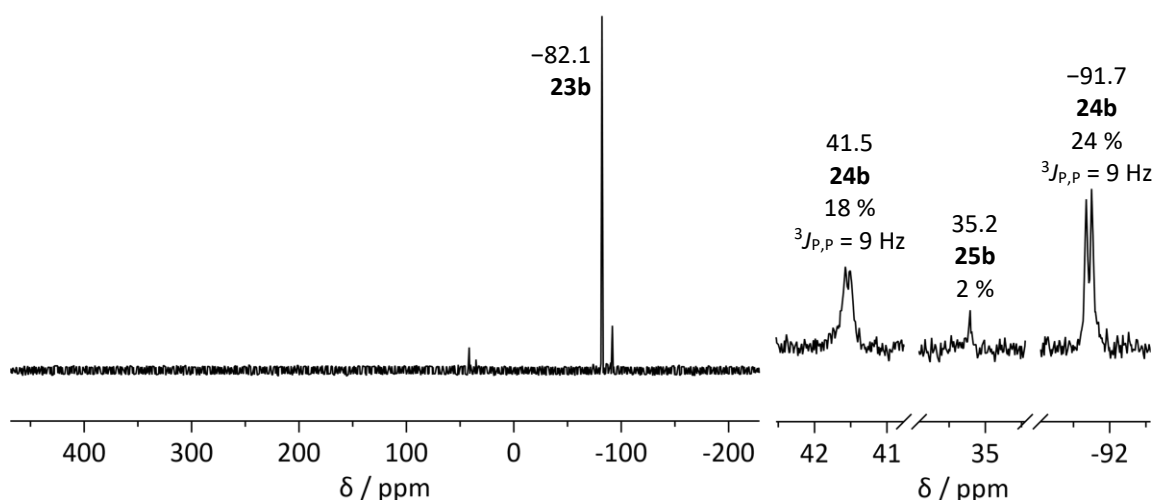
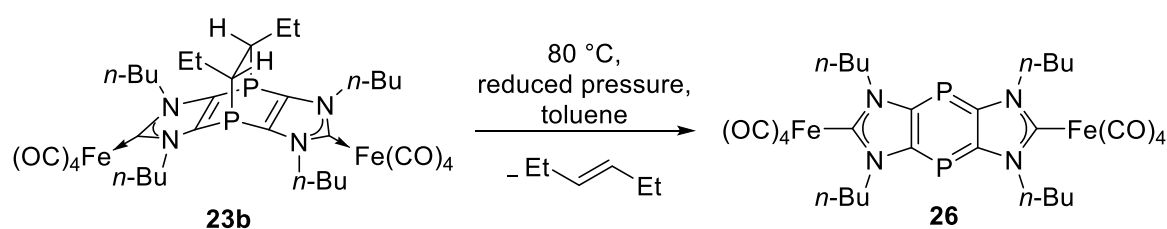


Figure 48. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction mixture of **17b** with 2.3 equivalents $\text{Fe}_2(\text{CO})_9$ in toluene. Magnification of the product signals on the right.

For the sterically less hindered derivative **17a** even less tri- and tetracoordination was observed – probably due to the energetically lower lying phosphorus lone pairs and the aforementioned oligomer or polymer formation. The poor performance of **17** as phosphane ligand could not only be explained by its weak σ -donor ability but also the combination with an $\text{Fe}(\text{CO})_4$ fragment that already contains four very strong donors where the electron donation from the diphosphane's s-type lone pair is insufficient to form a strong metal-phosphorus bond. On the contrary, the reaction of **23a** with $[\text{Rh}(\text{cod})\text{Cl}]_2$ seems to fully consume the starting material but produces a hardly soluble solid that could not be further investigated. Reacting **23a** with an excess of the borane dimethylsulfide adduct also consumes the initial Fe(0) complex but yields an unselective reaction mixture that contains tri- and or

tetracoordinated products including those of $P\text{-Fe}(\text{CO})_4$ coordination. The Fe-C bond seems to be labile enough for dissociation and thus, enables a substitution by BH_3 and coordination to the phosphorus centres. The bond dissociation energy for one $\text{Fe}(\text{CO})_4$ fragment in **23a**^{Me} amounts to $36.1 \text{ kcal mol}^{-1}$ which could explain the traces of P-coordination.

The formation of **23a** required elevated temperatures already but the heating of reaction mixtures targeting tri- or tetranuclear complexes did not have any effect. In case of **23b** heating was not necessary for its formation and could not be applied later on as an occurring retro-[4+2]-cycloaddition (Scheme 29) was indicated by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopic measurements and a colour change.



Scheme 29. Thermal retro-[4+2]-cycloaddition of **23b** yielding 1,4-diphosphinine bis(NHC) $\text{Fe}(0)$ complex **26**.

For **2** and **17** the 7,8-diethyl-substituted derivative **b** proved to be the one to enable a retro-[4+2]-cycloaddition most easily as shown by experiments and calculations. Theoretical calculations on the same reaction for **23b**^{Me} revealed an approximately thermoneutral pathway with a reaction barrier of $\Delta\Delta_rG^\ddagger = 24.8 \text{ kcal mol}^{-1}$ (Figure 49) which can easily be overcome at elevated temperatures.

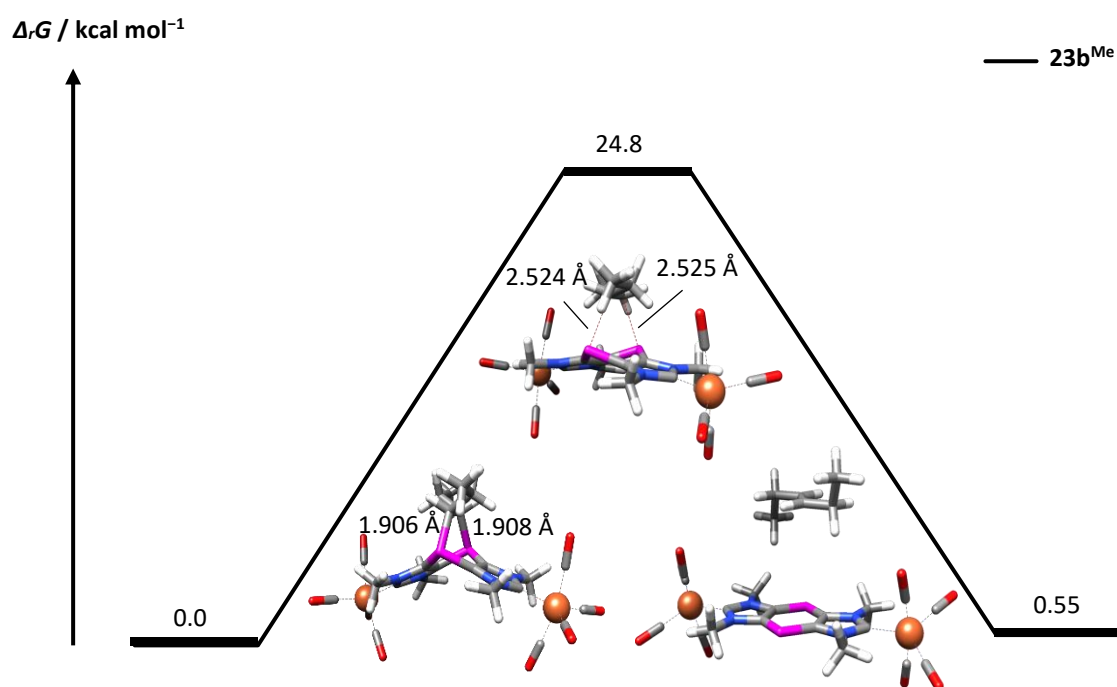


Figure 49. Gibbs reaction energies and transition state barriers for the retro-[4+2]-cycloaddition of model compound **23b**^{Me}.

The FMOs that are involved in the retro-[4+2]-cycloaddition step are displayed in Figure 50 and are very similar to what was observed for **2**. The occupied orbital of **26^{Me}** that participates in the critical step constitutes HOMO-4 which should stabilise the 1,4-diphosphinine scaffold to make it observable or isolable, respectively.

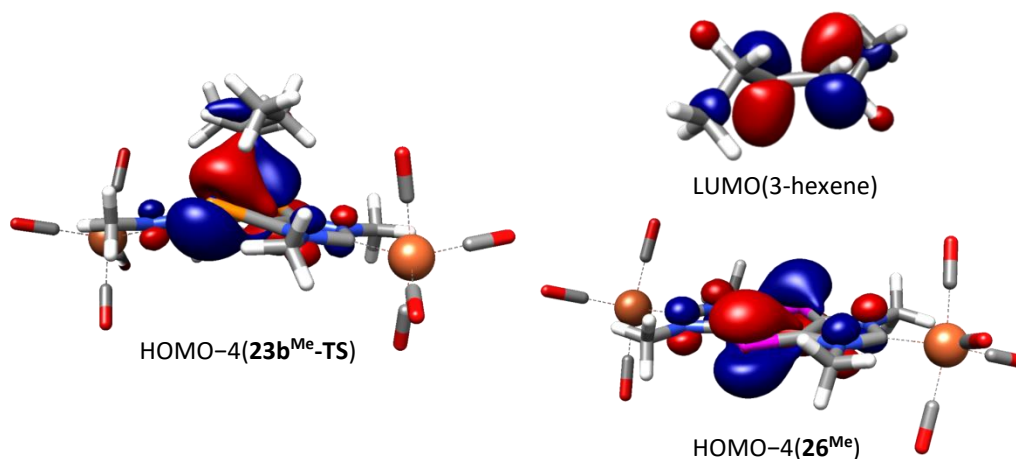


Figure 50. FMOs involved in the concerted step of the retro-[4+2]-cycloaddition reaction to form **26^{Me}** from **23b^{Me}**.

When **23b** is heated as a solid at 80 °C *in vacuo* a colour change from orange to dark brown occurs that indicates the formation of a new compound but the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum in diethyl ether still showed only the starting material (Figure 51).

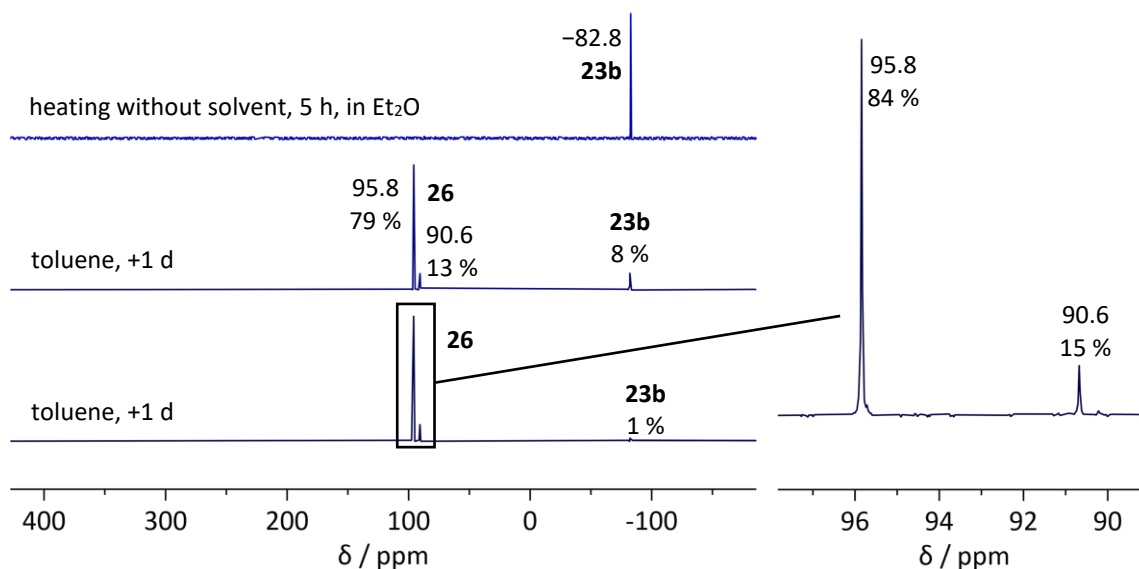


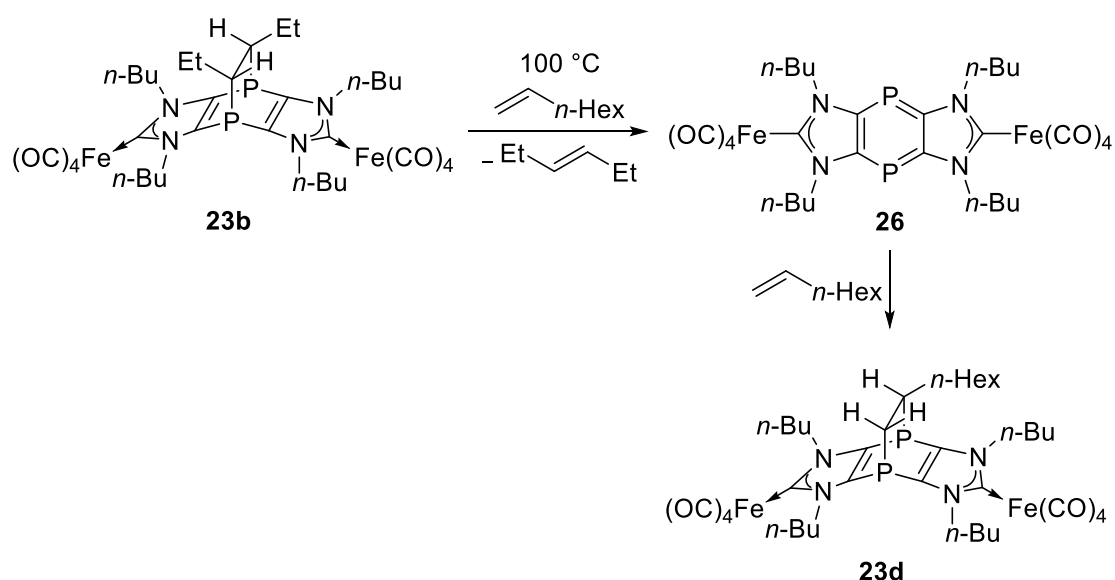
Figure 51. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the heating of **23b** at 80 °C at reduced pressure (≈ 0.1 mbar). Magnification of the product signals from the bottom spectrum on the right.

Only when heating in toluene the intense brown colour goes along with the appearance of two new signals at 90.6 and 95.8 ppm in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. They lie in the typical downfield region for

imidazole-annulated 1,4-diphosphinines like **1** but for the highly symmetrical compound **26** only one signal is expected. Similarly to **23a^{Me}**, the energy to dissociate an $\text{Fe}(\text{CO})_4$ fragment is around $34.3 \text{ kcal mol}^{-1}$ for **26^{Me}**; for the Fe-C bond of the first CO ligand it is only $18.9 \text{ kcal mol}^{-1}$ – both values that can easily be overcome by heating to 80°C . The liberation of one carbon monoxide molecule is favoured even more due to its volatile nature. Therefore, the additional signal probably stems from the loss of either an $\text{Fe}(\text{CO})_4$ unit or a CO ligand while still keeping the tricyclic 1,4-diphosphinine core intact.

The reaction did not go to completion under any tested circumstances regarding temperature, pressure and reaction time. Furthermore, no separation of the different products from the small amounts of starting material or each other could be achieved due to very similar solubilities. **26** also presented more moisture and air sensitive than the corresponding diselone **1**. However, the ^1H NMR spectrum of a mixture containing only 3 % starting material clearly shows four multiplets that can be assigned to the methylene/methyl groups of the *n*-butyl substituents. Their chemical shifts are almost identical to those of 1,4-diphosphinine diselone **1⁸¹** and are slightly highfield-shifted in comparison to **23b**.

Further proof of the formation of **26** could be achieved analogously to **19** when **23b** was heated in 1-octene to 100°C (Scheme 30) and the reaction was monitored via $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. After only seven hours all of **23b** was consumed and a new A,B spin system with resonances at -89.1 ppm ($^3J_{\text{P,P}} = 18.2 \text{ Hz}$) and 83.7 ppm ($^3J_{\text{P,P}} = 18.2 \text{ Hz}$) could be observed (Figure 52).



Scheme 30. Formation of bis(NHC) $\text{Fe}(\text{0})$ complex **23d** from bis(NHC) $\text{Fe}(\text{0})$ complex **23b** via retro-[4+2]-cycloaddition, followed by [4+2]-cycloaddition in 1-octene.

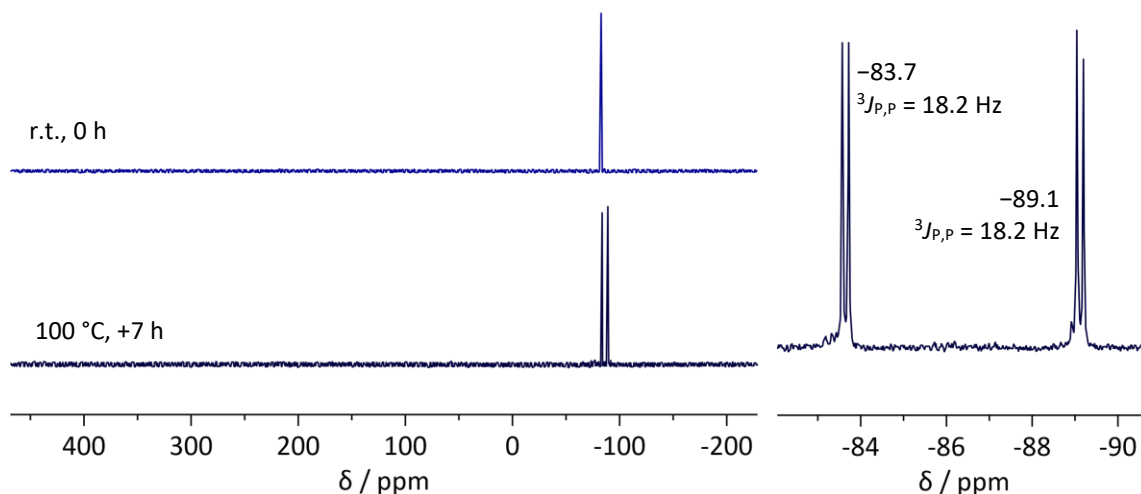
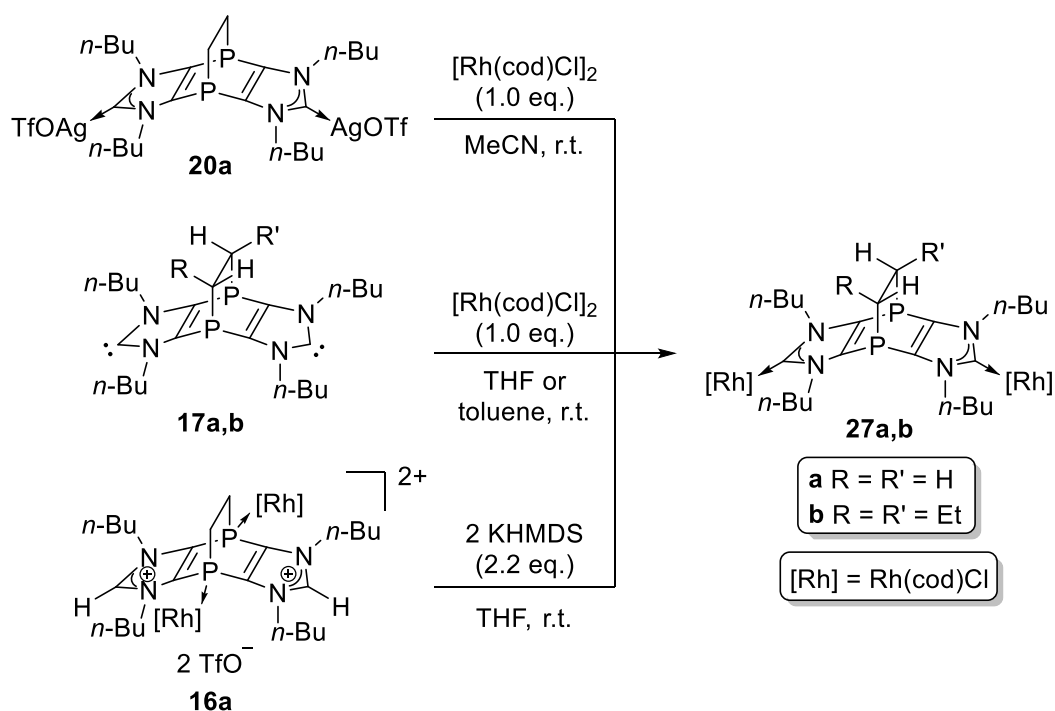


Figure 52. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the of heating a solution of **23b** in 1-octene. Magnification of the product signals on the right.

The signals are downfield-shifted in comparison to the free bis(NHC) **17d** and show a larger coupling constant than for the diselone **1** or imidazolium-containing scaffolds like **10** or **11**. As expected, the Fe(0) complexes are more closely related to the bis(NHCs) than the diselones. One effect of this relation is that *in situ* generated **26** not only reacts with the alkyl substituted alkene 1-octene but also the more electron-rich *trans*-1,2-diphenylethene – a [4+2]-cycloaddition that could not be achieved with **1**. Performing the reaction analogously to Scheme 30 with a large excess of *trans*-1,2-diphenylethene in C_6D_6 after circa one week yields a new singlet at -71.7 ppm in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (34 %), accompanied by the formation of 3-hexene as seen in the ^1H NMR spectrum. However, the completion of this exchange reaction could not be achieved in a reasonable time frame as the alkyl-substituted bridge in **23b** is still favoured over the aryl-substituted one but is a first example how manipulation at the C^2 -carbon atoms can influence the reactivity of the 1,4-diphosphinine centre.

3.2.3 Synthesis of Rh(I) complexes

To further extend the scope of transition metal complexes of **17**, investigate the influence of the metal centre and its ligands, thus being able to compare the diphosphane properties with diselones **2** and bis(imidazolium) salts **11**, complexes to the Rh(cod)Cl unit were targeted. For planar P-bridged bis(NHCs) **LII** dinuclear Rh(I) and Ir(I) could be achieved in a direct synthesis but no SCXRD analysis or tetranuclear metal complexes were obtained. Here, for aforementioned reasons again only the symmetric derivatives (**a,b**) were investigated. First, dinuclear complexes **27** were targeted through three different reaction paths (Scheme 31).



Scheme 31. Attempted formation of dinuclear Rh(I) complexes **27a,b** through three different pathways.

As mentioned above, experiments aiming at the formation of a heterometallic tetranuclear complex with **21a** and [Rh(cod)Cl]_2 remained unsuccessful, instead the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum showed signals that could be explained via occurring transmetalation reactions (Figure 53, top spectrum). Unfortunately, the reaction mixture appeared to be very unselective which could be explained by the heterogeneous reaction conditions and the tendency of **21** to undergo oligomerisation. The attempted direct synthesis of **27** from the bis(NHCs) **17** and [Rh(cod)Cl]_2 was performed with both derivatives **17a,b**. In both cases the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows three main signal groups that are in the region of either the bis(NHCs) or metal complexes thereof (Figure 53, 2nd and 3rd spectrum). In each case the two outer signals are singlets and the most downfield-shifted resonance has the lowest amount in the reaction mixture. As for the other synthesised transition metal complexes, a downfield shift is expected in comparison to bis(NHCs) **17** which makes the signals at -93.2 ppm and -82.0 ppm the most likely to belong to desired products **27a** and **27b**, respectively. The most highfield-shifted resonances could belong to unreacted starting material although most reactions with the free bis(NHCs) happen quickly at room temperature. The signal group in the middle of these peaks is a singlet for unsubstituted **17a** and two belonging and close-lying doublets with a $^3J_{\text{P,P}}$ -coupling of 17.3 Hz for 7,8-diethyl substituted **17b**. One possibility is that the central signal belongs to a mixed compound **28** where, *e.g.*, one carbene unit is metal-ligated and the other one is not and only the presence of an alkyl substituent on each side of the molecule as in **17b** generates two diastereotopic phosphorus centres (Figure 54).

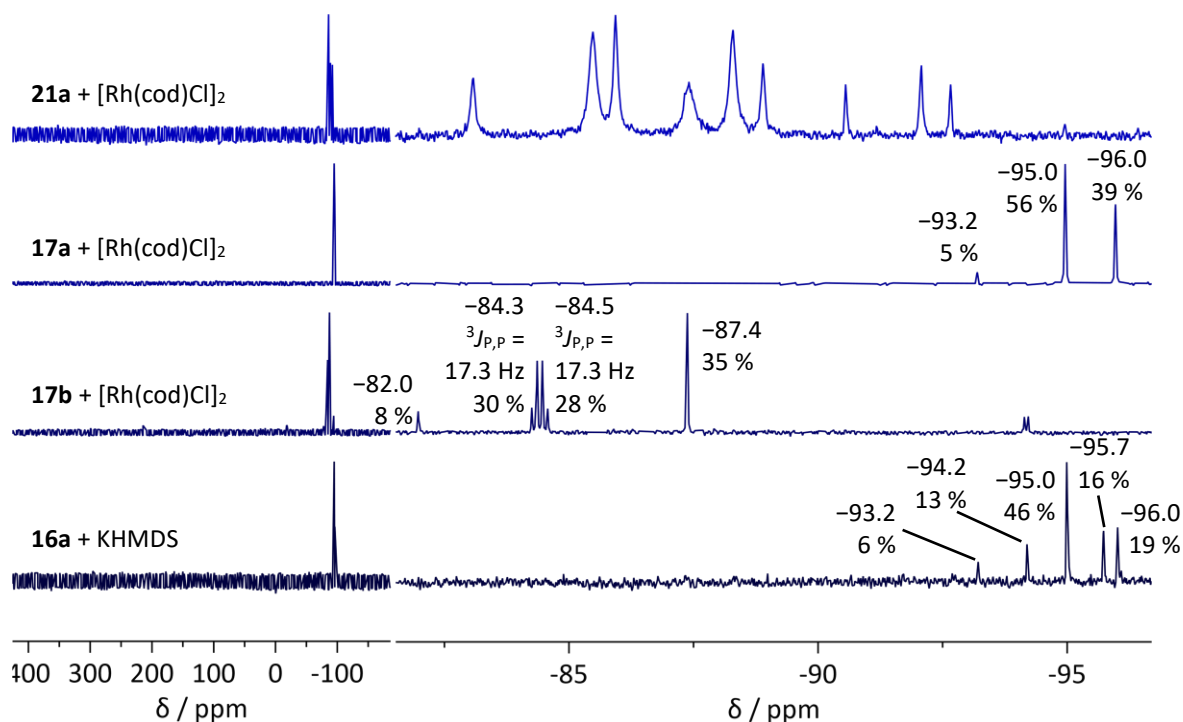


Figure 53. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the attempted syntheses of **27a,b** according to Scheme 31. Magnification of the product signals on the right.

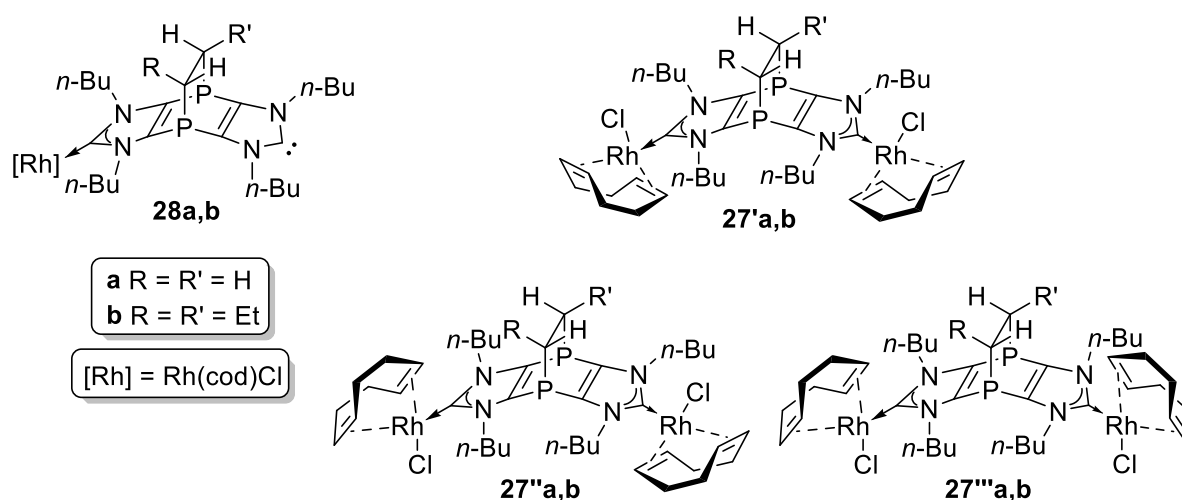


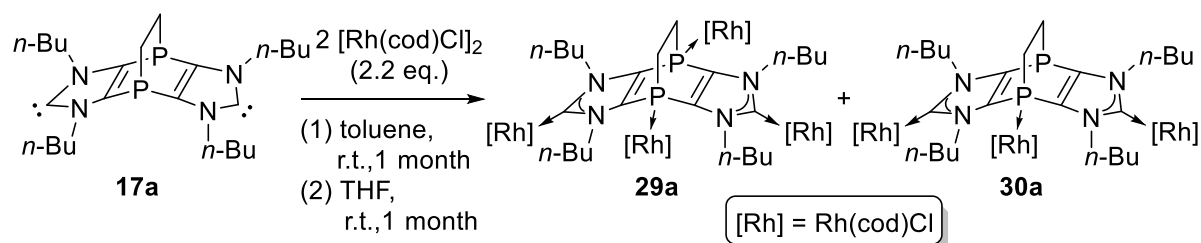
Figure 54. Possible Rh(I) complexes to explain the observed diastereotopicity and signal groups in Figure 53.

Another option would be the generation of three diastereomers **27'**–**27'''** through differently oriented Rh(cod)Cl units with the chloride ligand pointing upwards or downwards. Nothing similar was observed for **9a** but the extension through the selenium atoms provided a different coordination environment for the sterically demanding COD ligands that would bring them much closer to the C₂-bridge (see crystal structure of **9a**, Figure 24). Even after continuous stirring, the mixtures do not react to yield only one resonance/product in the end, which would speak for an isomer mixture of **27**. Theoretical

calculations on model systems of **27'a^{Me}** (with two ethene ligands instead of the COD ligand) prove that the three isomers are all local minima and are almost identical in energy with a slight preference for **27'a^{Me}** ($\Delta\Delta G = -0.45 \text{ kcal mol}^{-1}$ vs. **27'''a^{Me}**) that might be more pronounced for the actual system. In both cases partial coordination to one phosphorus centre – often only occurring after solvent removal – and complex ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra prevented isolation or further characterisation of the product mixtures.

Upon deprotonation of the ligated bis(imidazolium) salt **16a** all $^{31}\text{P}\{^1\text{H}\}$ NMR resonances in the downfield-region that indicate P-coordination vanished (Figure 53). Instead, several new signals in the highfield region appeared that also suggest that the Rh(I) fragments have dissociated from the phosphorus centres. This is only reasonable considering the significantly better donor ability of the carbene centres compared to the phosphorus centres. Among the signals are the three resonances at -93.2 , -95.0 and -96.0 ppm that also appeared in the direct reaction of **17a** with $[\text{Rh}(\text{cod})\text{Cl}]_2$ which supports the assumption that this is a product mixture of, *e.g.*, **27'–27'''**. The reaction proceeds unselectively and no product could be isolated from the mixture. Attempts to synthesise tetranuclear heterometallic complexes from **16a** with Ag_2O directly or deprotonation with KHMDS in the presence of AgOTf only yielded insoluble solids or very unselective reaction mixtures.

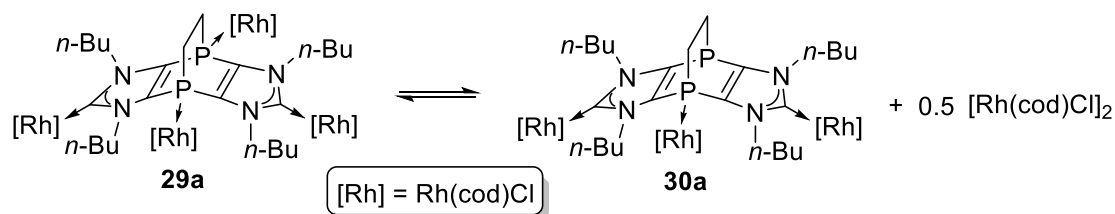
As none of the synthetic methods displayed in Scheme 31 afforded a clearly defined, isolable dinuclear Rh(I) complex, a tetranuclear homometallic complex **29a** was targeted. The $\text{Rh}(\text{cod})\text{Cl}$ unit appeared to be the transition metal fragment that binds the strongest to the poor σ -donating and π -accepting phosphorus centres in **2** and **11** and, hence, a tetranuclear complex containing this was most promising. Performing the reaction displayed in Scheme 32 in toluene yields a hardly soluble yellow solid while the (poorly resolved) $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum indicates a still significant amount of only mono-P-coordinated complex **30a**. Dissolving the reaction mixture in THF after solvent removal *in vacuo* yields a cleaner reaction mixture that contains 15 % of **30a**.



Scheme 32. Formation of tetranuclear Rh(I) complex **29a** in a mixture with trinuclear complex **30a**.

The reaction could not be driven to completion in solution as NMR spectroscopy always showed at least the aforementioned amount of trinuclear complex despite $[\text{Rh}(\text{cod})\text{Cl}]_2$ still being present. As **17a** – especially when already Rh(I)-coordinated at the carbene centres – poses as worse donor than

2a it is also possible that small amounts always dissociate in solution following the equilibrium shown in Scheme 33.



Scheme 33. Possible equilibrium present in solutions of **29a**.

Nevertheless, the mixture was isolated and characterised as a yellow solid while also containing residual [Rh(cod)Cl]₂. Following the observations made for **27a** with **27'a–27'''a** the ³¹P NMR spectrum (Figure 55) shows two doublets for **29a** at –29.5 and –33.8 ppm with ¹J_{Rh,P}-coupling constants of 163.7 and 160.8 Hz, respectively.

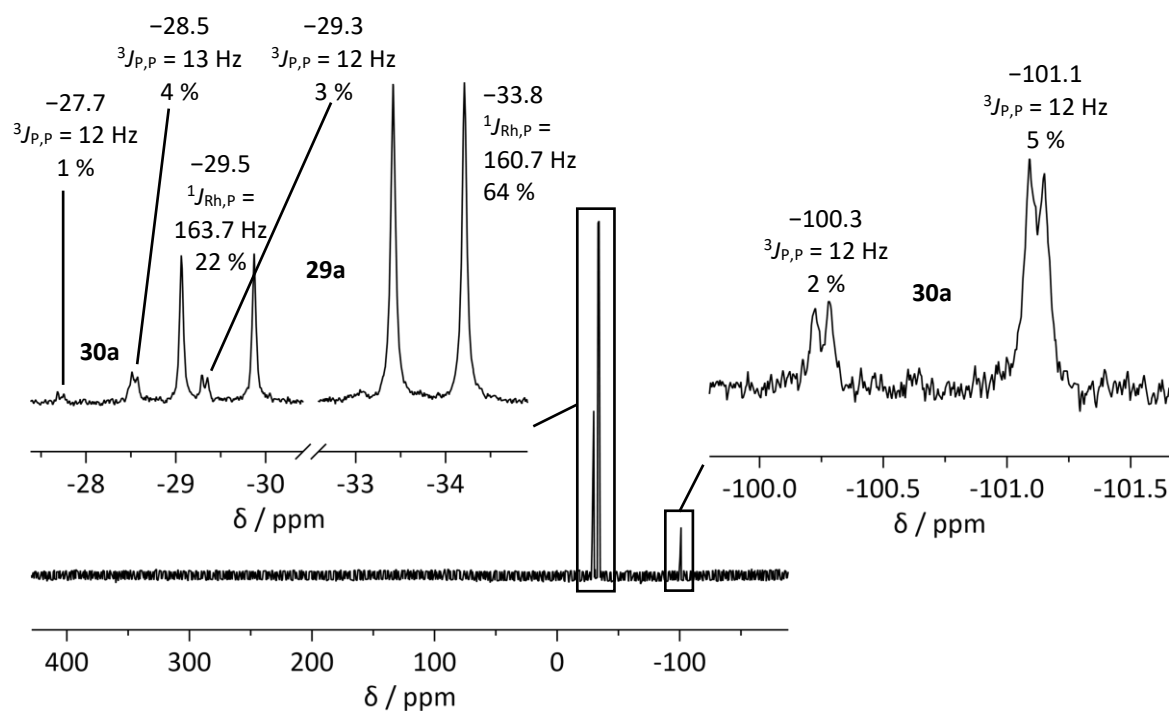


Figure 55. ³¹P{¹H} NMR spectrum of **29a** and **30a** after isolation in CD₂Cl₂.

They present in a ratio of approximately 1:3 that can also be observed in **30a** which supports the hypothesis of the above-shown equilibrium. After comparing with the crystal structures of **9a** and **16a** and because the deviations in the ³¹P NMR spectroscopic shifts are relatively small, it can be assumed that no isomerisation happens at the P-bound Rh(I) units. The comparison with **9a** as well as the obtained SCXRD analysis (*vide infra*) of **29a** also suggests that the main product carries Rh(I) fragments with upwards oriented chloride ligands at both carbene centres (**29'a**, Figure 56). Subsequently, as

diastereomer **29'''a** should carry the highest steric strain and is therefore the least favoured one, the observed isomer in lower amount is probably **29''a**.

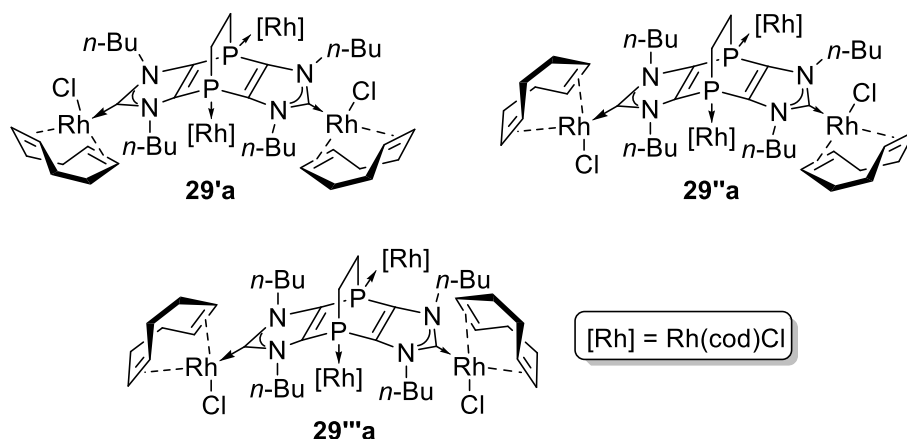


Figure 56. Possible diastereomers of **29a**.

The observed $\Delta\delta$ value of approximately 61 ppm is comparable to those for **9a** and **16a**, albeit a little bit smaller; the same is true for the $^1J_{\text{Rh,P}}$ -coupling constants that are still larger than for Dielmann's 7,8-dihydro-1,4-diphospha-barrelenes⁵¹ due to the large s-character of the phosphorus lone pair. When comparing the P-donor ability of **17a** with those of **2a** and **11a**, it should be placed in between those two's due to its more accessible lone pairs (Figure 36) and the less pronounced electron-withdrawing effect of the imidazole-2-ylidene units in comparison to the imidazolium rings. However, as coordination always happens at the carbene centres first electron density is already withdrawn from the system which further lowers the σ -donor ability of the P centres. Both the carbene carbon atoms as well as the phosphorus atoms possess only moderate or poor π -acceptor abilities which disfavours the coordination to phosphorus. This effect can be observed very well in **29a** where never all phosphorus centres are coordinated in solution – in contrast to **2a** and even poorer donor **11a**. The $^{13}\text{C}\{^1\text{H}\}$ NMR resonance for the carbene carbon atom is highfield-shifted to 191.7 ppm with a $^1J_{\text{Rh,C}}$ -coupling constant of 52 Hz. This value is around 10 ppm higher than for, *e.g.*, the same complex of IMes. Although according to previous investigations bis(NHCs) **17** should resemble IMes the additional coordination to the phosphorus centres changes the NHC unit's electronic properties.

The formation of **29a** could further be proven by high-resolution mass spectrometry and SCXRD analysis with single crystals obtained from a saturated toluene solution (Figure 57). The SCXRD analysis confirms the molecular structure of **29'a**. All four Rh(I) centres are in a square planar environment with either the carbene or phosphane ligand. As for **9a** and **16a**, the angular sum around phosphorus in the phosphane ligand is increased to 294 ° while the N-C-N angle in the imidazole units averages to 105(4) ° which is close to the corresponding value in **23b**. The Rh-P bond lengths are almost identical to the

ones in **9a** and **16a** but slightly shorter than in Dielmann's Rh(I) complexes due to the reduced electron density in the bent scaffold. The Rh(I)-ligand-Rh(I) angle between the two Rh-P bonds amounts to circa 168 ° which is a value in between those of **9a** and **16a**. The overall folding angle amounts to 132 ° which is only slightly wider than for **9a**, considering that the protons are substituted by much bulkier Rh(cod)Cl fragments. The N-C-N angles as well as the Rh-C2/C21 bond lengths of on average 2.02(4) Å compare very well to literature-known Rh(cod)Cl complexes to unsaturated mono(NHCs) with N-cycloalkyl substituents.¹⁵⁷

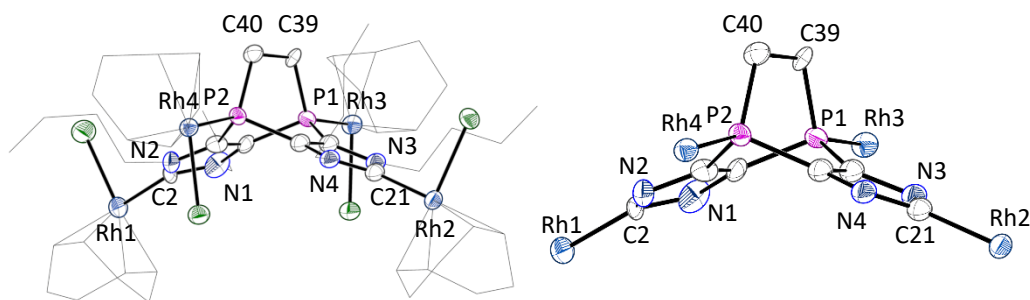


Figure 57. Molecular structure of **29a** in the single crystal. Thermal ellipsoids are set at 50 % probability. Hydrogen atoms and solvent molecules were omitted for clarity. *n*-Butyl chains and COD ligands are simplified as wires (left) or omitted, together with Cl ligands, for additional clarity (right).

29a does not show thermal retro-[4+2]-cycloaddition behaviour – as does none of the compounds that possesses at least one four-coordinate phosphorus centre. While this does not allow the synthesis of new 1,4-diphosphinine scaffolds this way, it could offer stabilisation and protection of the bent scaffold and the phosphorus centres for selective manipulation on the carbene centres even at higher temperatures in solution.

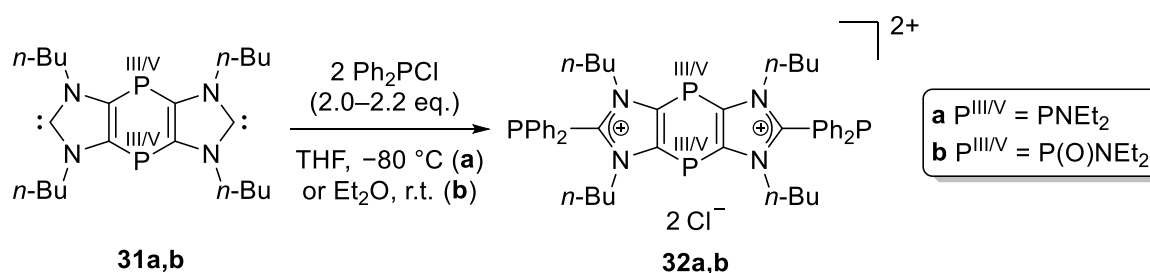
3.3 Main group element adducts of P-bridged, bent and planar bis(NHCs)

While transition metal complexes of bis(NHCs) have been investigated in great depth, comparatively few reports on adducts of small, flexible bis(NHCs) to main group element compounds have been reported and none on adducts of rigid bis(NHC) scaffolds although they offer another entry point into supramolecular chemistry. Main group element adducts to mono(NHCs) are well established and have been used to access new transition metal complexes as well as main group elements in unusual oxidation states. Thus, this third chapter focuses on the synthesis of carbene adducts from previously reported planar and new bent, P-bridged bis(NHCs) to reagents from groups 13 to 15. Their analytical properties were explored and significant experimental differences between both scaffolds were investigated and explained via theoretical calculations. Moreover, the possibility of additional coordination to the phosphorus centres with group 13 reagents as well as retro-[4+2]-cycloadditions were studied.

3.3.1 Synthesis of tricyclic bis[(diphenylphosphino)imidazolium] salts

3.3.1.1 Reactions of planar, P-bridged bis(NHCs)

Previous work on the synthesis and reactivity of planar, phosphorus-bridged bis(NHCs) did not include the synthesis or investigation of main group element adducts to these bis(NHCs). Main group adducts can often be easily accessed and hold potential for extending the scaffold, introducing additional functional sites, *e.g.* for coordination, or polymer formation. Many NHC adducts to group 15 compounds contain phosphorus for aforementioned reasons and they can usually be characterised as P^V , P^{III} or P^I complexes.⁹⁹ Due to their structures they are better looked at as “imidazoliumyl-substituted phosphorus compounds” as summarised by Weigand in 2018.¹⁵⁸ To gather first insight into the reactivity of planar, phosphorus-bridged bis(NHCs) towards phosphorus compounds the formation of diphenylphosphanyl-substituted imidazolium salts **32** from planar bis(NHCs) **31** (formerly **LII**) and chlorodiphenylphosphane according to Scheme 34 was targeted.



Scheme 34. Attempted formation of bis[(diphenylphosphino)imidazolium] salts **32** from bis(NHCs) **31**.

For both the P^{III} - and P^V -bridged bis(NHCs) $^{31}P\{^1H\}$ NMR monitoring of the reactions solutions did not show the formation of the desired product but instead a mixture of other products (Figure 58). Kuhn had synthesised the first diphenylphosphanyl-substituted imidazolium salt in 1999,¹⁵⁹ describing a ^{31}P NMR spectroscopic shift of -27.1 ppm for the corresponding product of an unsaturated *N*-iso-propyl substituted mono(NHC) which is structurally and electronically comparable to the investigated bis(NHCs). In case of the P^V -bridged bis(NHC) **31b** the $^{31}P\{^1H\}$ NMR spectrum in diethyl ether shows unambiguously identifiable signals for residual Ph_2PCl , $Ph_2P(O)H$ and tetraphenyldiphosphane *P*-oxide ($Ph_2P-P(O)Ph_2$). Kuhn had observed his product to be stable in solution for 30–60 minutes and described a decomposition mechanism involving the hydrolysis of Ph_2PCl and the formation of the tetraphenyldiphosphane *P*-oxide under assistance of the carbene as base. A similar mechanism can be assumed for the reaction of **31b** with Ph_2PCl as the $^{31}P\{^1H\}$ NMR spectrum also shows two resonances at -6.6 and -6.7 ppm that fit the corresponding bis(imidazolium) chloride **33** (Scheme 35).

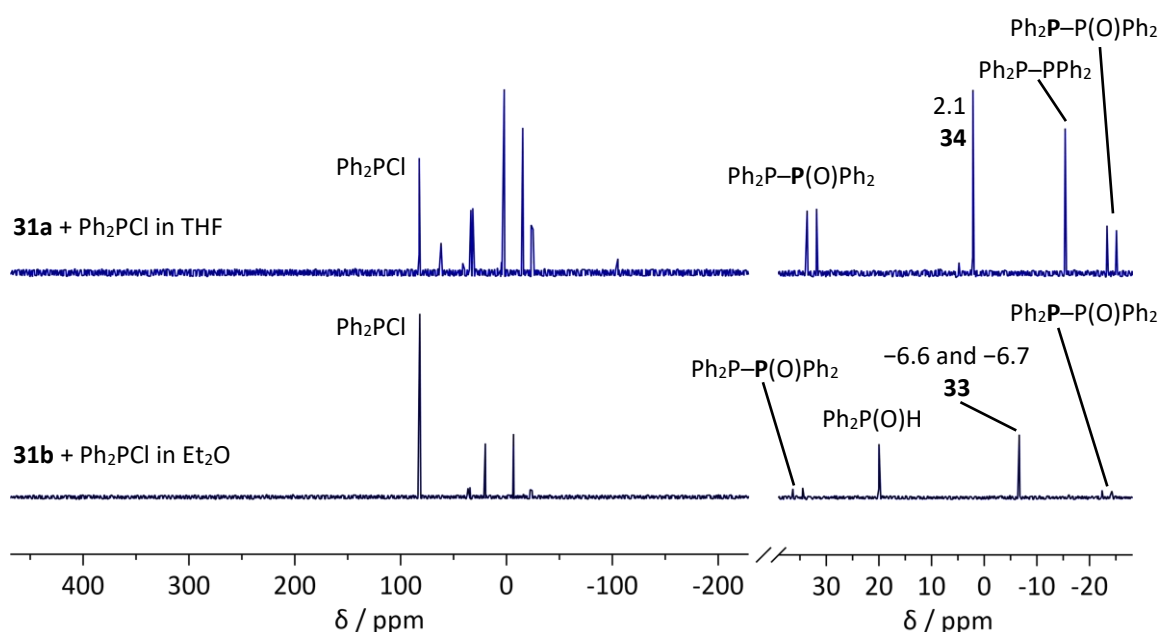
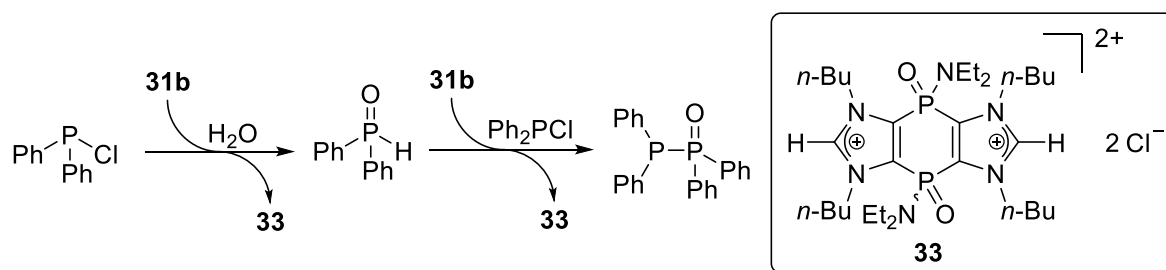


Figure 58. $^{31}P\{^1H\}$ NMR spectra of the attempted syntheses of **32a,b** according to Scheme 34. Magnification of the product signals on the right.



Scheme 35. Possible decomposition mechanism explaining the absence of **32b** and presence of **33**.

The formation of the observed products could not be prevented although thoroughly dried solvents were used. Lower temperatures, change of solvent as well as immediate NMR spectroscopic measurements of the reaction mixture did not lead to the observation of the desired product. Furthermore, the *in situ* use of **31b** in THF – with residual KHMDS potentially present, too – does not improve or change the reaction outcome, and the synthesis of **32b** (Scheme 34) could not be achieved.

The reaction mixture of P^{III}-bridged bis(NHC) **31a** also contains the diphosphane *P*-oxide as well as tetraphenyldiphosphane (Ph₂P–PPh₂) alongside a new, slightly broadened signal at 2.1 ppm. While the mechanism described in Scheme 35 explains the formation of the former, the diphosphane could be formed via a reductive coupling involving the NHC – a pathway that was originally proposed by Kuhn¹⁵⁹ – under generation of the corresponding C²-chloro imidazolium chloride. The formation of the diphosphane is also accompanied by the formation of Ph₂PNEt₂ ($\delta(^{31}\text{P}\{^1\text{H}\}) = 61.8$ ppm) which can be explained by taking the FMO situation of **31a**^{Me} (*n*-butyl and ethyl groups substituted for methyl) into consideration (Figure 59).

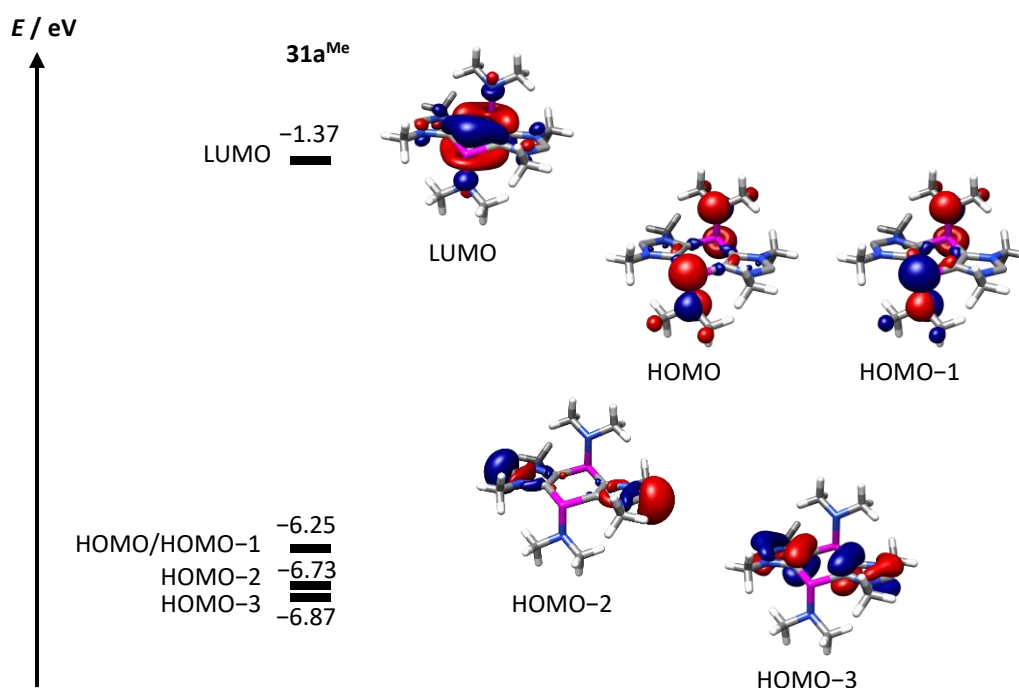


Figure 59. Selected calculated FMOs of compound **31a**^{Me} (trans-isomer).

In contrast to previous calculations the HOMO has its largest contribution from π^* -type orbitals of the P–N bond and is very closely followed by a similarly looking HOMO–1. The electron lone pairs at the carbene centres only constitute the HOMO–2 which is not much lower in energy but the energetic proximity of these MOs and the resulting competing reactivity towards some reagents has not been acknowledged before. The presence of Ph₂PNEt₂ in the reaction solution suggests that a metathesis reaction happened involving the phosphorus centres in Ph₂PCl and the tricyclic compound. The

additional participation of the two phosphorus centres of **31a** might allow new pathways to the formation of the tetraphenyldiphosphane and more complicated reaction mixtures. Thus, the new product **34** (Figure 60) could also belong to combinations that contain a *P*-Cl functionality as well as intact carbene centres. Compound **34** could not be isolated and further characterised as separation from the other products proved to be difficult and more decomposition happened upon work-up.

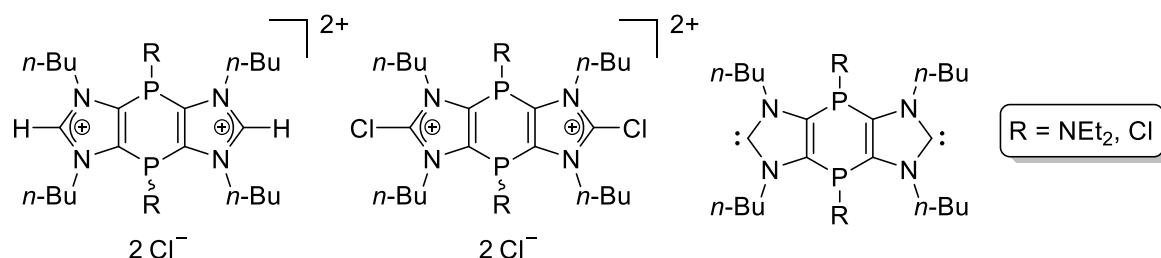


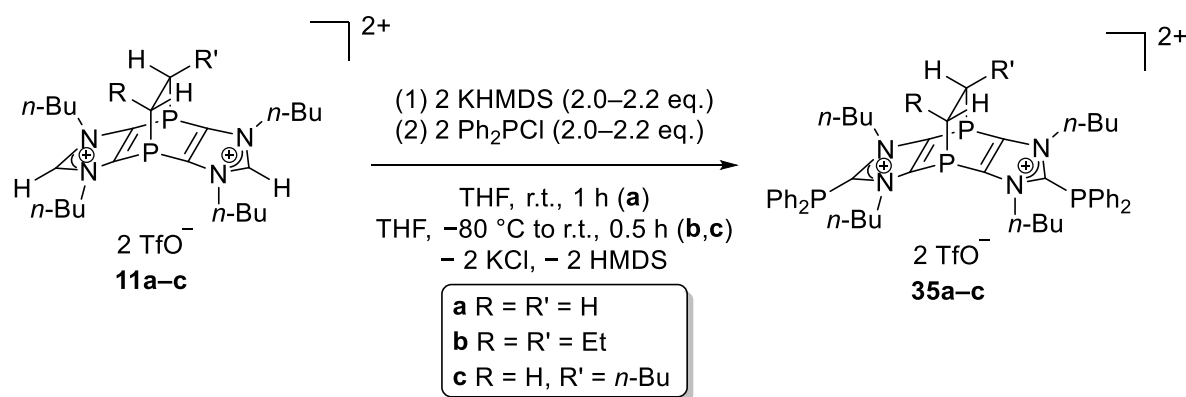
Figure 60. Possible structures of **34**.

The FMO situation of bis(NHC) **31b** looks analogously to the one describe for bent bis(NHCs) **17** and thus, no metathesis reaction could be observed and only the aforementioned decomposition mechanism can be applied.

In conclusion, the observed reaction behaviour implies that for **31a** the selective formation of main group adducts (or related compounds) containing polar E-X bonds (X = Cl, Br) will be prevented while for **31b** adduct formation with suitable reagents should be possible. This reactivity pattern will be investigated further in chapter 3.3.3.1.

3.3.1.2 Reactions of bent, P-bridged bis(NHCs)

Bent, phosphorus-bridged bis(NHCs) **17** do not possess P-functionality and, thus, the carbene centres are not heavily influenced by the P-bridging in the backbone which makes them better candidates for the synthesis of diphenylphosphanyl-substituted bis(imidazolium) salts. Indeed, performing the reaction displayed in Scheme 36 using *in situ* generated bis(NHCs) **17a–c** yields triflate salts **35a–c**. The initially formed KOTf undergoes an anion exchange to give KCl and the corresponding imidazolium triflates which have proven to be of extraordinary stability. The reactions proceed quickly in all cases and show product formation in high selectivity. $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopic monitoring of the reaction mixtures reveals the formation of the (di-)phosphane oxides only for **35a** and **35b**. Compounds **35a–c** are well soluble in toluene and could be separated almost completely from the side products; for **35a** and **35b** traces of diphenylphosphane oxide and tetraphenyldiphosphane *P*-oxide remained. They present as colourless to yellow solids and show typical NMR spectroscopic features (Table 9).



Scheme 36. Formation of Ph_2P -substituted bis(imidazolium) salts **35a-c** from in situ generated bis(NHCs) **17**.

Table 9. Selected NMR data for compounds **35a-c** in C_6D_6 .

	$\delta(^{31}\text{P})(\text{bridgehead})$ / ppm	$^3J_{\text{P,P}}$ / Hz	$\delta(^{31}\text{P})(\text{Ph}_2\text{P})$ / ppm	$\delta(^{13}\text{C}\{^1\text{H}\})(\text{C}^2)$ / ppm	$^1J_{\text{P,C}}$ / Hz
35a	-92.2	-	-25.1	146.2	58.5
35b	-84.3	-	-25.3	147.1	59.1
35c	-87.1, -86.6	15.7	-25.5, -25.1	146.1, 146.8	58.6, 57.9

While the resonances for the central phosphorus nuclei remain in the typical region for 1,4-diphospha-barrelenes, the signals for the newly introduced phosphorus nuclei appear at around -25 ppm in the ^{31}P NMR spectrum for all derivatives. This value is very close to the one observed by Kuhn¹⁵⁹ and fits a dichlorophosphane with an aromatic carbon-bound substituent. The asymmetric derivative shows two resonances for each phosphorus nucleus type because, as for **2c**, the diastereotopicity due to the bridge's asymmetric substitution is translated outwards. Furthermore, a $^3J_{\text{P,P}}$ -coupling of 15.7 Hz can be determined which is a first confirmation of the displayed imidazolium units as it is very close to the value observed for **11c**. The carbon NMR resonance of the former carbene can be found at around 146 ppm with $^1J_{\text{P,C}}$ -coupling constants of circa 58 Hz which additionally confirms the proposed structure and the imidazolium units drawn in Scheme 36.

Single crystals of both the unsubstituted derivative **35a** and asymmetric derivative **35c** could be analysed, confirming the proposed structure and counter anion, and are displayed in Figure 61. They are of relatively poor quality but share some distinct structural features that can be determined. The value for the N-C-N angle in the imidazole units lies between 106.4(13) and 109.0(13)°, which is getting close to the angle determined for the imidazolium salt **11b** and is larger than for the bis(NHCs) **17** and their metal complexes. The angle sum around the bridged phosphorus atom averages to 283° for all

the corresponding centres in **35a** and **35c** while the angle sum around the *P*-diphenyl substituted centres amounts to 310–312 ° which is expectedly much less constrained.

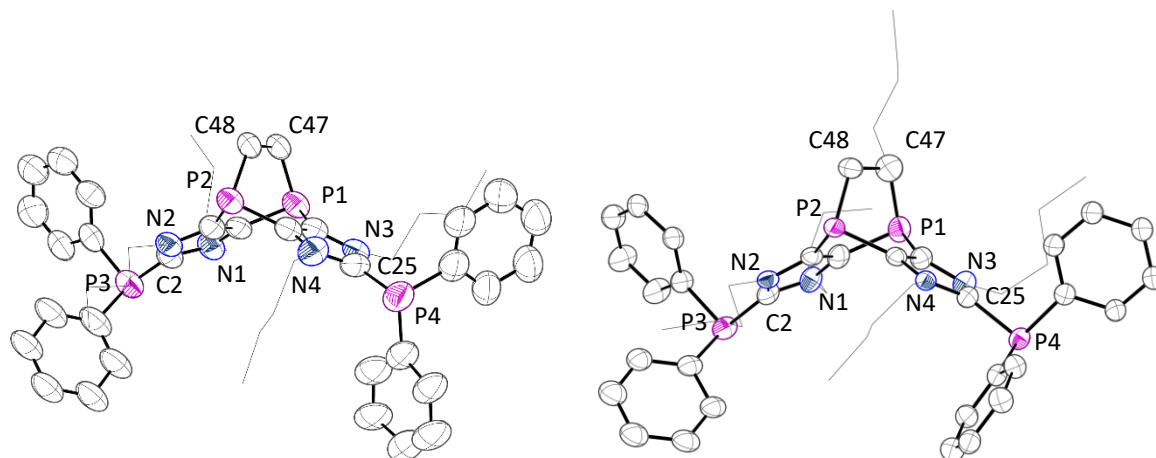


Figure 61. Molecular structure of **35a** (left) and **35c** (right) in the single crystal. Thermal ellipsoids are set at 50 % probability. Hydrogen atoms, solvent molecules and OTf anions were omitted for clarity. *n*-Butyl chains are simplified as wires for additional clarity.

Kuhn's diphenylphosphanyl-substituted imidazolium chloride could easily be reacted with negatively charged MCl_3 ($M = Pd, Pt$) fragments to yield the corresponding complexes.¹⁶⁰ Salts **35** can be viewed as tetraphosphanes containing four possible coordination sites. Theoretical calculations on **35b^{Me}** show that it is energetically as stabilised as the corresponding bis(imidazolium) salt **11b^{Me}** but the lone pairs at the central phosphorus atoms, albeit being at the same energy level, constitute the HOMO–8. Two almost degenerate HOMO and HOMO–1 are largely centred at the lone pairs of the other phosphorus atoms making them the preferred coordination site. $^{31}P\{^1H\}$ NMR spectroscopic monitoring of a reaction solution of **35a** with an approximately 40-fold excess of the borane dimethylsulfide adduct in toluene after only two and half hours shows the complete disappearance of the resonance around –25 ppm. Instead, new signals at 20.0 and 21.8 ppm appeared which fit the coordination compound and the resonance for the caged phosphorus nuclei moved slightly highfield to –90.9 ppm. Thus, functionalised bis(imidazolium) salts **35** could be used as an extended linker between two metal centres coordinated to the Ph_2P units while the caged phosphorus centres can probably be addressed with suitable reagents like $[Rh(cod)Cl]_2$.

Theoretical calculations also revealed the typically high aromaticity of the imidazolium units with NICS(1) values of –9.1 ppm accounting for aromaticity levels of up to 91 % of benzene or 96 % of 1,3-dimethylimidazolium. Consequence of the resemblance to bis(imidazolium) salts **11** is that a thermal retro-[4+2]-cycloaddition does not occur. NMR spectroscopic monitoring of samples of **35a–c** in C_6D_6 does not show the formation of the respective alkene and no change in the $^{31}P\{^1H\}$ NMR spectrum. The high stability of the bis(imidazolium) scaffold, which lowers the MOs energetically, greatly disfavours the retro-[4+2]-cycloaddition.

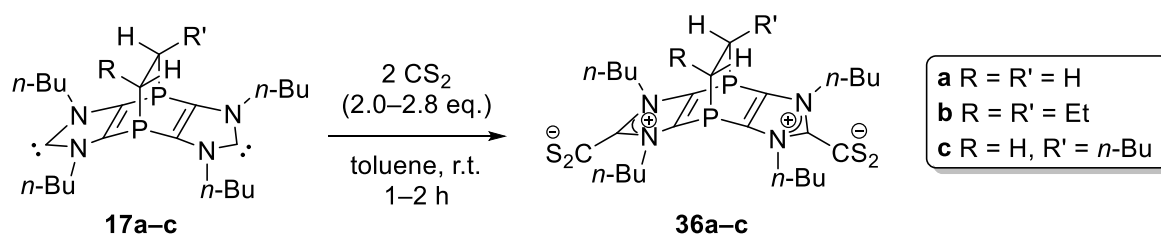
3.3.2 Synthesis and investigations of carbon dichalcogenide bis(NHC) adducts

3.3.2.1 Synthesis and characterisation of carbon disulfide bis(NHC) adducts

NHCs react with a multitude of group 14 compounds with the element in oxidation state II or IV. Adducts to carbon dioxide are usually obtained easily and present with varying stability often enabling the thermal liberation of the free NHC *in situ* which makes them good NHC transfer reagents. Similarly, adducts to carbon disulfide are accessible but they show increased stability and excellent crystallisation behaviour which makes them possible targets for the study of stereoelectronic parameters of different NHCs.¹⁶¹ The chemistry of NHC betaines has been reviewed in 2009¹⁶² and some investigations on the complexation and cluster formation of CS₂ adducts have been performed more recently.¹⁶³ For phosphorus-bridged bis(NHCs) **17** and **31** the reactivity towards carbon disulfide was investigated first, to create a baseline for the reactions with a large excess of carbon dioxide, and due to the increased reaction control in working with liquids instead of gases.

Unfortunately, reactions of planar bis(NHCs) **31a** and **31b** with two equivalents of carbon disulfide only yielded unselective reaction mixtures. Surprisingly, NMR spectroscopic monitoring showed more than five resonances in the expected region of the ³¹P{¹H} NMR spectrum for **31a** and more than twenty for **31b**. Changes in the reaction conditions like reaction time, solvent and equivalents of carbon disulfide did not lead to improved reaction outcomes. As for the reactions with chlorophosphanes (*vide supra*), the energetically favourable *P*-NEt₂ functionality might cause side reactions. For **31b** a clean reproducibility of the synthesis according to provided protocols^{136,137} could only be achieved in some cases. Thus, impurities contained in the batches of **31b** used for the reactions with carbon disulfide could also cause the unselective reaction outcome.

In contrast, reactions of bent bis(NHCs) **17** with two equivalents of carbon disulfide in toluene cleanly yielded the corresponding adducts **36** (Scheme 37).



Scheme 37. Formation of CS₂ adducts **36a–c** from bis(NHCs) **17**.

36a–c could be isolated as typically burgundy-coloured solids in moderate to good yields up to 61 %. The ³¹P NMR spectra show resonances that are slightly highfield-shifted in comparison to the free bis(NHCs)' and the former carbene carbon signals are shifted to around 152 ppm which NMR

spectroscopically confirms the betaine type structure containing imidazolium units (Table 10). The carbon resonances for the CS₂ units lie around 224 ppm in the ¹³C{¹H} NMR spectrum which corresponds well with reported values of mono(NHC) CS₂ adducts.¹⁶¹

Table 10. Selected NMR and UV/vis data for compounds **36a–c** in THF-*d*₈ (**36a,c**) or C₆D₆ (**36b**).

	$\delta(^{31}\text{P})$ / ppm	$^3J_{\text{P,P}}$ / Hz	$\delta(^{13}\text{C}\{^1\text{H}\})(\text{C}^2)$ / ppm	$\delta(^{13}\text{C}\{^1\text{H}\})(\text{CS}_2)$ / ppm	$\lambda(\text{CS}_2)$ / nm
36a	−95.4	−	152.4	224.9	363
36b	−87.1	−	152.7	223.8	361
36c	−88.6, −92.0	17.0 Hz	152.4, 152.8	224.8, 224.8	364

The UV/vis spectra of circa 10^{−6} molar toluene solutions of **36a–c** all show an absorbance maximum between 361 and 364 nm which corresponds to the burgundy colour of the solids. TD-DFT calculations on the TPSS-D4/CPCM_{toluene}/def2-TZVPPD//TPSS-D4/CPCM_{THF}/def2-TZVP level of theory for **36b**^{Me} confirm the absorbance to belong to π - π^* -transitions in the CS₂ units which is in accordance with the literature.¹⁶¹ Furthermore, the IR spectra of **36a–c** show a strong band each for the CS₂ unit at 1052–1054 cm^{−1} which are typical for backbone-unsaturated mono(NHC) adducts like the IMes CS₂ adduct.¹⁶¹

As mentioned above CS₂ adducts of NHCs tend to crystallise very well which allows for the determination and comparison of the structural features of different adducts. Only in this case, for all derivatives **36a–c** single crystals could be obtained from toluene solutions and analysed via X-ray diffraction studies (Figure 62). However, the structure of derivative **36c** is of poor quality and thus, will not be discussed. Though, the structural motif and orientation of the CS₂ units were confirmed and are comparable to the other two derivatives.

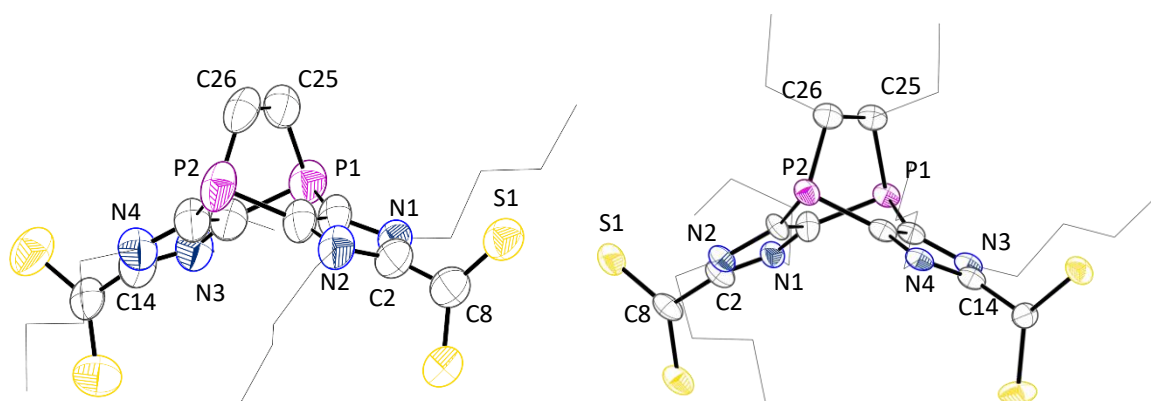


Figure 62. Molecular structure of **36a** (left) and **36b** (right) in the single crystal. Thermal ellipsoids are set at 50 % probability. Hydrogen atoms and solvent molecules were omitted for clarity. *n*-Butyl and ethyl chains are simplified as wires for additional clarity.

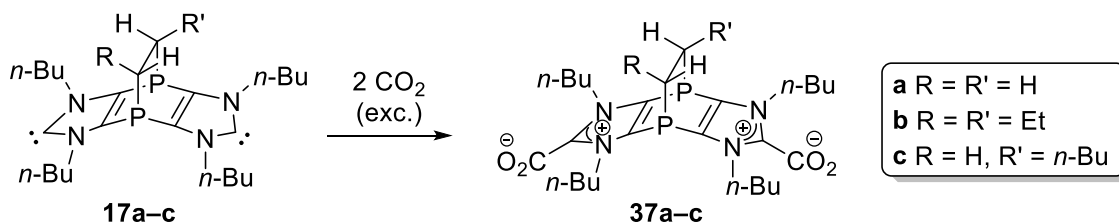
The CS₂ units are oriented perpendicular to the imidazole plane with N1-C2-C8-S1 torsion angles between 78.705(7) (**36a**) and 99.512(3) ° (**36b**) which is the known configuration for NHCs with bulkier

N-substituents.¹⁶¹ The average N-C-N angle in the imidazole unit amounts to circa 108 ° which is expectedly closer to the value for the bis(imidazolium) salts and further confirms the betaine-style drawing of the CS₂ adducts. As seen before, the effect of the adduct formation on the central phosphorus centres is small and their average angle sum is still relatively small ($\sum \angle(P) = 283^\circ$ for **36a**, $\sum \angle(P) = 284^\circ$ for **36b**).

Theoretical calculations on derivative **36b**^{Me} reveal FMOs that are centred in p-type orbitals of the CS₂ units making them the preferred coordination site. The NICS(1) value of the imidazolium ring, albeit being larger than for above-described imidazolium scaffolds ($\delta = -7.7$ ppm), still allocates an aromatic character of 78 % of that of benzene. Both the positive and negative charges in the CS₂ adducts are delocalised well over three atoms each, which increases their stability and makes them air-stable for several days. As seen for the other imidazolium-containing derivatives above, a thermal retro-[4+2]-cycloaddition did not occur for any of **36a–c** and they remained stable in solution; the loss of CS₂ was also not observed.

3.3.2.2 Investigations on carbon dioxide bis(NHC) adducts

Having collected data for the closely related CS₂ adducts, CO₂ adducts **37** of bis(NHCs) **17** were targeted as well (Scheme 38).



Scheme 38. Targeted formation of CO₂ adducts **37a–c** from bis(NHCs) **17**.

Following protocols for the synthesis of CO₂ adducts to IMes from the free carbene,¹⁶⁴ bubbling thoroughly dried CO₂ with a pressure of circa 1 bar through a toluene solution of **17a** immediately yielded a colourless to yellow precipitate. ³¹P{¹H} NMR spectra did not show any signals due to the low solubility in all common organic solvents which could indicate the formation of the inner salt **37a** or oligomer formation through unknown reaction pathways. Performing the reaction analogously with **17b** afforded a colourless to yellow solid, as well, which was insoluble in toluene. The ³¹P{¹H} NMR spectrum recorded after solvent removal *in vacuo* and redissolving in dichloromethane shows the almost selective formation of a bis(imidazolium) salt **38b** related to **11b** with unknown counter anions X[−] ($\delta(^{31}\text{P}\{^1\text{H}\}) = -89.4$ ppm). Adding dry ice to a THF solution of **17b** leads to the formation of three major signal groups in the ³¹P{¹H} NMR spectrum (Figure 63). The reaction mixture, redissolved in dichloromethane, contains about 12 % of **38b** and 56 % of another symmetric compound with a resonance at

–92.1 ppm. The latter could be the desired product **37b** as the pronounced imidazolium-character induced by the CO₂ addition should lead to a highfield shift in comparison to **17b**. In between the two singlets are two doublets that can be assigned to a common asymmetric compound. Their position in the spectrum as well as the comparably small $^3J_{P,P}$ -coupling of 16 Hz point to a mixed salt **39b** (Scheme 39) where a similar effect as in **28b** leads to diastereotopic phosphorus nuclei.

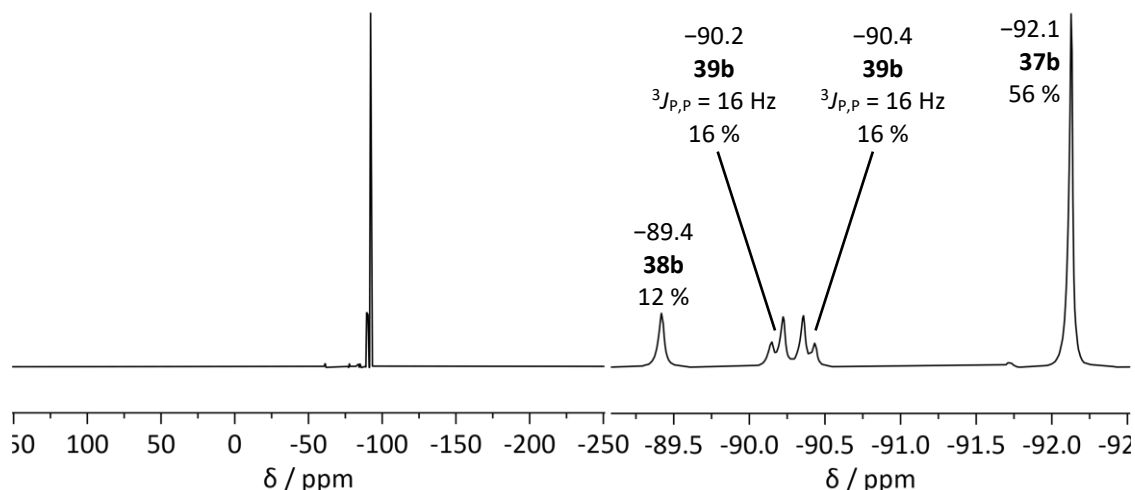
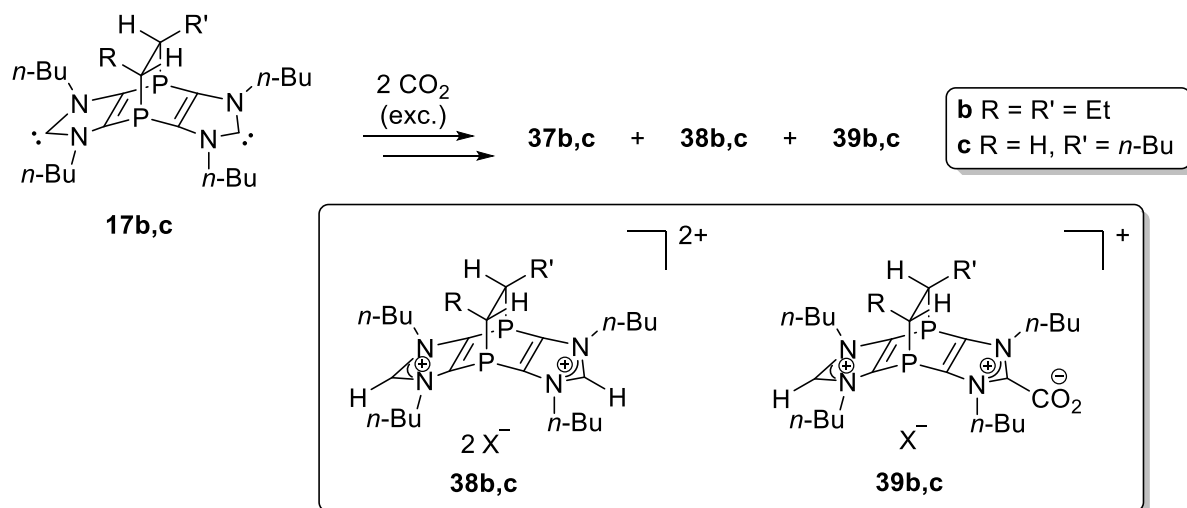


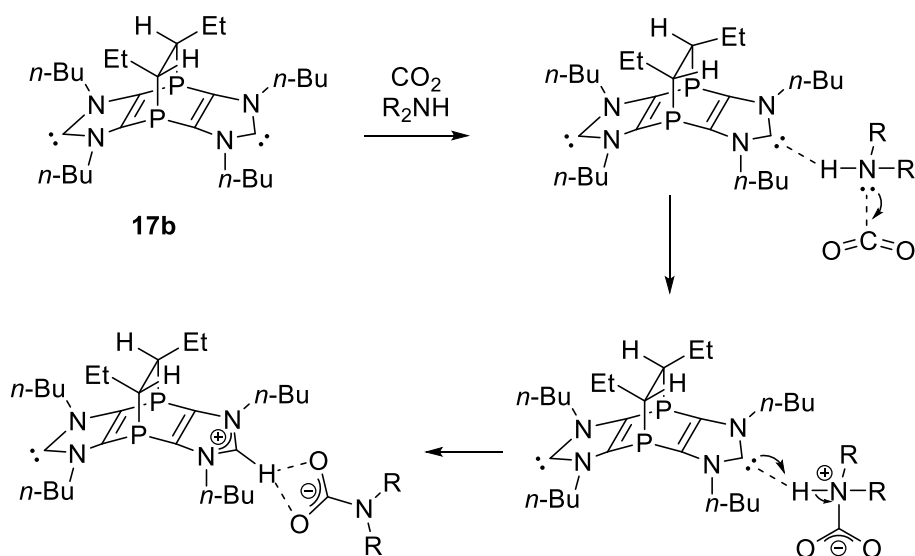
Figure 63. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the attempted synthesis of **37b** in dichloromethane. Magnification of the product signals on the right.



Scheme 39. Possible products from the reaction of bis(NHCs) **17b,c** with CO₂.

The reaction of **17c** with dried CO₂ leads to similar but more complex spectra due to the already present asymmetry even in the twofold adducts. The presence of protonated imidazolium salts is also confirmed by ^1H NMR spectra that show typical C²-H signals in the aforementioned region, including the respective $^4J_{P,H}$ -coupling constant.

The formation of protonated imidazolium salts in large amounts in dried, aprotic solvents suggests an alternative proton source. It is known that NHC CO₂ adducts with small N-alkyl substitution react with acids to the corresponding imidazoliumcarboxylic acid, which after decarboxylation (*e.g.* thermally) gives the respective imidazolium salt.¹⁶² The acid can be carbonic acid which could form in traces from CO₂ and water but this is improbable in this case as already pure ($\geq 99.995\%$) carbon dioxide was used and dried thoroughly in a tower filled with a molecular sieve (pore size 3 Å). A different proposed mechanism can be deduced from extensive calculations on the reductive functionalisation of CO₂ that were performed to determine the role of the NHC in the catalytic conversion of CO₂ into formamides with silanes as reductant and amines as functionalising reagents.¹⁶⁵ The study finds that the NHC reacts with CO₂ in the presence of an amine to give an imidazolium carbamate as contact ion pair which poses the catalytically active system.¹⁶⁶ As alluded to above, **17b** and **17c** always contain small amounts of HMDS that cannot be removed via washing or drying. For, *e.g.*, **17b** this amount usually is around 0.30 equivalents while the batch that produced the spectrum in Figure 63 contained circa 0.65 equivalents which correlates well with the observed ratios. A possible reaction pathway in agreement with conclusions from the literature¹⁶⁶ is depicted for one carbene centre in **17b** in Scheme 40.



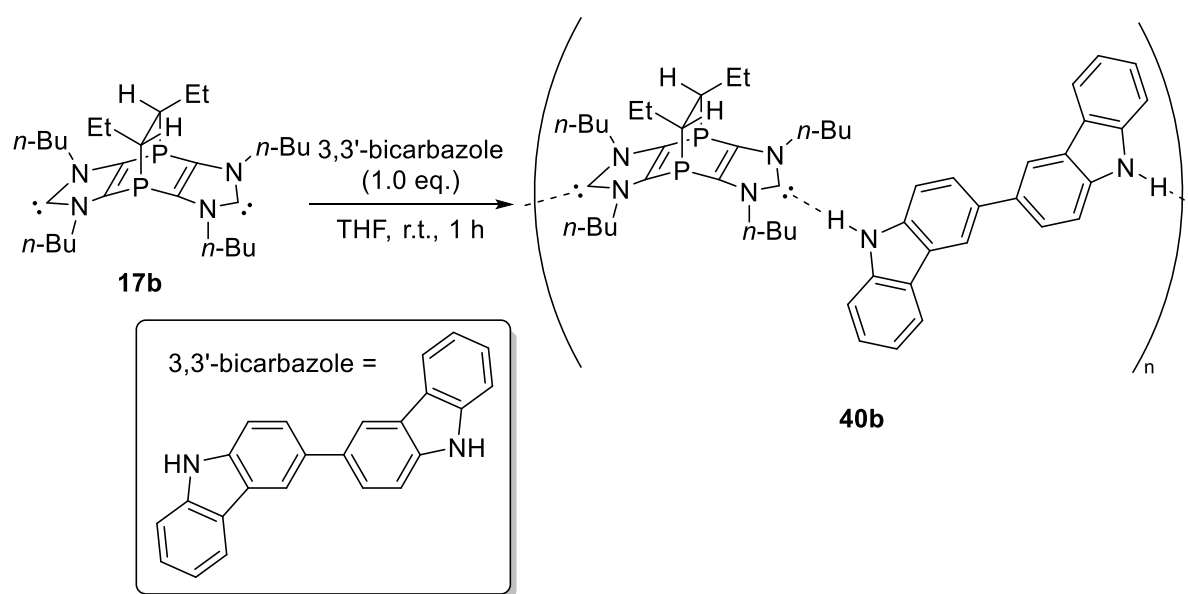
Scheme 40. Possible mechanism for the formation of imidazolium carbamates in the reaction of **17b** with CO₂.

The contact ion pair was displayed as such for the calculated catalytic system described in the literature, but depending on the used amine and the solvent the ion pair could also dissociate in solution. The reaction only occurring with carbon dioxide but not carbon disulfide is in line with the increased electrophilicity of the carbon centre in CO₂ compared to CS₂.¹⁶⁷

Further proof of the hypothesis could be obtained by the targeted synthesis of the hydrogen bonded adduct **40b** of **17b** to 3,3'-bicarbazole (Scheme 41). The behaviour of isolable mono(carbenes)

towards NH-containing fluorophores had been investigated by Protasiewicz in 2019¹⁶⁸ and 2020¹⁶⁹ showing that the formation of hydrogen bonded adducts of a mono(NHC) towards carbazole or 3,3'-bicarbazole quenches their fluorescence and significantly shifts the N-H ¹H NMR resonance. Liberation of the fluorophore via, *e.g.*, dilution reinstates the fluorescence.

Performing the reaction displayed in Scheme 41 yields a yellow, in common organic solvents only sparingly soluble solid. The NMR spectra of a circa 25 mM solution in deuterated THF shows a ³¹P NMR resonance at -86.9 ppm which is expectedly only slightly highfield-shifted in comparison to **17b**. The broad N-H ¹H NMR signal at 11.0 ppm as well as the highfield-shifted C²-carbon resonance at 214.8 ppm confirm the formation of the hydrogen bonded adduct **40b**.



Scheme 41. Proposed formation of bis(NHC) bicarbazole adduct **40b** from bis(NHC) **17b**.

The addition of equimolar amounts of **17b** to a fluorescing 10 mM THF solution of 3,3'-bicarbazole quenched the fluorescence immediately upon formation of **40b**. The subsequent addition of an excess of carbon dioxide led to the formation of a beige solid and does not reinstate the fluorescence of the 3,3'-bicarbazole which excludes the clean formation of a bis(NHC) adduct under liberation of the fluorophore. Analogously, direct addition of carbon dioxide to an 8 mM THF solution of **40b** produces the same result and an almost identical ³¹P NMR spectrum in dichloromethane (Figure 64). It shows the same signal groups that were observed in the reaction of **17b** with carbon dioxide but the bis(imidazolium) salt **38b** has the largest percentage in solution. This correlates well with the increased acidity of 3,3'-bicarbazoles ($pK_a \approx 19.9$)¹⁷⁰ in comparison to HMDS ($pK_a \approx 30$)¹⁷¹ and the only trace amounts of the latter contained in the isolated bis(NHCs). Unfortunately, the ¹H NMR spectrum does not show any distinct proton signal for the C-H/N-H functionality and no further proof of the constitution of the proposed bis(imidazolium) carbamate could be obtained.

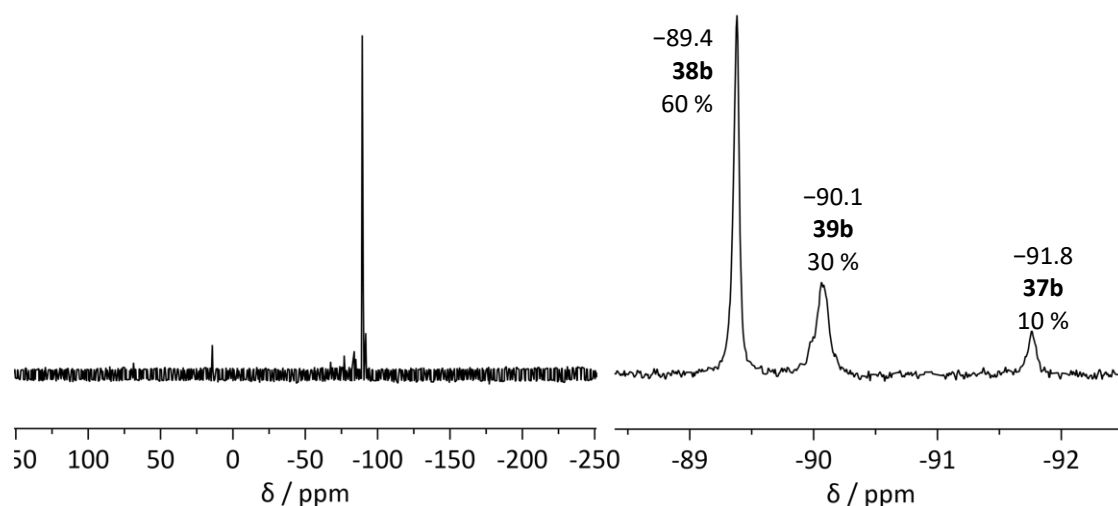
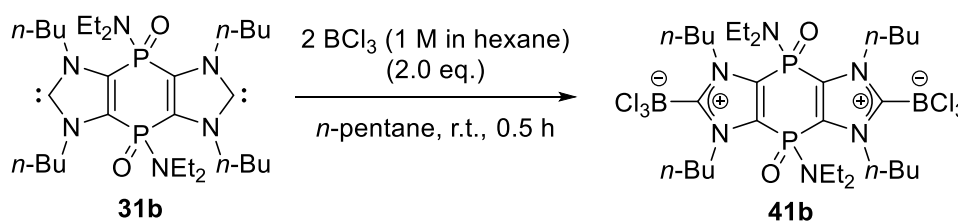


Figure 64. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the reaction of **40b** with CO_2 in dichloromethane. Magnification of the product signals on the right.

3.3.3 Synthesis of borane bis(NHC) adducts

3.3.3.1 Reactions of planar, P-bridged bis(NHCs) with boron trichloride

NHC adducts to boron halides – often chlorides – are valuable precursors in main group chemistry as they can be easily functionalised further or reduced to entry the field of low-valent boron compounds like NHC stabilised diborenes.^{99,98} For bis(NHC) scaffolds this reactivity might enable the synthesis of boron-bridged oligomers. Thus, due to its more inert P-functionality, P^{V} -bridged bis(NHC) **31b** was reacted first according to Scheme 42 to yield BCl_3 adduct **41b**.



Scheme 42. Synthesis of BCl_3 adduct **41b** from bis(NHCs) **31b**.

Immediately upon addition of the BCl_3 solution to **31b** a beige solid precipitated out of solution that, dissolved in deuterated dichloromethane, showed several signals between -4 and -7 ppm in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. Column chromatography over aluminium oxide at -20 °C and under argon atmosphere enabled the isolation of a colourless solid with a single resonance at -4.7 ppm in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, therefore proving the inherent stability of the newly formed adduct **41b**. As expected, this signal is almost unvaried in comparison to the starting material. Proof of the formation of the boron trichloride adduct was obtained from the $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum that displayed a single

resonance at 1.8 ppm which agrees very well with previously published values of adducts to mono(NHCs).¹⁷² No signal for the former C^2 -carbon nuclei could be observed due to the broadening upon coupling to the quadrupolar ^{11}B nuclei. **31b** was used as a mixture of the *trans*- and *cis*-isomer and presumably both reacted with boron trichloride at the carbene centres but the work-up only allowed the isolation of one isomer. SCXRD analysis revealed this to be the *trans*-isomer (Figure 65).

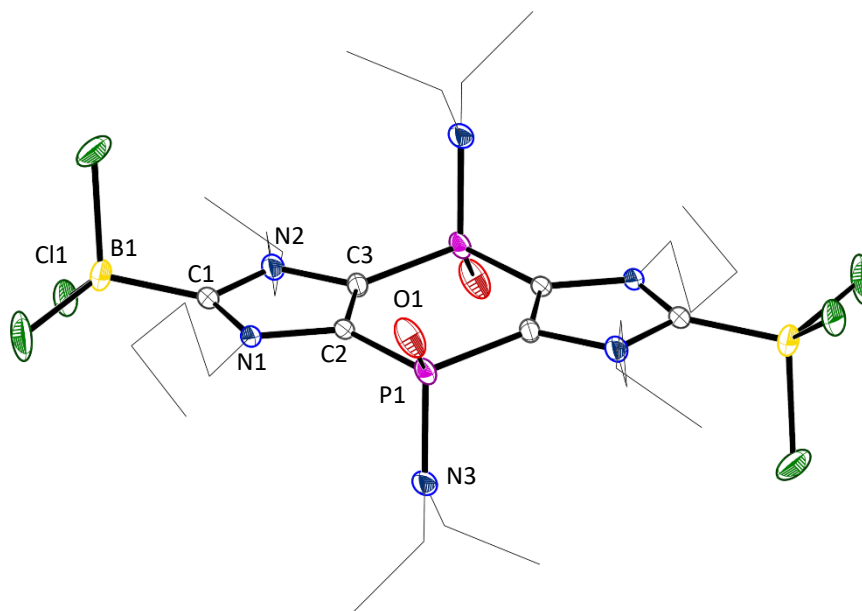
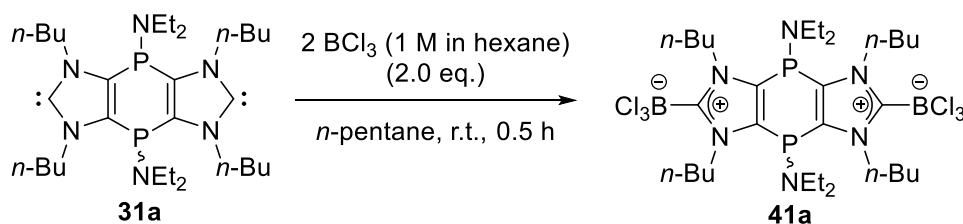


Figure 65. Molecular structure of **41b** in the single crystal. Thermal ellipsoids are set at 50 % probability. Hydrogen atoms were omitted for clarity. *n*-Butyl and ethyl chains are simplified as wires for additional clarity.

In comparison to the free bis(NHC) **31b** whose crystal structure was previously published^{136,137} the bond lengths of the tricyclic systems do not change significantly but the N1-C1-N2 angle is widened to 106.4(2) ° which is expected upon adduct formation. However, the angle in the imidazolium unit is comparable to the one observed for the Au(I) complex **LVib**.¹³⁷ The C1-B1 bond length of 1.641(5) Å as well as the B1-Cl1 bond length of 1.854(4) Å are in the range of analogous bond lengths obtained for various mono(NHC) BCl₃ adducts.¹⁷² The structural and NMR data show the relatively small influence that the backbone P-substitution has on the carbene centres as all values are in line with those of unsubstituted mono(NHCs) adducts.

After the successful synthesis of **31b**, P^{III}-bridged bis(NHC) **31a** was treated similarly with boron trichloride targeting the corresponding BCl₃ adduct **41a** (Scheme 43). As for **31b**, the addition of boron trichloride immediately resulted in the formation of a solid which surprisingly undergoes a colour change from blue over green to yellow-red leaving a colourless solution, finally.



Scheme 43. Attempted synthesis of BCl_3 adduct **41a** from bis(NHCs) **31a**.

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (Figure 66) of the solid after solvent removal, dissolved in dichloromethane, shows several resonances, mainly between 0 and 12 ppm, but the complete consumption of the starting material **31a**. The $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum reveals two major signals at 6.7 and 2.0 ppm where the latter could belong to the desired adduct while the former is indicative of the tetrachloroborate anion ($[\text{BCl}_4]^-$).¹⁷³

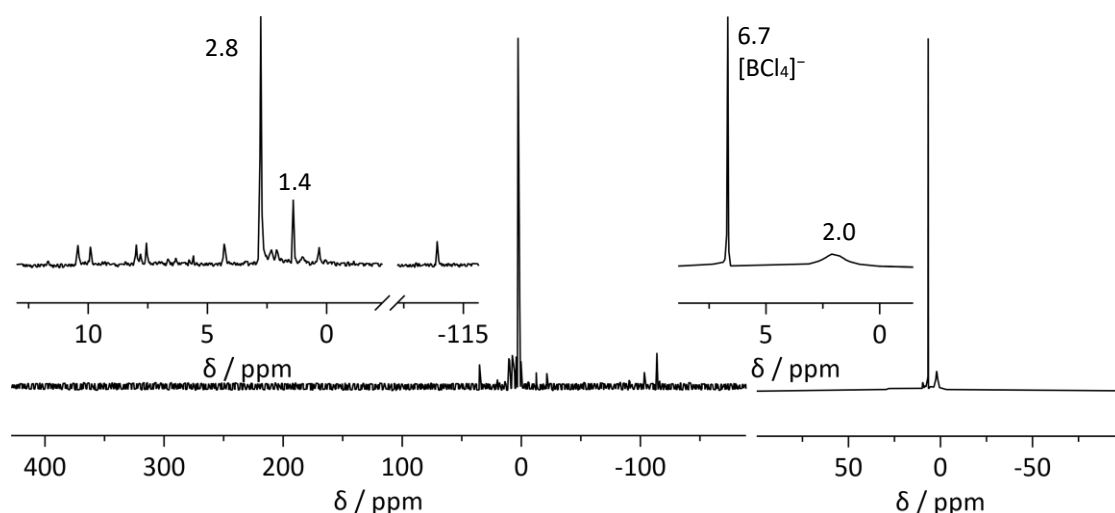
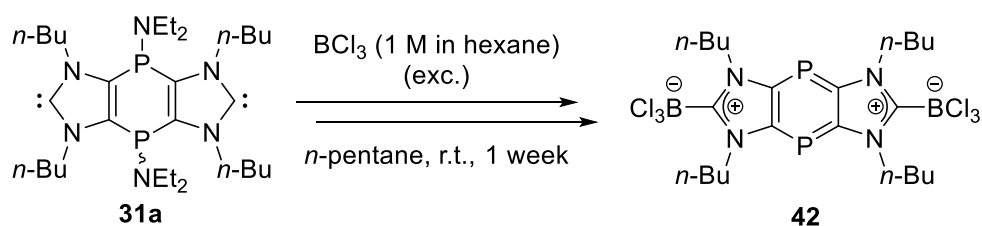


Figure 66. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction of **31a** with BCl_3 in dichloromethane (left) and $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of the same reaction mixture (right).

The mixture could not be further purified due to too similar solubilities of the various products and decomposition occurring during column chromatography. However, the formation of the tetrachloroborate and the intriguing colour change of the formed solid prompted the investigation of the reaction of **31a** with an excess of boron trichloride (Scheme 44). In the reaction of less than 0.08 mmol **31a** with six equivalents BCl_3 the already observed colour change from blue over green to yellow happened within four hours. After washing with *n*-pentane the reaction mixture, dissolved in deuterated dichloromethane, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum showed an almost selective conversion to a compound with a resonance at 118.6 ppm (94 %) (Figure 67). The main signal at 118.6 ppm is significantly highfield-shifted in comparison to the starting material and all transition metal complexes **LVIa** which suggests a drastic change in the phosphorus environment.



Scheme 44. Synthesis of BCl_3 adduct **42** from bis(NHCs) **31a**.

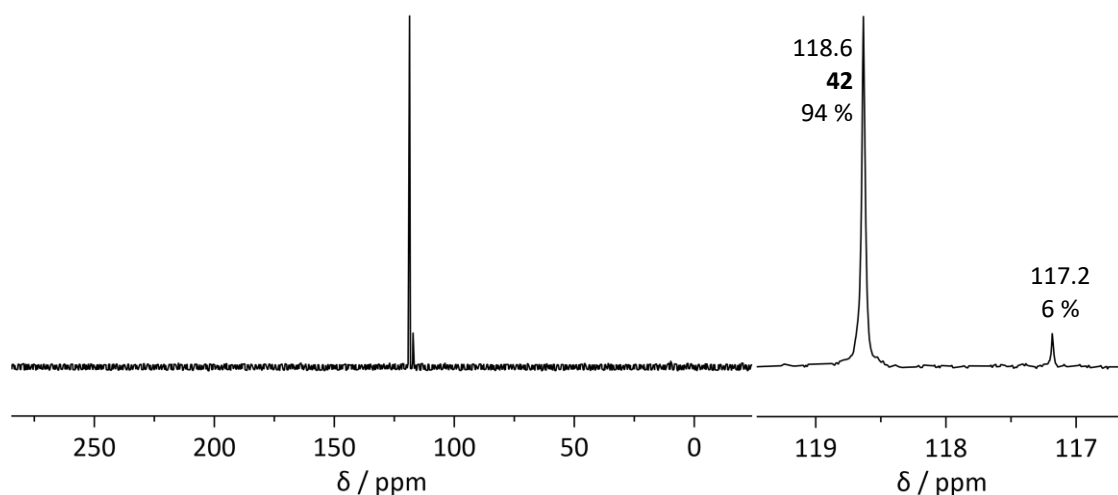


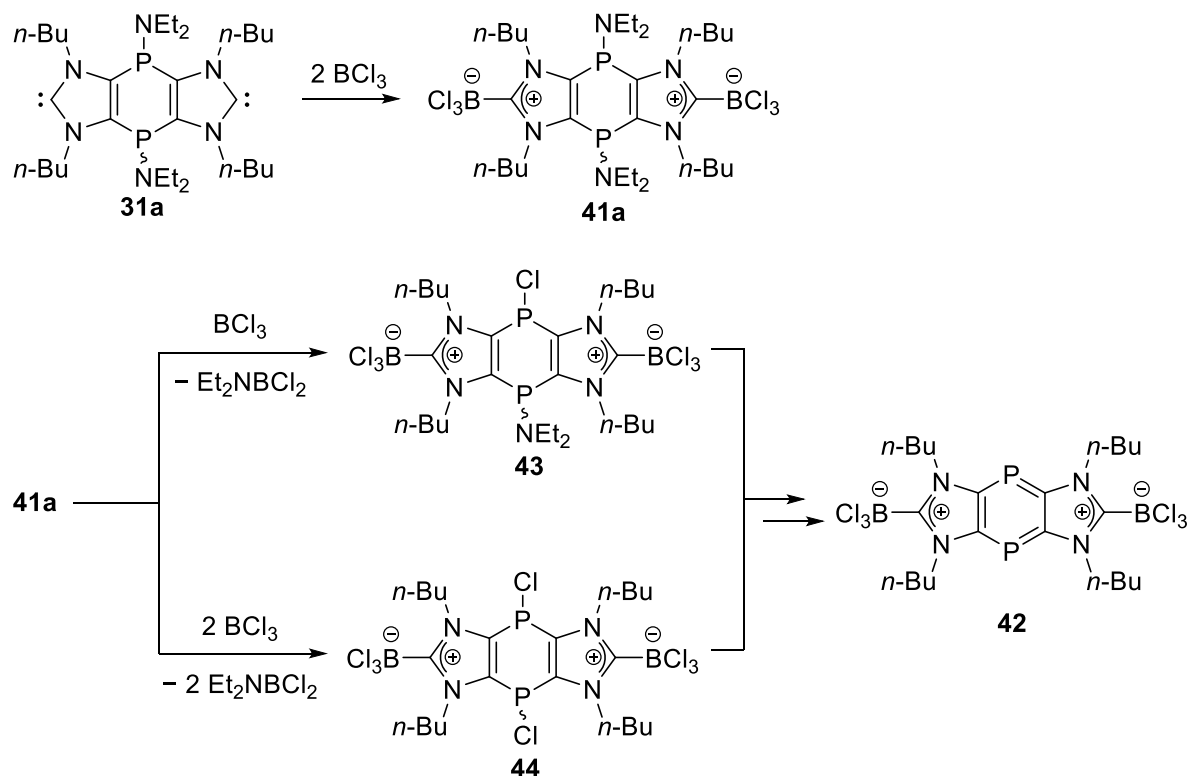
Figure 67. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction of **31a** with six equivalents BCl_3 in CD_2Cl_2 . Magnification of the product signals on the right.

The observed $^{31}\text{P}\{^1\text{H}\}$ NMR shift is very close to the resonance reported for the triflate salt resulting from the Se methylation of **1** ($\delta(^{31}\text{P}) = 120.0 \text{ ppm}$)⁸¹ where the only two-coordinate phosphorus nuclei are additionally deshielded by the electron-withdrawing imidazolium units. As **42** has an identical motif in the tricycle, a similar shift in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum is reasonable. The yellow colour of **42** is in contrast to previously reported tricyclic 1,4-diphosphinines which are red or violet in appearance^{53,82,81} or orange in case of Ghadwal's 1,4-diphosphinine bis(imidazolium) salt.⁸⁶ However, it is similar to the Se-methylated bis(imidazolium) salt of **1** which is light yellow⁸¹ and TD-DFT calculations confirmed only a few weak excitations between 367 and 431 nm which correspond to a visible yellow colour. Unfortunately, **42** could not be isolated since it could not be separated from the formed side products with similar $^{31}\text{P}\{^1\text{H}\}$ NMR shifts and due to its remarkable air and moisture sensitivity. Increasing the reaction scale to around 0.35 mmol of **31a** led to an increased number of undesired products which additionally hindered isolation and characterisation. Nevertheless, **42** could be identified and characterised via (2D-)NMR spectroscopy in mixtures: In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum the signal for the P-adjacent carbon nuclei is a doublet of doublet at 155.7 ppm with a $J_{\text{P,C}}$ -coupling of 24.7 Hz which compares very well with reported data of **1** and its methylation product.⁸¹ Due to the direct coupling to the quadrupolar boron nuclei no signal for the former C^2 -carbon nuclei could be observed in the 1D- $^{13}\text{C}\{^1\text{H}\}$ NMR

spectrum but the 2D- $^{13}\text{C}\{^1\text{H}\}$ - ^1H HMBC-NMR spectrum revealed coupling of the NCH_2 carbon atoms to a signal at 162.7 ppm. This value compares very well with, *e.g.*, the corresponding BCl_3 adduct to the tetramethyl-substituted mono(NHC).¹⁷² In the $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum one broadened signal at 2.1 ppm can be assigned to the NHC-bound boron nuclei while additional, sharper resonances at 6.8 as well as 7.8 ppm could belong to tetrachloroborate or trichloro(diethylamino)borate anions, respectively. The side product with a $^{31}\text{P}\{^1\text{H}\}$ NMR shift of 117.2 ppm in the spectrum in Figure 67 belongs to the 1,4-diphosphinine bis(imidazolium) scaffold **13** as the ^1H NMR spectrum shows a triplet at 9.83 ppm ($^4J_{\text{P,H}} = 2.3$ Hz) that indicates the C-H functionality. The formation is probably caused by traces of hydrogen chloride in the boron trichloride solution.

No single crystals suitable for SCXRD of **42** could be obtained from any of the reaction mixtures at various temperatures. A comparison of calculated structures of the in this work described tricyclic 1,4-diphosphinine compounds will be provided in chapter 3.4.1.

$^{11}\text{B}\{^1\text{H}\}$ NMR spectroscopic monitoring of the reaction also showed the formation of dichloro(diethylamino)borane ($\delta(^{11}\text{B}\{^1\text{H}\}) = 30.4$ ppm) which suggests a scrambling reaction (σ -bond metathesis) occurring leading to the formation of a *P*-Cl substituted species (Scheme 45). This is in line with the observations made in chapter 3.3.1.1 and the calculated FMO diagram which predicts a highly reactive P-N bond towards reagents with polarised E-Cl bonds.



Scheme 45. Plausible steps in the formation of BCl_3 adduct **42** starting from bis(NHCs) **31a**.

The formation of **42** probably starts with the generation of the bis(NHC) BCl_3 adduct **41a** (Scheme 45) as theoretical calculations for **41a**^{Me} could only find an energy path that was strictly decreasing in energy when approaching the carbene centre with a BCl_3 molecule, indicating a very fast reaction. This should be followed by partial (**43**) or complete (**44**) chlorination at the phosphorus centres (Scheme 45). The spontaneous formation of the 1,4-diphosphinine scaffold from the *P*-chlorinated precursor was also observed in the generation of **1** where the corresponding intermediate could not be isolated¹³⁷ but the actual mechanism was never investigated. Chapter 3.4.1 will focus on the synthesis of **13** via the route with BCl_3 and more detailed mechanistic insights will be provided there.

The generation of **42** is largely driven by the aromatisation of the central ring that shows a remarkable aromaticity of 102 % of that of benzene according to NICS(1) calculations. Furthermore, the two imidazolium units provide additional aromatic stabilisation with NICS(1) values of -9.1 ppm. Still, **42** is extremely air and moisture sensitive which becomes clearer when looking at the FMO diagram of **42**^{Me} (Figure 68).

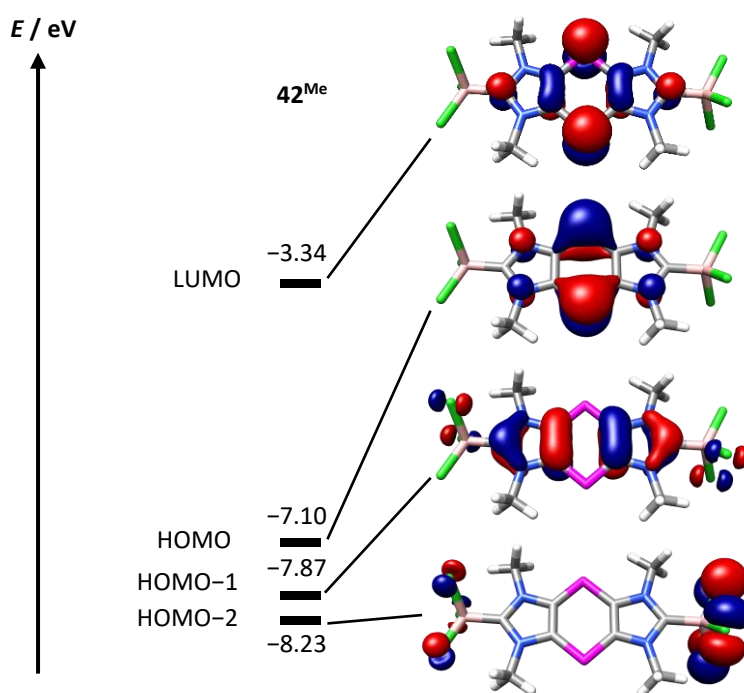
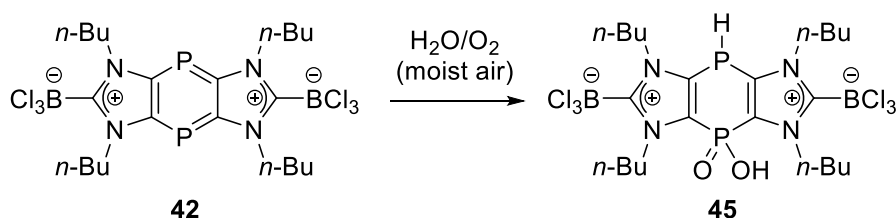


Figure 68. Selected calculated FMOs of compound **42**^{Me}.

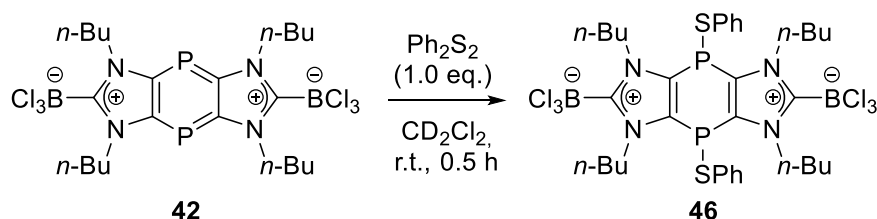
The distribution and shape of the MOs of **42**^{Me} is very similar to those of the free bis(NHC) **19**^{Me} and in contrast to **1**^{Me} the HOMO is centred in allyl-type MOs around the two phosphorus centres. With the HOMO being located there, this new 1,4-diphosphinine scaffold should show enhanced reactivity in reactions targeted at one or both phosphorus centres despite its aromaticity. In fact, **42** quickly decomposes under moist air under a visible fading of the yellow colour. While the $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum in dichloromethane remains unchanged, the $^{31}\text{P}\{^1\text{H}\}$ shows two main signals at 14.2 ppm and -127.5 ppm where the latter possesses a $^1J_{\text{P,H}}$ -coupling of 234.7 Hz according to the ^{31}P NMR spectrum.

This indicates the formation of compound **45** (Scheme 46) with one oxidised phosphorus centre and a P-H motif, so far not reported in 1,4-dihydro-1,4-diphosphinine chemistry, which was supported by observation of a confirming peak pattern in the negative ESI mass spectrum. Theoretical calculations confirm **45^{Me}** to be a local minimum.



Scheme 46. Reaction of **42** with moisture from air exposure.

Furthermore, **42** was reacted with Ph_2S_2 which was shown before to react selectively with the aromatic 1,4-diphosphinine centre in a 1,4-addition.⁵² While **XVIIIa** took 110 °C and two days to fully convert into the corresponding 1,4-addition product, full conversion of **42** to **46** (Scheme 47) could be determined from the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum after only half an hour at room temperature. The $^{31}\text{P}\{^1\text{H}\}$ NMR resonance at -34.9 ppm compares very well with the previously reported resonance of -34.1 ppm.⁵²



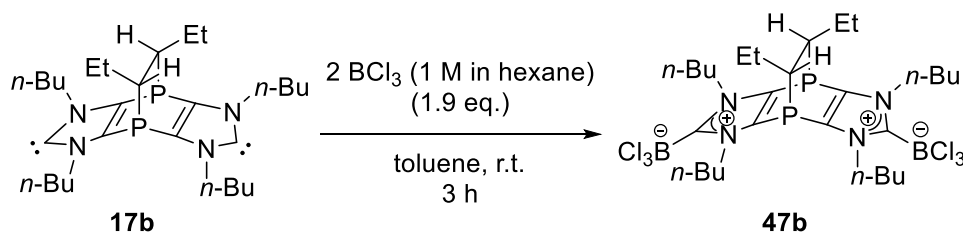
Scheme 47. Formation of **46** from **42** with Ph_2S_2 .

Both these test reactions lend strong support to the constitution of the central ring system, the stability of the BCl_3 -substituted imidazolium units and, most importantly, the new and increased reactivity of the 1,4-diphosphinine annulated to imidazolium units in **42**.

3.3.3.2 Reactions of bent P-bridged bis(NHCs)

The reaction of bent bis(NHCs) **17** with boron trichloride was investigated using **17b** as example, especially as it should allow for the easiest retro-[4+2]-cycloaddition if possible. **17b** was reacted according to Scheme 48 yielding a colourless solution and an oily, orange precipitate. **47b** could be isolated from the reaction mixture as colourless solid in only 6 % yield which is due to the fact that large amounts of bis(imidazolium) salt **11b** (with unidentified counter ions) were formed during the reaction, precipitating as an oily, orange solid. Despite working under strict exclusion of air and moisture, its formation could not be prevented. **47b** shows a ^{31}P NMR resonance at -86.8 ppm and an $^{11}\text{B}\{^1\text{H}\}$ NMR

shift of 2.6 ppm which agrees well with the resonance described for **41b** and literature values.¹⁷² In the 1D-¹³C{¹H} NMR spectrum no signal was observed for the boron-bound carbon nuclei due to the coupling to the quadrupolar nuclei but again, the 2D-¹³C{¹H}-¹H HMBC-NMR spectrum showed a corresponding resonance at 158.4 ppm which confirms the imidazolium character in **47b**.



Scheme 48. Formation of BCl_3 adduct **47b** from bis(NHC) **17b**.

X-ray diffraction analysis of single crystals of **47b** confirm the structure of the BCl_3 adduct (Figure 69).

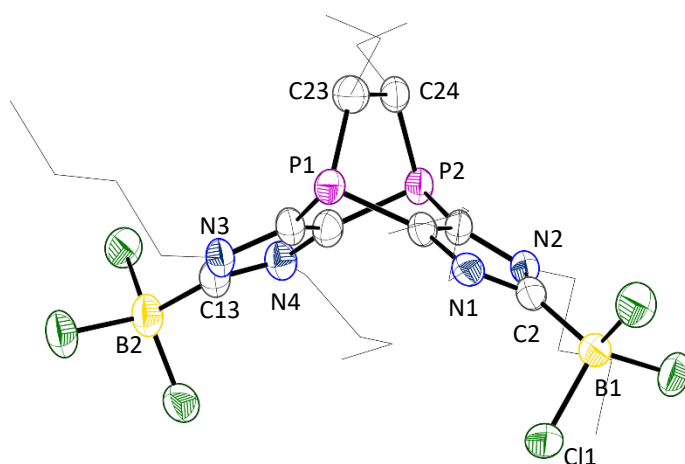


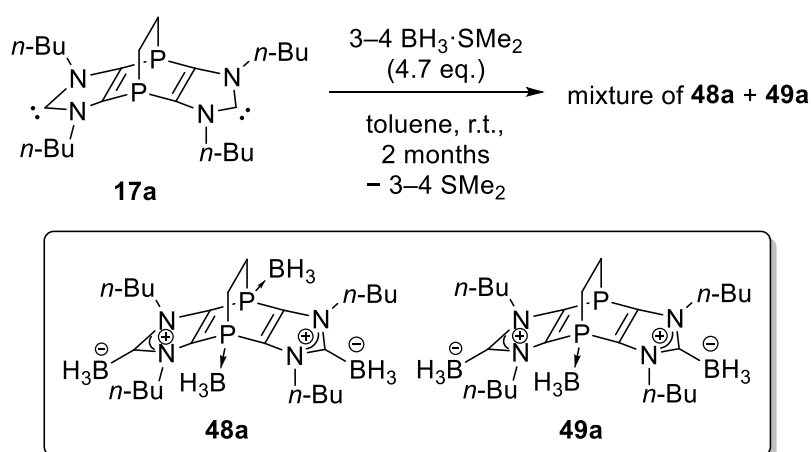
Figure 69. Molecular structure of **47b** in the single crystal. Thermal ellipsoids are set at 50 % probability. Hydrogen atoms were omitted for clarity. n-Butyl and ethyl chains are simplified as wires for additional clarity.

In contrast to **17b**, the N1-C2-N2 angle is widened to 106.3(6) ° which is almost identical to the angle in **41b** but slightly smaller than for the other above-described salts and adducts **11b**, **35b** and **36b**, respectively and still larger than for the previously discussed transition metal complexes. The C2-B1 bond length of 1.649(11) Å and B1-Cl1 bond length of 1.865(9) Å are equally comparable to the ones in **41b** which emphasises the little influence the very differently substituted phosphorus in the backbone has on the NHC units' reactivity. The 7,8-dihydro-1,4-diphosphabarrelene framework is almost unvaried with an average angle sum of 283 ° around the phosphorus centres and unchanged P-C and C-C bond lengths.

Analogously to **11b**, **35b** and **36b** no thermal retro-[4+2]-cycloaddition and no other decomposition could be observed for **47b**. Theoretical calculation confirm that – similarly to **11b** – the retro-[4+2]-

cycloaddition of **47b**^{Me} yielding **42**^{Me} is about 7.2 kcal mol⁻¹ endergonic with a reaction barrier of 26.7 kcal mol⁻¹. NICS(1) calculations assign aromaticity values of almost 92 % of that of benzene to the imidazolium units in **47b**. Thus, in conclusion, a thermal retro-[4+2]-cycloaddition for bis(NHC) adducts (or salts like **35b**) containing imidazolium units with a large aromatic stabilisation is not possible.

In addition to the BCl₃ adduct **47b** the reaction of **17a** with BH₃·SMe₂ was investigated to compare the P-donor ability to **2a** and **11a** and the reactivity with the tetranuclear Rh(I) complex **29a** (Scheme 49). Reacting **17a** with an excess of, *e.g.*, 4.7 equivalents of the borane dimethylsulfide adduct yields an invariable mixture of the two products **48a** and **49a** with **48a** being the major product with 62 % in the reaction mixture. In the ³¹P{¹H} NMR spectrum the only threefold substituted adduct **49a** shows one highfield-shifted signal at -99.2 ppm with a 7.3 Hz ³J_{P,P}-coupling and one broadened downfield-shifted signal at -15.5 ppm which can be assigned to the BH₃-coordinated phosphorus nucleus. In the ¹³C{¹H} NMR spectrum a very broad signal at 178 ppm belongs to **49a** confirming the coordination of BH₃ to the two carbene centres. **48a** shows a ³¹P{¹H} NMR resonance at -17.7 ppm which is comparable to two- and four-fold adducts **6a** and **8a**. As for tetranuclear Rh(I) complex **29a** the carbene units clearly react preferably which lowers the donor ability of the phosphorus lone pairs and induces the observed equilibrium between one and two coordinated phosphorus centres. In the ¹³C{¹H} NMR spectrum a signal at 180 ppm can be assigned to the BH₃-coordinated carbon nuclei of **48a** which is much more downfield-shifted than for any of the other main group element adducts described above. It is also significantly downfield-shifted in comparison to BH₃ adducts to alkyl-substituted mono(NHCs) as reported by Kuhn ($\delta(^{13}\text{C}\{^1\text{H}\}) \approx 167 \text{ ppm}$)¹⁷⁴ which shows the mutual influence of C- and P-coordination on the increasingly lower donor capacity of the scaffold.



Scheme 49. Formation of BH₃ adducts **48a** and **49a** from bis(NHC) **17a**.

Single crystals grown from the reaction mixture in dichloromethane are of relatively poor quality but confirm the main product **48a** as four-fold BH_3 adduct (Figure 70). The structural features cannot be discussed in great detail but seem to be very similar to those of **6a**.

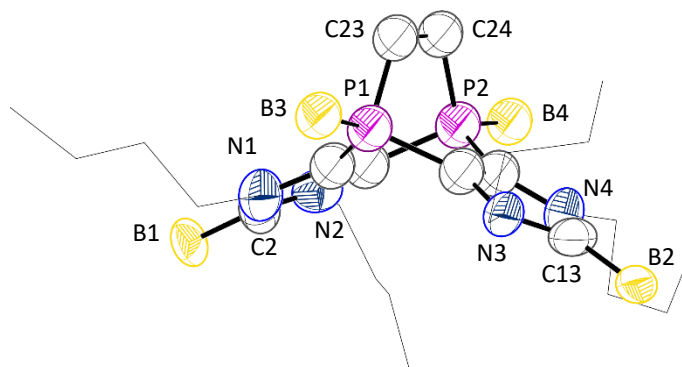


Figure 70. Molecular structure of **48a** in the single crystal. Thermal ellipsoids are set at 50 % probability. Hydrogen atoms were omitted for clarity. *n*-Butyl and ethyl chains are simplified as wires for additional clarity.

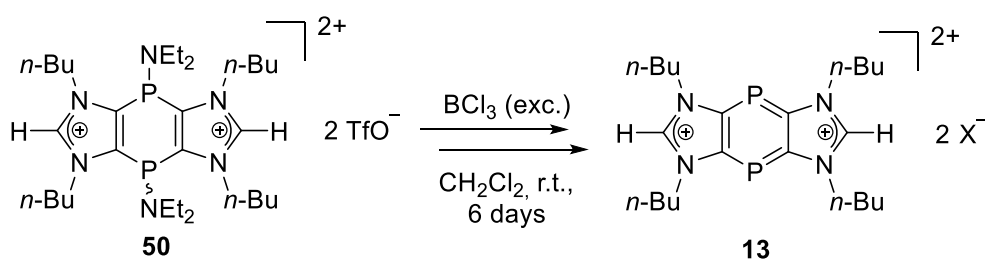
The ability to coordinate the phosphorus centres in bis(NHC) **17a** is largely dependent on the substitution on the carbene centres and is preferred for, *e.g.*, electron-rich transition metal fragments that can provide π -back-bonding. Thus, scaffolds containing aromatic, electron-withdrawing imidazolium units are worse P-donors than for instance disilone **2a**.

3.4 Synthesis and investigations on a salt with 1,4-diphosphinine bis(imidazolium) cation 13

The synthesis of a 1,4-diphosphinine bis(imidazolium) salt with N-alkyl substitution in the imidazolium units has remained elusive so far, as the reaction conditions of a reductive deselenisation were not suitable to retain the aromatic central ring. Ghadwal has reported on a C²-phenyl substituted 1,4-diphosphinine bis(imidazolium) salt that experiences a large kinetic stabilisation by *N*-Dipp substitution but has not been investigated regarding its reactivity.⁸⁶ In this following chapter, the conversion of the tricyclic *P*-NEt₂ substituted 1,4-dihydro-1,4-diphosphinine bis(imidazolium) salt into its aromatic 1,4-diphosphinine counterpart via chlorination and reduction that was observed in chapter 3.3.3.1 will be explored. Furthermore, theoretical calculations were conducted to elucidate a possible reaction mechanism and the special phosphorus-centred properties of this new scaffold in comparison to known 1,4-diphosphinines. First reactivity studies in [4+2]-cycloadditions, towards transition metal complexes and in reduction reactions were performed to assess the phosphorus-centred reactivity and confirm the theoretically predicted properties.

3.4.1 Synthesis of a salt with 1,4-diphosphinine bis(imidazolium) cation 13

The observations made in the attempted synthesis of **41a** and the unexpected formation of **42** are an ideal starting point to target the synthesis of a 1,4-diphosphinine bis(imidazolium) scaffold **13** that is not accessible through the reductive deselenisation of **1** or the retro-[4+2]-cycloaddition of **11**. Thus, planar *P*-bridged bis(imidazolium) triflate **50** (formerly **LV**) was reacted with boron trichloride in dichloromethane (Scheme 50).



Scheme 50. Generation of 1,4-diphosphinine bis(imidazolium) cation **13** from bis(imidazolium) triflate **50**.

In a first step six equivalents of BCl₃ (1 M in hexane) were added to **50** in dichloromethane, as it is not soluble in *n*-pentane which was used in the synthesis of **42** and had the advantage of precipitating the product. As seen before, the solution underwent a rapid colour change from brown over green to yellow. After six hours all volatiles were removed and the residue was redissolved in dichloromethane and another six equivalents of BCl₃ were added leading to a colour change from red to yellow. After

stirring for five days, the reaction course was monitored via $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy (Figure 71) which showed approximately 81 % conversion to the product **13** with a resonance at 121.4 ppm. One other signal at 1.4 ppm belongs to a symmetrically substituted intermediate like *P*-chlorinated compound **51** (Scheme 51). The $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of this reaction mixture does not show any residual BCl_3 but small amounts of Et_2NBCl_2 ($\delta(^{11}\text{B}\{^1\text{H}\}) = 30.3$ ppm) and several signals that could belong to tetracoordinate borate species (0.6–7.7 ppm). As the reaction seemed to be dependent on an excess of BCl_3 , another six equivalents were added to the reaction mixture and after stirring overnight, the solvent was removed and washed with *n*-pentane yielding a yellow, slightly sticky solid that did not contain the previously in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum observed side product anymore. **13** could be obtained with a clean ^{31}P NMR spectrum but showed impurities in the ^1H as well as $^{11}\text{B}\{^1\text{H}\}$ NMR spectra that could not be removed due to the similar solubility of the salts and the sensitivity of **13** towards even traces of air or water.

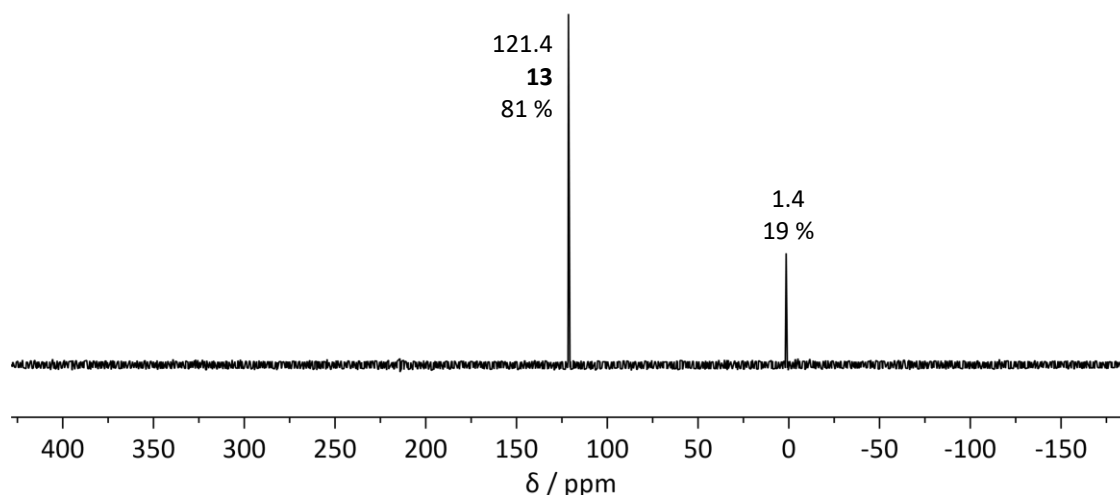


Figure 71. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction of **50** with an excess of BCl_3 in CH_2Cl_2 .

13 was characterised via NMR and IR spectroscopy as well as mass spectrometry. The observed ^{31}P NMR shift of 121.3 ppm is comparable to the previously reported Se-methylated triflate of **1**⁸¹ and compares well to the resonance observed for **42**. It reflects the symmetrical, only two-coordinate phosphorus centres with annulation of the central ring to the imidazolium units which are significantly more electron-withdrawing than the imidazole-2-selones in **1**. In comparison to **1** the multiplet signals for the CH_3 and CH_2 protons in the ^1H NMR spectrum are slightly downfield-shifted while the acidic C-H proton shows a resonance at 9.6 ppm. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum a broadened triplet at 144.4 ppm ($^3J_{\text{P,C}} = 3.0$ Hz) can be assigned to the respective C-H functionality. The carbon nuclei of the central ring are characterised by a doublet of doublet at 154.5 ppm ($J_{\text{P,C}} = 26.6$ Hz) which is comparable to the corresponding values of **1** and expectedly downfield-shifted with larger $J_{\text{P,C}}$ -coupling constants in

comparison to 1,4-dihydro-1,4-diphosphinine scaffolds like **50**. The $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum reveals four major resonances at 4.0 ppm (7 %), 6.1 ppm (20 %), 6.5 ppm (48 %) and 7.7 ppm (25 %) where the signal at 6.5 ppm could very well belong to the tetrachloroborate anion making $\text{X} = \text{BCl}_4$ in Scheme 50. The former triflate anion could still be identified in traces in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum ($\delta(^{13}\text{C}\{^1\text{H}\}) = 118.6$ ppm, $^1J_{\text{F,C}} = 318.1$ Hz). One impurity in the ^1H NMR spectrum could be identified as the diethylamino boron trichloride adduct ($\delta(^1\text{H}) = 1.40, 3.04, 3.71$ ppm) with two inequivalent methylene groups due to the tetravalent nitrogen centre.¹⁷⁵ In the IR spectrum the bands for the C-H vibrational modes are shifted towards higher wave numbers (3140 and 3069 cm^{-1}) compared to bis(imidazolium) salts **11** (≈ 3110 and 3040 cm^{-1}). High-resolution positive ESI mass spectrometry confirms the composition of **13** with a triflate counter anion and as decomposition product with (formally) OH^- – a decomposition product that was also observed for **42** in the negative ESI mass spectrum (Figure 72).

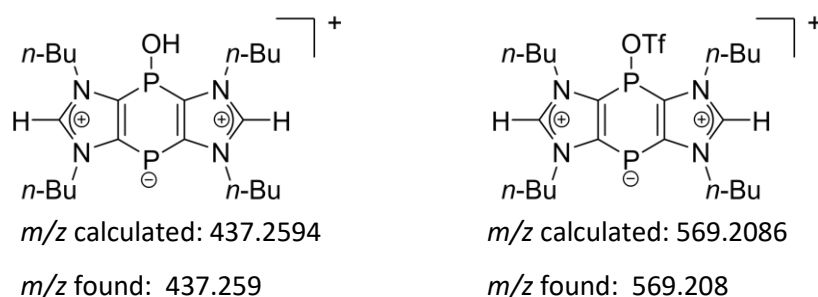


Figure 72. Proof of **13** according to the high-resolution positive ESI mass spectrum (structure examples for the observed compositions).

The synthesised tricyclic scaffold **13** bears a very strong resemblance with the 1,4-diphosphinine scaffold **XXXVII** by Ghadwal⁸⁶ but exhibits a very different ^{31}P NMR resonance ($\delta(\text{XXXVII}) = 16.5$ ppm). The difference in substitution in comparison to **13** are firstly, phenyl substituents instead of the protons at the imidazolium units and secondly, 2,6-diisopropylphenyl substituents at the nitrogen atoms. Ghadwal attributes stronger σ -donating properties to their phenyl substituted imidazolium unit than to, *e.g.*, IPr (= *N*-Dipp substituted mono(NHC)) that might cause the highfield shift in the ^{31}P NMR in comparison to other imidazolium-substituted phosphorus compounds.⁸⁶ Nevertheless, the $\Delta\delta$ value of almost 105 ppm is significant and indicates a more serious change of **13** compared to **XXXVII** that will be further investigated in the next chapter.

Unfortunately, no single crystals suitable for SCXRD analysis could be grown from solutions containing **13**. To get an overview of the structural features and differences that might influence the reaction behaviour of the different 1,4-diphosphinine scaffolds described in this work so far, calculated structures and properties of diselone **1**^{Me}, bis(imidazolium) cation **13**^{Me}, bis(NHC) **19**^{Me}, bis(NHC) $\text{Fe}(\text{CO})_4$ complex **26**^{Me}, bis(NHC) BCl_3 adduct **42**^{Me} and Ghadwal's 1,4-diphosphinine salt **XXXVII** are presented in Table 11.

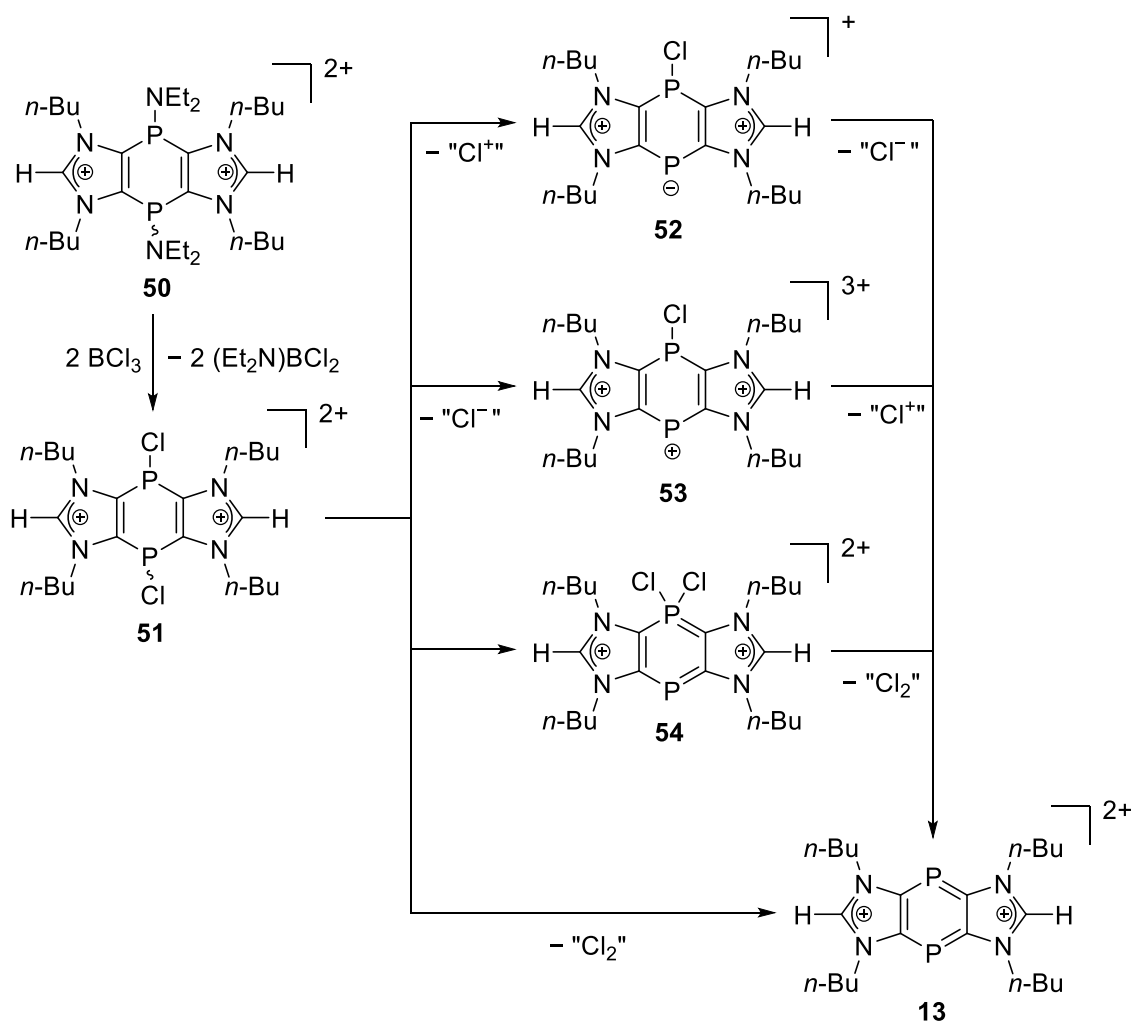
Table 11. Selected structural features and properties of calculated structures of **1^{Me}**, **13^{Me}**, **19^{Me}**, **26^{Me}**, **42^{Me}** and **XXXVII**.

	1^{Me}	13^{Me}	19^{Me}	26^{Me}	42^{Me}	XXXVII
$\angle(\text{C-P-C}) / ^\circ$	97.6	96.2	98.3	97.5	97.1	95.1
$\angle(\text{N-C-N}) / ^\circ$	105.8	110.2	103.0	104.8	106.8	107.0
$d(\text{P-C}) / \text{\AA}$	1.749	1.745	1.745	1.746	1.745	1.748
MBO(P-C)	1.35	1.36	1.36	1.42	1.44	1.22
$d(\text{C-C}) / \text{\AA}$	1.413	1.417	1.415	1.411	1.410	1.407
Löwdin atomic charge at P	0.59	0.68	0.57	0.61	0.64	0.71
NICS(1)(1,4-diphosphinine) / ppm	-8.07	-10.8	-10.4	-9.86	-10.1	-8.80*
NICS(1)(imidazole) / ppm	-6.32	-9.46	-9.51	-8.42	-9.10	-6.43*

* own calculations; TZVPP instead of TZVPPD basis set, which slightly underestimates the NICS(1) value in comparison (circa 1 %).

First of all, the P-C as well as C-C bond lengths of the central 1,4-diphosphinine ring are almost invariant and seemingly independent on the substitution in the imidazole rings. On all other values bis(NHC) **19^{Me}** stands out as a consequence of having four low-valent centres in one molecule. The N-C-N angle in the respective imidazole/-ium units is a clear indicator on how to describe the five-membered ring and characterises **13^{Me}** and **42^{Me}** as bis(imidazolium) compounds while **1^{Me}** and **26^{Me}** carry more imidazole character. The latter possess lower aromaticity values, albeit **26^{Me}** still being almost as aromatic as benzene, and react much slower in [4+2]-cycloadditions and with nucleophiles or electron-rich reagents. This is also reflected in the slightly lower Löwdin atomic charge at the phosphorus atoms. The imidazolium-annulated 1,4-diphosphinines on the other hand, show increased reactivity in [4+2]-cycloadditions without any back-reaction and react readily with traces of air and water at the phosphorus centres. Ghadwal's 1,4-diphosphinine scaffold can also be categorised as bis(imidazolium) compound as indicated by the N-C-N angle. However, it shows the smallest C-P-C angle and the highest Löwdin charge at the phosphorus centres. It can be expected that the Dipp instead of alkyl substitution at the nitrogen atoms affects the electronic properties of the adjacent carbon atoms as can be seen in the synthesis of selones and phosphinidene adducts to NHCs^{176,147} which is likely to cause the difference between, e.g., **13** and **XXXVII**. The imidazolium units being better π -acceptors and therefore even more electron-withdrawing can be seen by the decreased MBO of 1.22 of the P-C bonds. As a consequence, the Löwdin charge at phosphorus is slightly increased and the C-P-C angle decreased. Surprisingly, **XXXVII** shows decreased aromaticity in the central 1,4-diphosphinine as well as the imidazolium rings in comparison to, e.g., **13** with values that more resemble the ones for **1**. This could also contribute to the relative shielding of the phosphorus – and adjacent carbon – nuclei in the respective NMR spectra.

As alluded to above, the spontaneous formation of **1** from its *P*-Cl-substituted precursor has been observed before but an exact mechanism has not been investigated so far. Similarly to **41** it is reasonable to assume the formation of the *P*-chlorinated compound **51** as first step (Scheme 51). This reaction was originally performed with PCl_3 to achieve the same metathesis reaction,⁵³ however, in case of the bis(imidazolium) salt **13** the use of PCl_3 yielded a zwitterionic compound with two anionic phosphorus centres.¹³⁷



Scheme 51. Possible formal reaction sequences in the formation of **13** from **50**.

The twofold chlorination at the phosphorus centres is a clearly exergonic process ($\Delta\Delta_r G^\circ = -53.8 \text{ kcal mol}^{-1}$ for **50**^{Me}) under liberation of dichloro(diethylamino)borane that was also observed NMR spectroscopically. In case of the synthesis of **1** or **XVIIIa,b** the reduction to the 1,4-diphosphinine is performed with $n\text{-Bu}_3\text{P}$ under formal elimination of Cl_2 . The reaction mixture of **50** with BCl_3 does not contain any reducing agents and **13** is still formed. The spontaneous formation of Cl_2 – potentially intra- or intermolecularly – is improbable as theoretical calculations assign a Gibbs reaction energy of $43.4 \text{ kcal mol}^{-1}$ at room temperature. The formation of scaffold **53**^{Me} through chloride

abstraction is even more endergonic when using BCl_3 or the newly formed chloro(diethylamino)borane as abstracting agent ($\Delta\Delta_r G^\circ = 65.5 \text{ kcal mol}^{-1}$ and $\Delta\Delta_r G^\circ = 89.2 \text{ kcal mol}^{-1}$, respectively) and therefore unlikely. The generation of monocationic **52** provides a more favourable product but the reaction mixture does not contain an obvious Lewis base to bind the formal chlorenium ion. The formal $1\lambda^3,4\lambda^5$ -diphosphinine **54**^{Me} is $17.2 \text{ kcal mol}^{-1}$ less favoured than **51**^{Me} and other scaffolds that contain a similar doubly chlorinated phosphorus centre are highly disfavoured as well. The latter rules out **51** as direct abstracting agent for a chloride or chlorenium ion. Reaction pathways that include the direct formation of a chloramine from intra- or intermolecular reactions also prove to be significantly endergonic. As shown by the presence of the boron trichloride amine adduct in the ^1H NMR spectrum, some kind of proton source – probably from impurities in the BCl_3 solution or the starting material **50** – could alter the reaction mechanism in unpredictable ways and assist in the formation of otherwise endergonic intermediates. However, the reaction mixture with BCl_3 does not allow the formation of anionic phosphorus centres which suggests a slightly different mechanism than with PCl_3 as chlorinating agent.

To further investigate the new tricyclic 1,4-diphosphinine scaffold **13** cyclic voltammetric measurements were performed using a circa 1 mM acetonitrile solution of **13** with a 0.1 molar concentration of tetra-*n*-butylammonium hexafluorophosphate as electrolyte, a platinum electrode and ferrocene ($\text{Fc}^{+/0}$) as internal reference (for further information see chapter 5.2.8). For the tricyclic 1,4-diphosphinines – and especially the dicationic scaffold **13** – the reductive region is of the greatest interest and is displayed in Figure 73. There are two distinct electrochemically irreversible reduction processes visible; the second reduction wave shows an additional almost degenerate reduction process at slower scan rates. The presence and distance of these two reduction processes is very similar to reports of **XVIIIa** which displays a first two-electron reduction at -1.74 V and a second one-electron reduction at -2.59 V vs. $\text{Fc}^{+/0}$. **13** possesses a higher electron affinity than previously investigated 1,4-diphosphinines as the reduction potentials are shifted significantly towards positive values ($E_p^{\text{Ic}} = -0.87 \text{ V}$ and $E_p^{\text{IIc}} = -1.63 \text{ V}$) which becomes evident when taking into account the much lower LUMO energy of **13** in comparison to, e.g., **XVIIIb** (see next chapter; Figure 75). The first reduction appears to be a two-electron process for **13** as well, yielding two anionic phosphorus centres, which is reasonable according to Ghadwal's report on related zwitterionic 1,4-diphosphinine-1,4-diide species.⁸⁶ For all two/three reduction processes the oxidative return waves are diminished in their current and cannot be unambiguously detected when analysing the isolated processes. This suggests that the electrochemical reductions are followed by chemical processes which consume the formed species (EC_{irr} or EEC_{irr}).

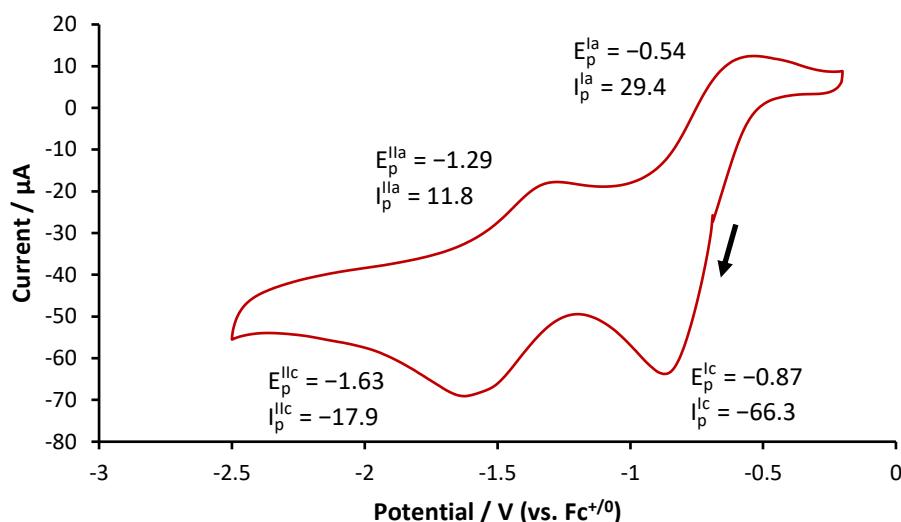


Figure 73. Cyclic voltammogram of **13** (circa 1 mM) at a Pt electrode in a 0.1 M $n\text{-Bu}_4\text{PF}_6/\text{MeCN}$ solution at a scan rate of 200 mV s^{-1} ; measurement with cathodic initial scan direction (indicated by an arrow) of the two reduction processes; potentials are referenced against $\text{Fc}^{+/0}$.

The two reduction processes were separately scanned at different scan rates between 50 mV s^{-1} and 1600 mV s^{-1} . Plotting the respective peak currents against the square root of the scan rate yields linear regressions with excellent fits ($R^2 > 0.99$) (Figure 74).

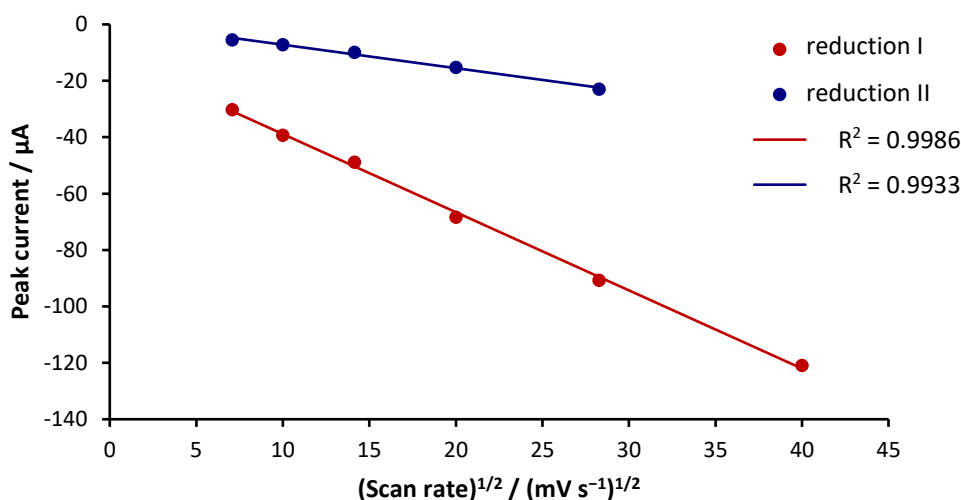


Figure 74. Plot of the peak currents against the square roots of the scan rate for the two reduction processes of **13** and their fitted regression lines.

According to the Randles-Ševčík equation¹⁷⁷ this linear relation proves a strictly diffusion controlled redox process – in contrast to the stripping oxidation observed for **21c**.

Cyclovoltammetric investigation of the oxidative region ($> 0 \text{ V}$) showed unreliable results for different measurements and were therefore not analysed. The reason for this are probably the impurities contained in the samples of **13** that are prone to oxidation or reaction with oxidised species of **13**.

3.4.2 Theoretical investigation and first studies on phosphorus-centred reactivity

The observations made for **42** as well as the sensitivity of **13** towards air and moisture in contrast to **1** and bis(imidazolium) salts **11** – as evidenced by the mass spectrometry – suggest that the electronic situation of **13** must be different to that of **1**. The FMO diagram of **13^{Me}** (Figure 75) reveals that the LUMO to HOMO–1 are identical to the ones found for **42^{Me}** but even lower in energy.

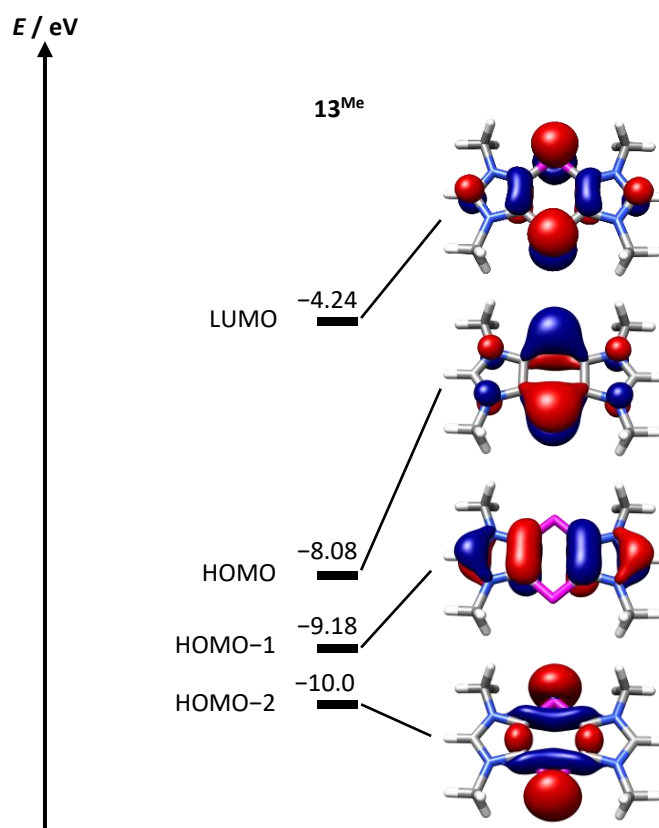


Figure 75. Selected calculated FMOs of compound **13^{Me}**.

As for **42** this should lead to an increased reactivity at the phosphorus centres which is even further enhanced by the HOMO–2 being largely centred in the phosphorus lone pairs which are in plane with the tricyclic scaffold. To exclude any discrepancy of the calculated results with the actual molecule, **13** was also optimised and analysed with its actual *n*-butyl substituents yielding an identical order of FMOs and very similar energies (Table 12). The order of MOs follows exactly that of the parent phosphinine for each phosphorus centre; for the parent 1,4-diphosphinine the calculated FMOs show a similar set-up with the HOMO–1 and HOMO–2 interchanged. Kobayashi's non-isolated 1,4-diphosphinine shows phosphorus-centred, π -type HOMO and LUMO followed by two occupied MOs that are constituted by the in-plane lone pairs at phosphorus – making it even more reactive at the P centres and thus more challenging to isolate.

Table 12. Comparison of orbital energies and HOMO-LUMO gap of calculated **13^{Me}** and **13**.

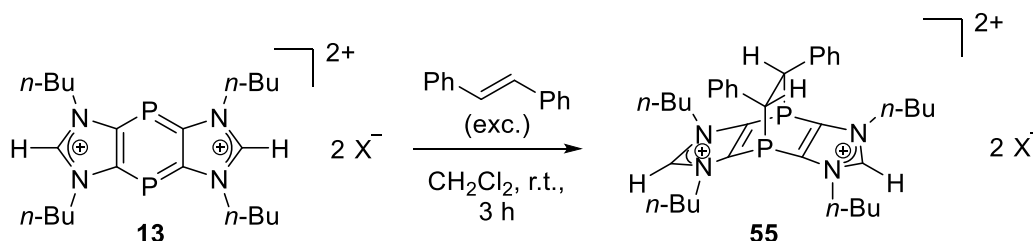
	13^{Me}	13
$E(\text{LUMO}) / \text{eV}$	-4.24	-4.15
$E(\text{HOMO}) / \text{eV}$	-8.08	-7.98
$E(\text{HOMO}-1) / \text{eV}$	-9.18	-9.05
$E(\text{HOMO}-2) / \text{eV}$	-10.0	-9.82
$\Delta E_{\text{L-H}} / \text{eV}$	3.84	3.83

Ghadwal's 1,4-diphosphinine **XXXVII**, according to their FMO calculations (BP86-D3/def2-SVP level of theory), presents with (at least) four degenerate occupied MOs (HOMO–HOMO–3) centred in the π -systems of the Dipp ligands while the LUMO looks similar to the one calculated for **13^{Me}**. For comparability and because the functional chosen by Ghadwal has significantly broader error margins in combination with the small def2-SVP basis set which makes their calculations less robust according to Grimme's benchmark publication,¹⁷⁸ **XXXVII** was also investigated on the same level of theory as **13** (PW6B95-D4/CPCM_{THF}/def2-QZVP//TPSS-D4/CPCM_{THF}/def2-TZVP level of theory). Calculations show a very similar HOMO-LUMO set-up as in Figure 75 with both MOs located in π -/ π^* -type orbitals at the phosphorus centres and a HOMO-LUMO gap of 3.58 eV. The in-plane lone pairs at phosphorus however, only constitute HOMO–14 albeit showing a similar energy difference to the HOMO. The MOs in between are centred in the ring systems of the Dipp or phenyl substituents, respectively. The shielding of the phosphorus nuclei – and the adjacent carbon nuclei – in their respective NMR spectra in comparison to **13** are therefore a consequence of the Dipp instead of *n*-butyl substitution and the overall lower aromaticity of the scaffold.

In contrast to **19**, **13** does not react intermolecularly and is stable which confirms the hypothesis of the formation of NHC adducts to the low-valent phosphorus centres in the observed product **20** in chapter 3.1.3.3.

As seen for **42** before, the new electronic situation allows for enhanced 1,4-reactivity targeted at the two phosphorus centres. Due to the unknown exact composition of **13** and its counter anions all reactions were performed with excesses of the respective reagents. Despite a concerted 1,4-addition of H₂ to **13** being thermoneutral with a moderate reaction barrier of $\Delta\Delta_r G^\ddagger = 26.4 \text{ kcal mol}^{-1}$, **13** does not react with H₂ in dichloromethane at temperatures of 60 °C over the course of six days. Similarly, it shows no reaction with carbon dioxide in deuterated dichloromethane at 60 °C over a one-month time period.

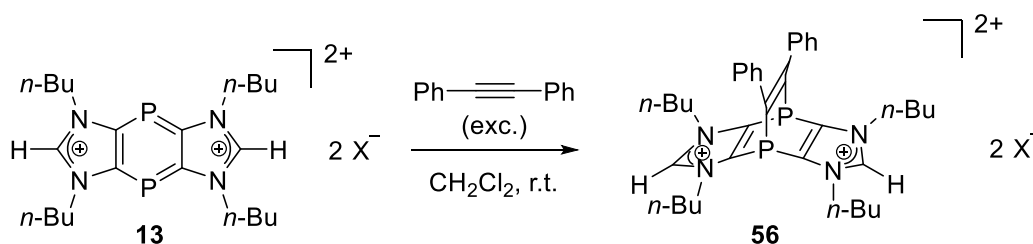
On the other hand, [4+2]-cycloaddition reactions with reagents that do not react with **1** under any circumstances are very feasible with **13**. With an excess of *trans*-1,2-diphenylethene **13** is fully converted into the 7,8-dihydro-1,4-diphosphabarrelene bis(imidazolium) scaffold **55** within three hours at ambient temperature (Scheme 52).



Scheme 52. Generation of bis(imidazolium) cation **55**.

55 is characterised by a ³¹P{¹H} NMR resonance at -80.6 ppm which is expectedly downfield-shifted in comparison to bis(imidazolium) salts **11** with alkyl-substitution. Furthermore, in the ¹H NMR spectrum a shift of 9.66 ppm can be assigned to the C-H protons in **55** which is also downfield-shifted compared to **11**.

More impressively, **13** immediately reacts with diphenylethyne to give the new 1,4-diphosphabarrelene scaffold **56** with 38 % conversion and a ³¹P{¹H} NMR shift of -81.7 ppm (Scheme 53). A [4+2]-cycloaddition with diphenylethyne could never be achieved with any of the tricyclic 1,4-diphosphinine scaffolds before and not even the trace formation of corresponding 1,4-diphosphabarrelene products could be observed.⁵²



Scheme 53. Generation of bis(imidazolium) cation **56**.

After one night only 32 % of the starting material **13** were left according to ³¹P{¹H} NMR spectroscopy (Figure 76) but a second product signal at -83.9 ppm had appeared that becomes the main product when **13** is fully consumed after 24 hours at 60 °C. As the intended reaction cannot produce an asymmetric molecule, there are no isomers that would have a similar shift. However, due to the unprecedented phosphorus-centred reactivity of **13** a two-fold [4+2]-cycloaddition constitutes a possible side reaction and would lead to a similar ³¹P{¹H} NMR spectroscopic shift. This is also confirmed by the

LUMO of **56**^{Me} not being embedded in the central ring but instead in a π^* -type orbital in the bridge – which is in contrast to derivative **2e** also stemming from the reaction with an alkyne and might explain the deviant reactivity.

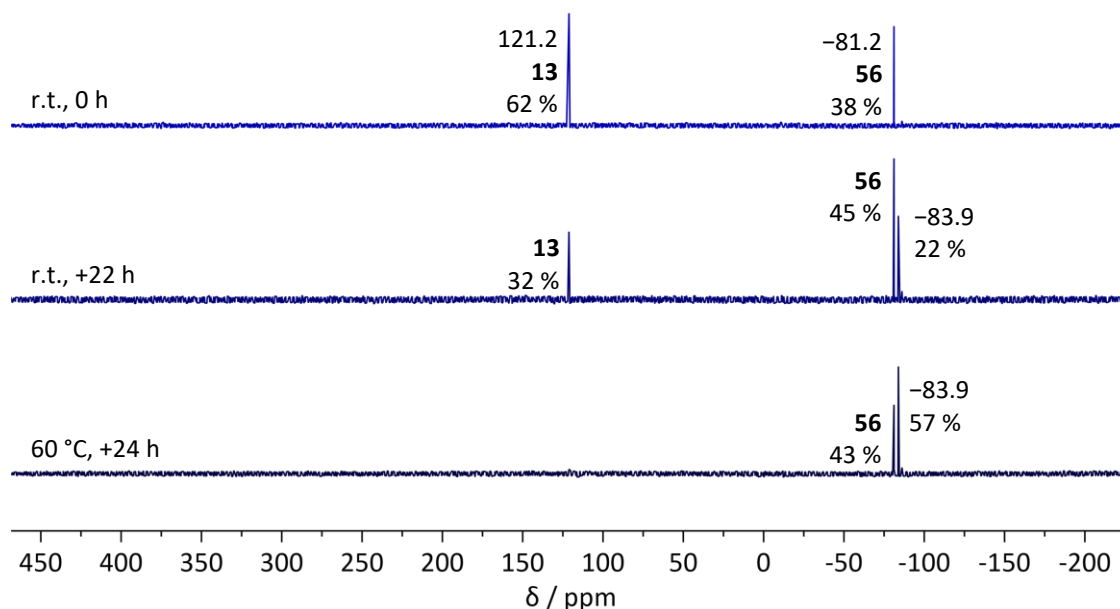
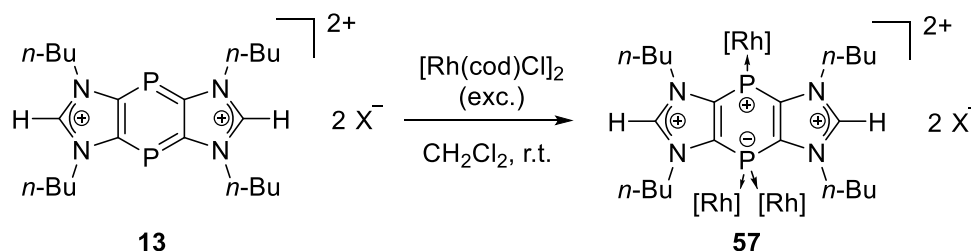


Figure 76. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the reaction of **13** with an excess of diphenylethyne in CH_2Cl_2 .

1,4-Diphosphinine diselone **1** or the related dithione **XVIIIa** could never successfully be reacted with transition metal complexes at the phosphorus centres; only the formation of 7-metall-1,4-diphosphanorborandienes with Al(I) and Ga(I) synthons has been reported.⁸⁵ Attempted reactions of **13** with metal complexes like, *e.g.*, $[\text{M}(\text{CO})_6]$ ($\text{M} = \text{Cr}, \text{W}$) or $[\text{M}(\text{CO})_5(\text{NCMe})]$ ($\text{M} = \text{Cr}, \text{W}$) did not yield any product or only unselective reaction mixtures according to the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra. Reacting **13** with an excess of more than four equivalents of $[\text{Rh}(\text{cod})\text{Cl}]_2$ (Scheme 54) resulted in a $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum with two main signal groups (content 100 %, $\text{S/N} \approx 4$): a doublet at 34.2 ppm ($^1J_{\text{Rh,P}} = 204$ Hz) and a triplet at -114.6 ppm ($^1J_{\text{Rh,P}} = 126$ Hz) in a 1:1 ratio (Figure 77).



Scheme 54. Reaction of **13** with an excess of $[\text{Rh}(\text{cod})\text{Cl}]_2$.

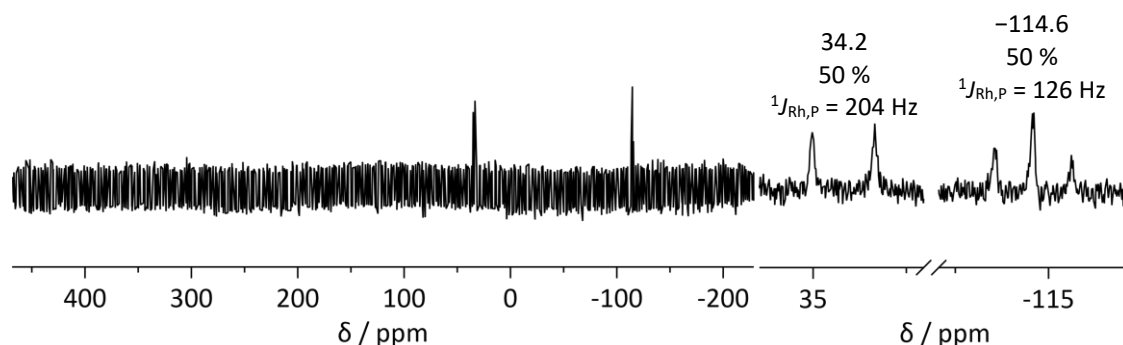
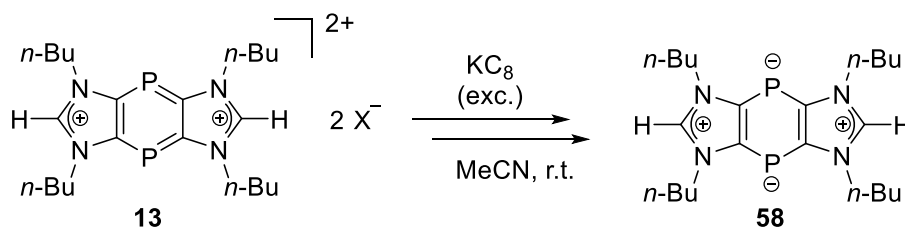


Figure 77. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction of **13** with an excess of $[\text{Rh}(\text{cod})\text{Cl}]_2$ in CH_2Cl_2 . Magnification of the product signals on the right.

The highfield-shifted resonance is indicative of a two-fold Rh(I)-coordinated phosphorus centre as the direct Rh,P-coupling is relatively small. The value compares well to an anionic phosphorus centre coordinated by two of the same Rh(I) fragments in **LVII**.⁸¹ The downfield-shifted doublet is in the region of Rh(I)-coordinated phosphanes with alkyl or aryl substituents but could also result from the shielding of a low-valent phosphorus centre. Due to the low solubility of the formed product further NMR experiments could not unambiguously determine whether both types of phosphorus centres are part of the same molecule as indicated by the signal integration. The in Scheme 54 proposed product **57** would also accommodate for only one observed isomer in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. In any case this reaction could prove that for the first time an aromatic 1,4-diphosphinine scaffold could be coordinated by transition metal fragments, enabled by the accessible made donor functionality of the phosphorus centres.

As the cyclic voltammogram of **13** clearly showed two reductive processes happening at chemically very accessible potentials, **13** was reacted with an excess of KC_8 in acetonitrile to achieve the synthesis of **58** (Scheme 55).



Scheme 55. Attempted generation of 1,4-diphosphinine-1,4-diide **58**.

58 had been proposed before by Naz as product of the reaction of **50** with an excess of PCl_3 via an unidentified reaction mechanism presenting with a $^{31}\text{P}\{^1\text{H}\}$ NMR shift of -50.2 ppm^{137} which fits very well with the $^{31}\text{P}\{^1\text{H}\}$ NMR shift of Ghadwal's 1,4-diphosphinine-1,4-diide ($\delta(^{31}\text{P}\{^1\text{H}\}) = -48\text{ ppm}$).⁸⁶ **58** could not be isolated as it decomposed upon evaporation of the solvent *in vacuo*. The reaction mixture of the reaction displayed above immediately turned brown upon addition of **13** to KC_8 in acetonitrile and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopic monitoring revealed three new signals at 62.5, 26.7 and -79.9 ppm (Figure 78). Over the course of four days only the broad signal at -79.9 ppm remained. The observed shift for **58** deviates significantly from the previously reported one ($\Delta\delta = -35.0\text{ ppm}$). A similar difference was observed for a tricyclic, imidazole-2-thione annulated 1,4-diphosphinine-1,4-diide when using KC_8 as reductant and was attributed to coordination, solvent and counter ion effects that could also come into play here, especially when taking into account the presence of further impurities in the mixture of **13**. Unfortunately, the NMR spectroscopically observed compound proved to not be stable in solution over time and under applied vacuum and could not be further investigated.

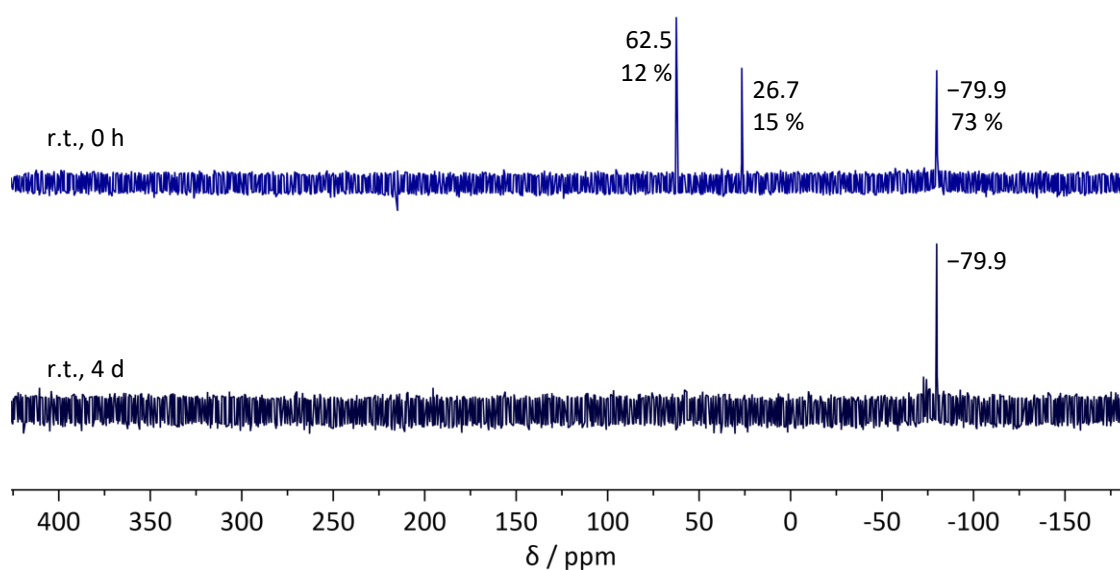
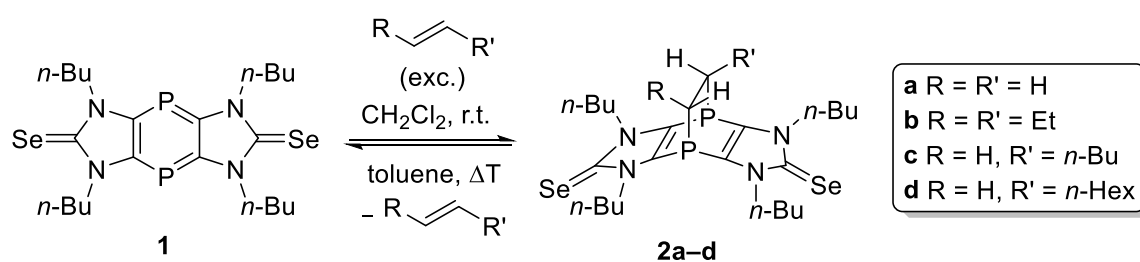


Figure 78. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the reaction of **13** with an excess of KC_8 in MeCN.

4 SUMMARY

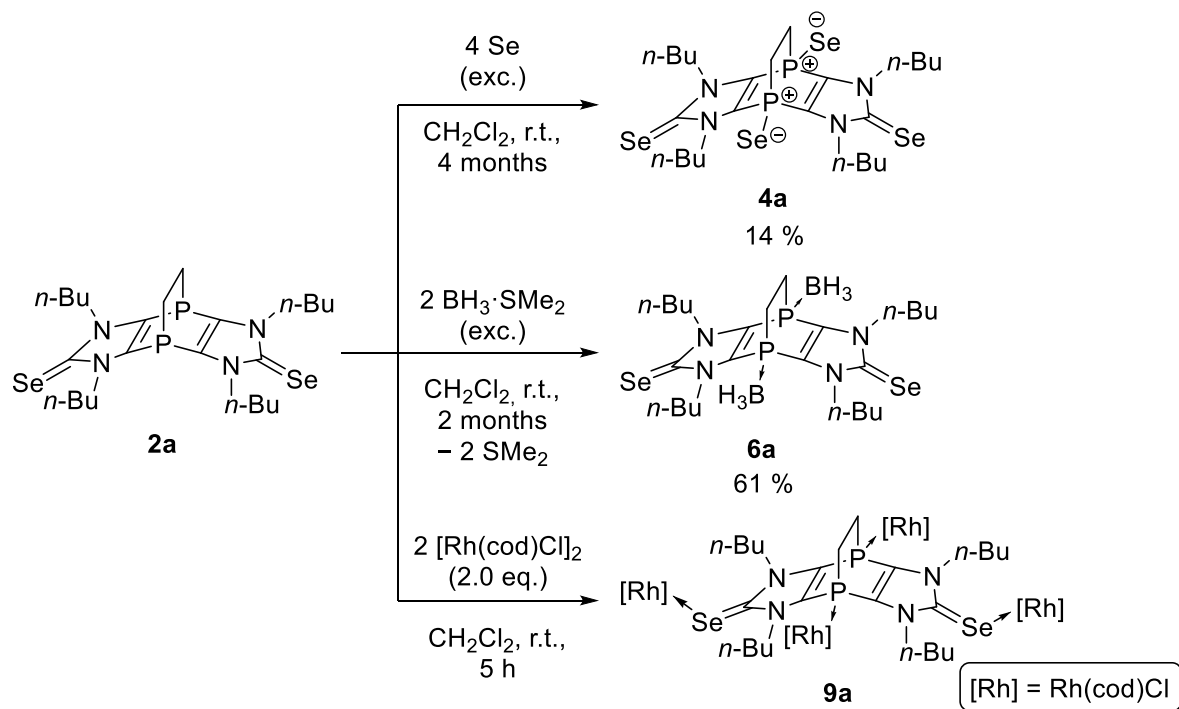
This PhD thesis described synthesis and properties of new 7,8-dihydro-1,4-diphosphabarrelenes and their subsequent conversion into novel P-bridged bis(imidazolium) salts and bis(N-heterocyclic carbenes). The latter display especially interesting building blocks having two sets of coordination sites of different basicity and were investigated regarding their reactions towards transition metal complexes and main group compounds and compared to previously published mono- and P-bridged bis(NHCs). The presence of a non-functionalised, saturated bridge in the different 7,8-dihydro-1,4-diphosphabarrelene scaffolds allowed the study of the thermal retro-[4+2]-cycloaddition behaviour to access new tricyclic, imidazole-annulated 1,4-diphosphinines.

Chapter 3.1 focused on the synthesis of 7,8-dihydro-1,4-diphosphabarrelenes **2** from 1,4-diphosphinine diselone **1** with non-functionalised, terminal or internal alkyl-substituted alkenes or ethene, respectively (Scheme 56).



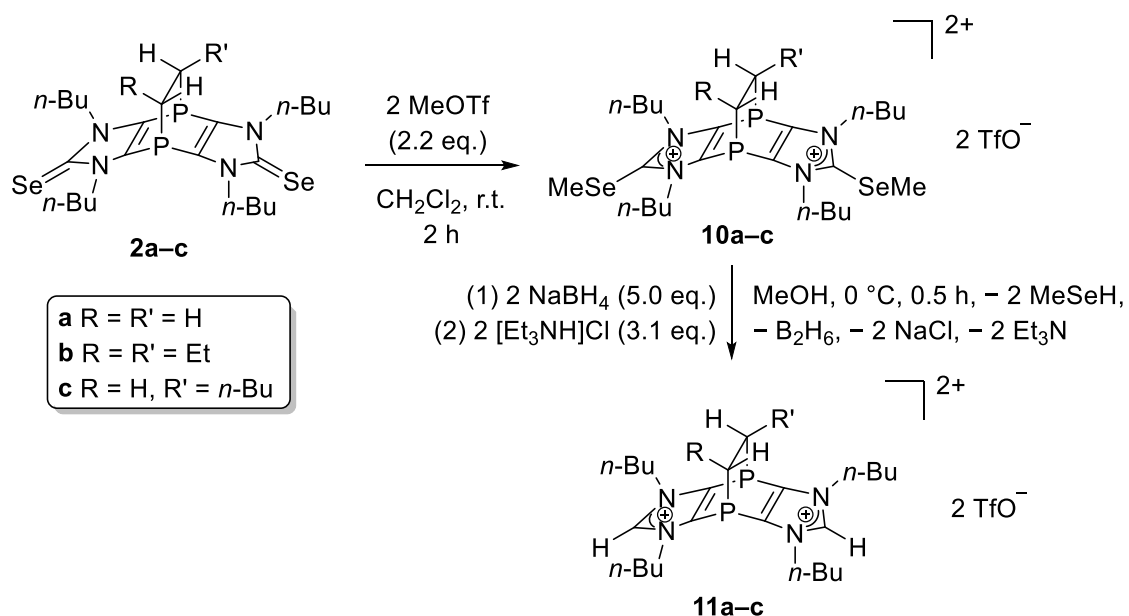
Scheme 56. Reversible [4+2]-cycloaddition of **1** with alkenes yielding 7,8-dihydro-1,4-diphosphabarrelenes **2a–c**.

2a–d could be isolated and fully characterised, and derivative **2b** was investigated via SCXRD confirming the scaffold's bent structure and typically small angular sum of only 285 ° around the phosphorus centres. Theoretical investigations on the possibility of retro-[4+2]-cycloadditions of **2^{Me}** showed approximately thermoneutral reaction energetics with moderate reaction barriers which could be confirmed experimentally. FMO analysis of **2^{Me}** revealed the phosphorus lone pairs to be of high s-character and constituting HOMO–4 making diphosphanes **2** relatively weak P-σ-donors. The generation and NMR spectroscopic analysis of diphosphane diselenide **4a** confirmed the lone pairs' large s-character (Scheme 57). The donor behaviour was investigated in reactions of **2a** with BH₃·SMe₂ and [Rh(cod)Cl]₂ resulting in the formation of **6a** as main product with the former and isolable, tetracoordinated complex **9a** in case of the latter (Scheme 57). This proved that **2a** reacts preferably at the Se centres with large, electron-rich coordination partners as determined from the FMO analysis.



Scheme 57. Reactions of **2a** yielding P-selenides, BH_3 adducts and Rh(I) complexes for characterisation of its lone pairs and donor behaviour.

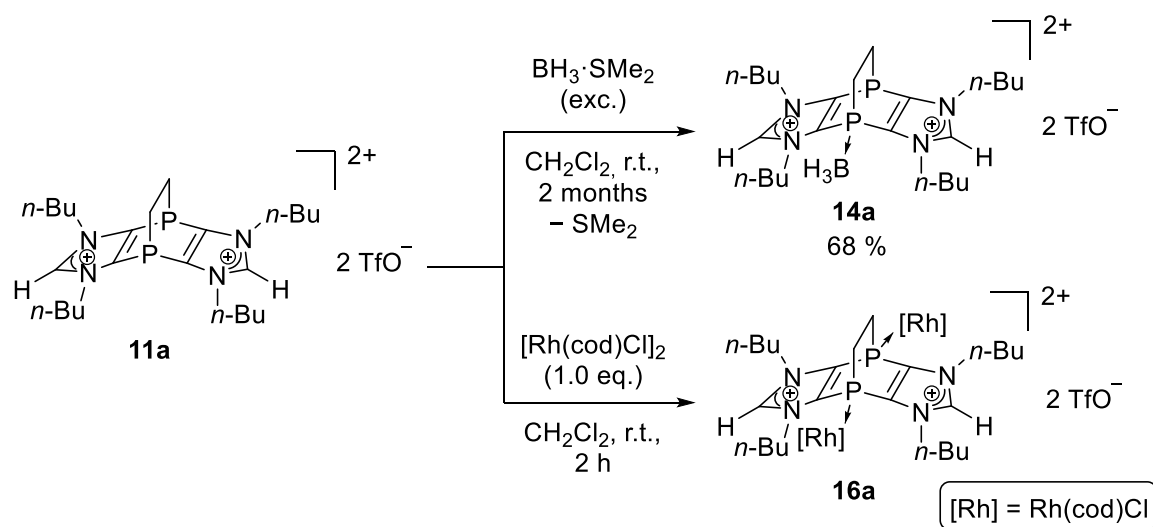
2a–c were successfully be converted into their corresponding bis(imidazolium) salts **11a–c** via an improved, two-step reductive deselenisation under retention of the bridge motif (Scheme 58).



Scheme 58. Synthesis of bis(imidazolium) salts **11a–c** from 7,8-dihydro-1,4-diphospha-barrelenes **2**.

11a–c pose remarkably stable compounds that show similar structural features to their precursors **2a–c** but possess characteristic N-C-N angles of 110° in their imidazolium units. Theoretical calculations

on the latter attribute aromaticity levels of up to 96 % of benzene which greatly factors into the stability of the salts. The accompanying electron-withdrawing effect on the central 7,8-dihydro-1,4-diphosphabarrelene not only further decreases the σ -donor ability of the phosphorus centres but also prevents a retro-[4+2]-cycloaddition from occurring. The poor σ -donor ability was demonstrated in the synthesis of BH_3 adduct **14a** where the generation of the twofold BH_3 adduct could only be observed in trace amounts. Nevertheless, **11a** could easily be coordinated to the electron-rich $\text{Rh}(\text{I})$ as evidenced by the isolation of **16a** (Scheme 59).



Scheme 59. Investigation of the donor behaviour of **11a** via the synthesis of **14a** and **16a**.

Bis(imidazolium) salts **11a–c** were deprotonated with the strong, weakly nucleophilic base KHMDs to yield bis(NHCs) **17a–c** which could be isolated and fully characterised. The symmetric derivative **17b** and asymmetric derivative **17c** could be analysed via SCXRD revealing that structural parameters of the bent framework remained almost unchanged but the transformation becomes evident from the narrowing of the N–C–N angle to 103° (Figure 79). Theoretical calculations showed a series of close-lying MOs from HOMO to HOMO–5 that are constituted by the lone pairs at the carbene centres, the phosphorus centres or mixtures of the two (Figure 79) which makes them ideal di- or tetratopic ligands, respectively, depending on the reagent and stoichiometry. The thermal retro-[4+2]-cycloaddition of derivative **17b** to access 1,4-diphosphinine bis(NHC) **19** proved to be most feasible according to calculations but experiments showed the formation of NHC-to-P adducts instead, formed via intermolecular reaction between the highly reactive low-valent phosphorus and carbon centres. The transient formation of **19** was proven via a trapping reaction performed in 1-octene yielding asymmetric bis(NHC) **17d**.

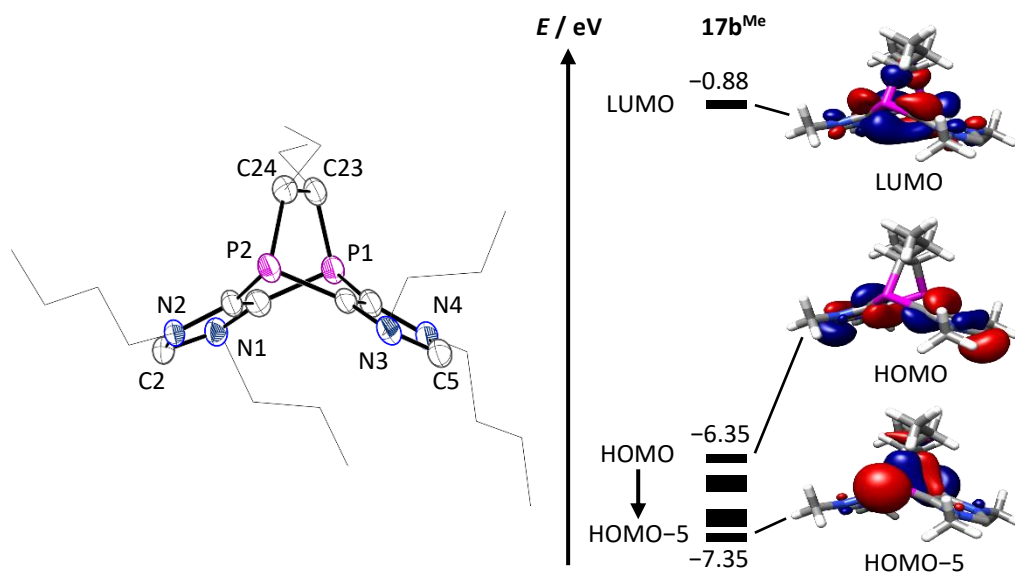
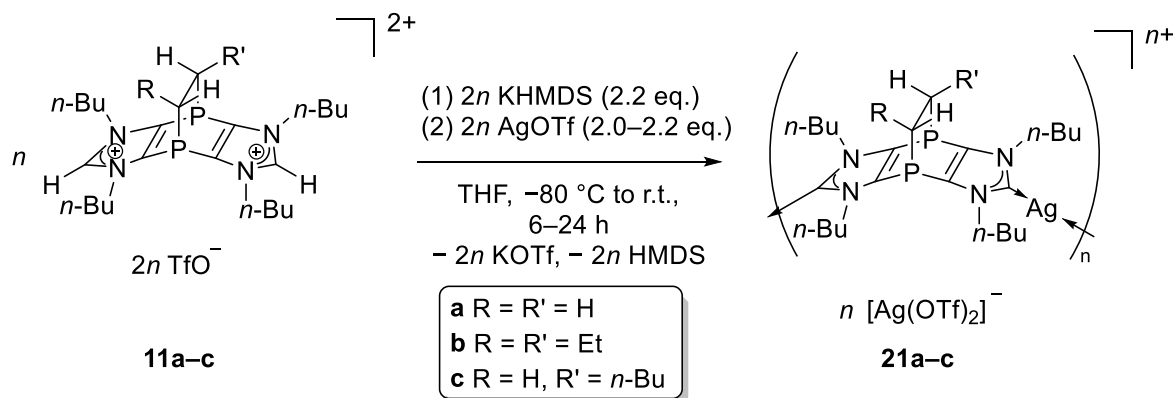


Figure 79. Molecular structure of **17b** (left) in the single crystal. Thermal ellipsoids are set at 50 % probability. Hydrogen atoms were omitted for clarity. *n*-Butyl and ethyl chains are simplified as wires for additional clarity. Selected calculated FMOs of compound **17b^{Me}** (right).

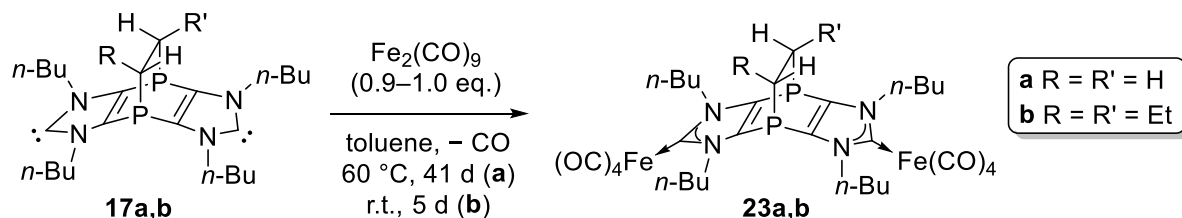
In chapter 3.2 bis(NHCs) **17** were investigated in reactions with transition metals from group 8, 9 and 11. While the inherent stability of **11** prevented the synthesis of coinage metal complexes via the route with M_2O ($M = Cu, Ag$), Ag(I) complexes **21a–c** could be synthesised from *in situ* generated **17a–c** with AgOTf (Scheme 60).



Scheme 60. Formation of oligomeric dinuclear Ag(I) complexes **21a–c** from *in situ* generated bis(NHCs) **17**.

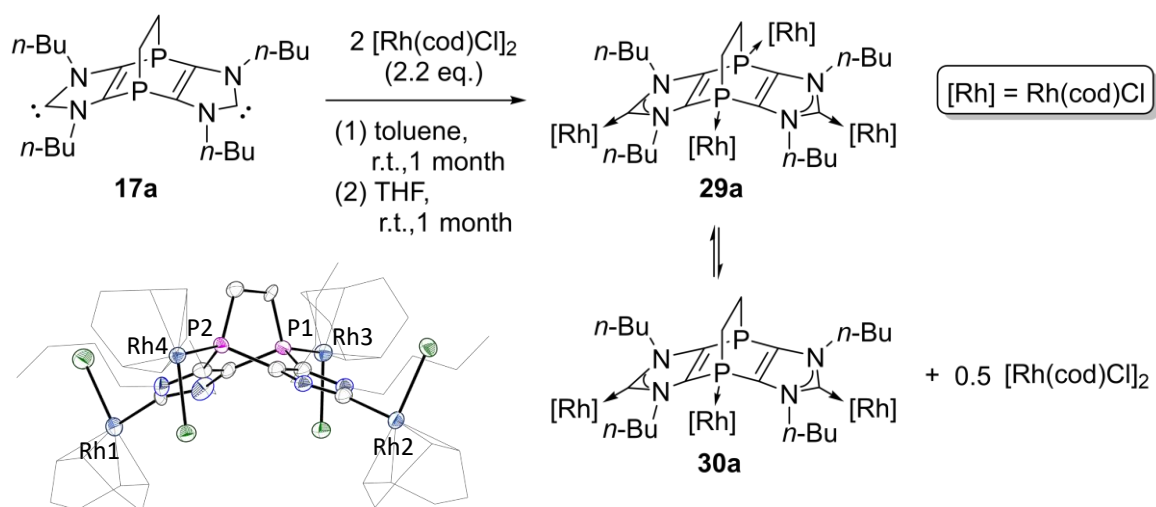
As expected with the weakly coordinating triflate anion, **21a–c** behave like organometallic oligo-/polymers and are insoluble in common organic solvents and only temporary solubility was observed in acetonitrile. **21** could not be further coordinated to other transition metal fragments via the phosphorus centres, showed no thermal retro-[4+2]-cycloaddition and, due to their structural nature, could not be used to access other coinage metal complexes via transmetalation.

Furthermore, dinuclear Fe(0) complexes **23a** and **23b** were synthesised (Scheme 61). Investigations on the possible formation of homo- or heterotetranuclear complexes revealed only incomplete coordination of even one phosphorus centre. However, thermal retro-[4+2]-cycloaddition of **23b** allowed access to 1,4-diphosphinine bis(NHC) Fe(0) complex **26** which could be trapped with 1-octene similarly to **19** yielding bent bis(NHC) Fe(0) complex **23d**.



Scheme 61. Formation of dinuclear Fe(0) complexes **23a,b** from bis(NHCs) **17**.

The synthesis of a tetranuclear transition metal complex of **17** was achieved with $[\text{Rh}(\text{cod})\text{Cl}]_2$ providing a suitable amount of back-bonding to enable the formation of **29a** which in solution is in equilibrium with trinuclear Rh(I) complex **30a** (Scheme 62). **29a** is formed as isomer mixture (ratio 3:1) due to different orientations of the chloride and COD ligands at the carbene-bound Rh(I) centres.

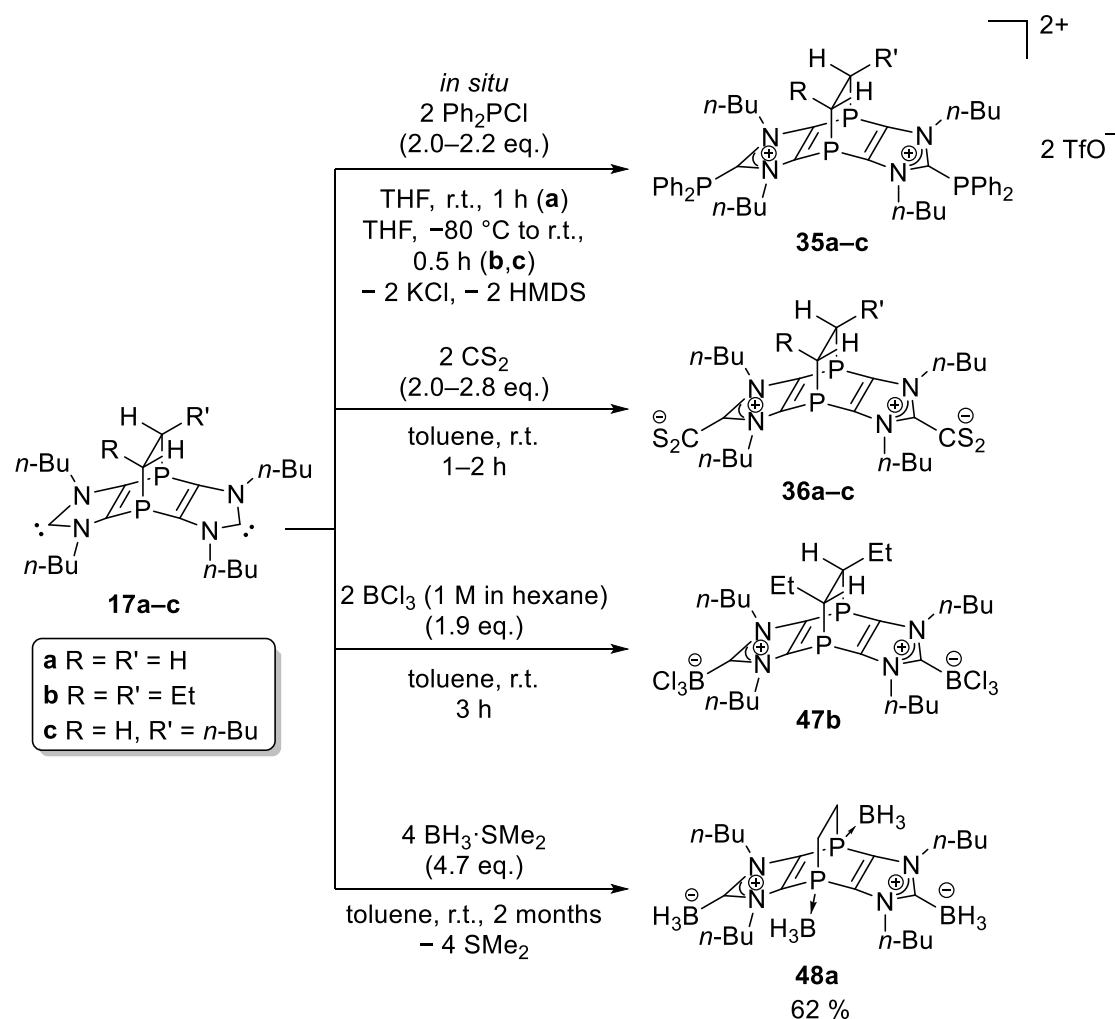


Scheme 62. Formation of tetranuclear Rh(I) complex **29a** in a mixture with trinuclear complex **30a**. Molecular structure of the major isomer of **29a** in the single crystal (bottom left). Thermal ellipsoids are set at 50 % probability. Hydrogen atoms and solvent molecules were omitted for clarity. *n*-Butyl chains and COD ligands are simplified as wires for additional clarity.

7,8-Dihydro-1,4-diphosphinine scaffolds that are coordinated to one or both phosphorus centres are not able to undergo thermal retro-[4+2]-cycloaddition, independently on the nature and substitution of the imidazole unit.

In chapter 3.3 the synthesis of main group adducts of bent bis(NHCs) **17** as well as previously reported planar bis(NHCs) **31** was described. **17a–c** were reacted with Ph_2PCl yielding Ph_2P -substituted

bis(imidazolium) triflates **35a–c** (Scheme 63). Carbon disulfide adducts **36a–c** could be easily synthesised and isolated as burgundy-coloured solids while carbon dioxide adducts remained elusive due to the formation of insoluble solids or bis(imidazolium) salts related to **11** due to the presence of amines. BCl_3 adduct **47b** was synthesised as derivative of group 13 to study the possibility of a retro-[4+2]-cycloaddition over several groups. None of the imidazolium-containing scaffolds **35**, **36** or **47** enabled a thermal retro-[4+2]-cycloaddition allowing to formulate the general rule that imidazolium units in the 7,8-dihydro-1,4-diphosphabarrelenes prevent thermal retro-[4+2]-cycloaddition.

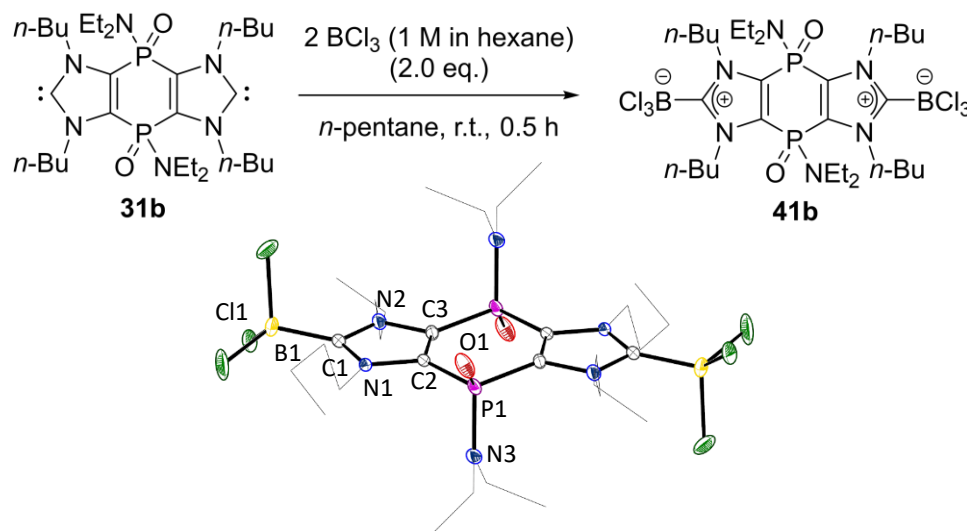


Scheme 63. Formation of main group adducts from bis(NHCs) **17**.

Furthermore, **17a** could be ligated to four borane molecules yielding **48a** as major product in solution and showing the mutual influence of C- and P-coordination on the decreasing donor ability of scaffold.

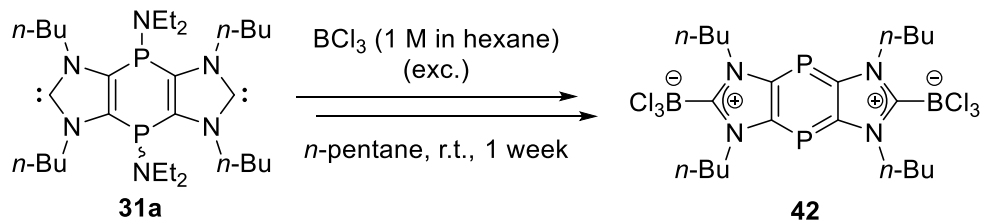
Planar, *P*- NEt_2 substituted bis(NHCs) **31** did not react with Ph_2PCl to yield the corresponding Ph_2P -substituted bis(imidazolium) salts **32a** and **32b**. Both attempted reactions showed decomposition to tetraphenyl *P*-oxide, while **31a** also underwent more complex reaction pathways due to the presence

of the P-N functionality where the HOMO and HOMO-1 are centred. **31b** reacts with BCl_3 to isolable adduct **41b** whose crystal structure shows typical features of mono(NHC) BCl_3 adducts (Scheme 64).



Scheme 64. Synthesis of BCl_3 adduct **41b** from bis(NHCs) **31b** and molecular structure of **41b** in the single crystal below. Thermal ellipsoids are set at 50 % probability. Hydrogen atoms were omitted for clarity. n -Butyl and ethyl chains are simplified as wires for additional clarity.

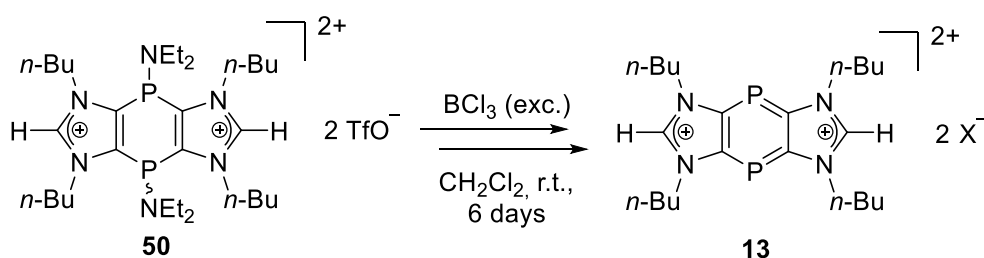
31a reacts with an excess of BCl_3 to spontaneously give the new 1,4-diphosphine bis(NHC) adduct **42** (Scheme 65).



Scheme 65. Synthesis of BCl_3 adduct **42** from bis(NHCs) **31a**.

In contrast to previous imidazole-2-thione or -selone-annulated 1,4-diphosphinines, **42** shows enhanced reactivity at the phosphorus centres due to both HOMO and LUMO being located there which was evidenced by the formation of 1,4-addition product **46** with Ph_2S_2 . Furthermore, theoretical calculations assign aromaticity levels of 102 % and 92 % of benzene to the central 1,4-diphosphinine and the imidazolium rings, respectively.

Chapter 3.4 described how the same route can be used to access a salt containing 1,4-diphosphinine bis(imidazolium) cation **13** with unknown counter ions X^- starting from P - NEt_2 substituted 1,4-dihydro-1,4-diphosphinine bis(imidazolium) salt **50** (Scheme 66).



Scheme 66. Generation of 1,4-diphosphinine bis(imidazolium) cation **13** from bis(imidazolium) triflate **50**.

13 presented with a similar FMO set-up as **42** (Figure 80) and the highest aromaticity values of all 1,4-diphosphinine scaffolds so far according to NICS(1) calculations – 109 % and 95 % of benzene for the 1,4-diphosphinine and imidazolium rings, respectively.

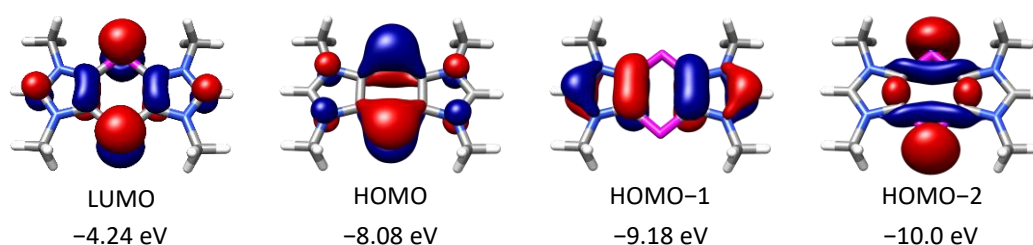


Figure 80. Selected calculated FMOs of compound **13^{Me}**.

Cyclic voltammetric studies on **13** showed similar behaviour in the reductive region as 1,4-diphosphinine dithione **XVIIIa** but with potentials shifted towards less negative values reflecting the new electronic situation at the phosphorus centres (Figure 81).

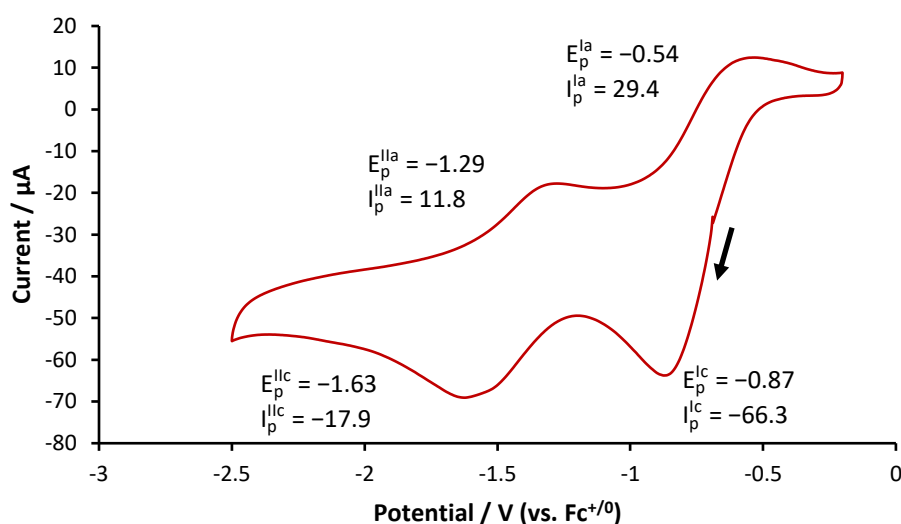
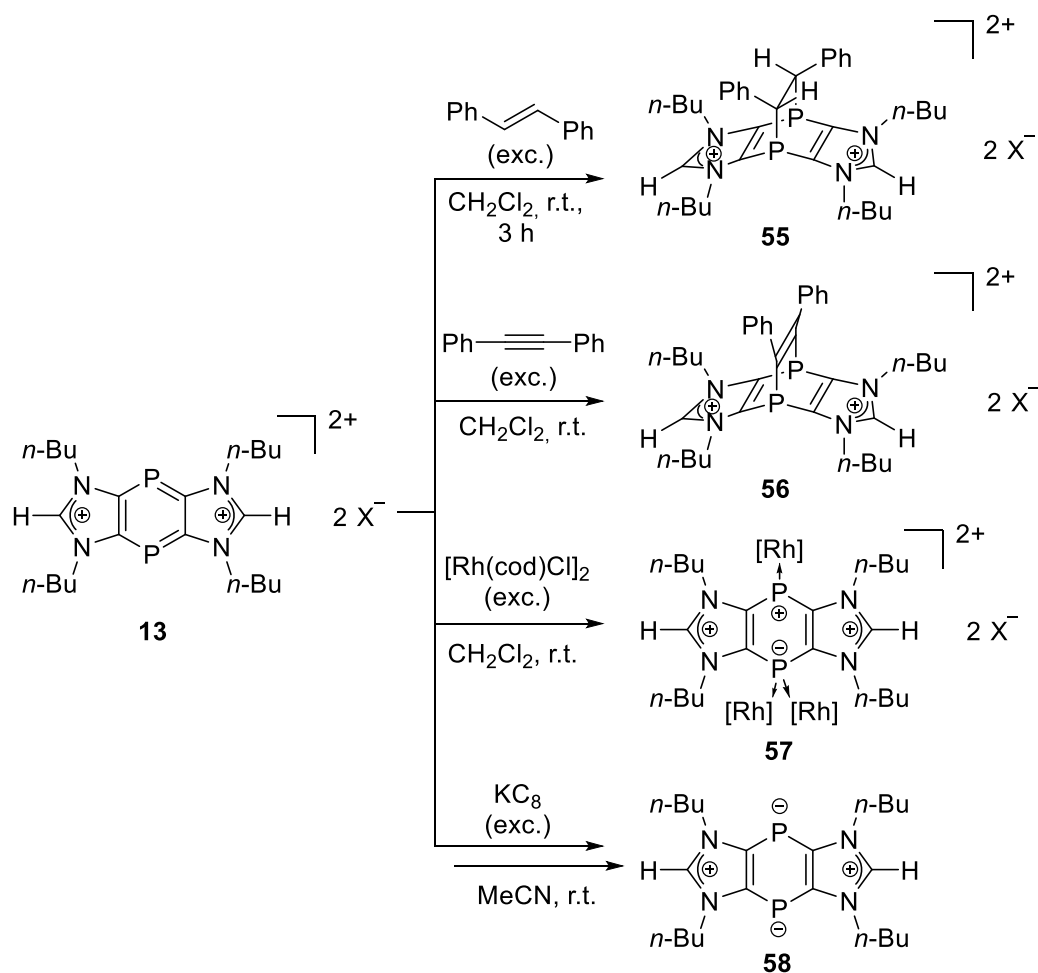


Figure 81. Cyclic voltammogram of **13** (circa 1 mM) at a Pt electrode in a 0.1 M *n*-Bu₄PF₆/MeCN solution at a scan rate of 200 mV s⁻¹; measurement with cathodic initial scan direction (indicated by an arrow) of the two reduction processes; potentials are referenced against Fc^{+/0}.

First reactivity studies to address the phosphorus centres were monitored via ³¹P{¹H} NMR spectroscopy and revealed fast reactions towards even electron-rich 2π-systems in [4+2]-

cycloadditions (**55** and **56**) and with transition metal complexes (**57**) – where no P-centred reaction could be observed for tricyclic 1,4-diphosphinines before. As predicted by the cyclovoltammetric experiment, **13** could easily be reduced with KC_8 at ambient temperature yielding zwitterionic **58**; unfortunately, it readily undergoes decomposition (Scheme 67).



Scheme 67. Overview of reactions performed with **13** to investigate the 1,4-reactivity.

5 EXPERIMENTAL SECTION

5.1 General working techniques

All reactions were performed under a dried and deoxygenated argon atmosphere using Schlenk or glovebox techniques under the exclusion of air and moisture. The used argon (>99.998 %) for the Schlenk line was purified by a system of three columns: 1. deoxygenation by a BTS copper catalyst (*BASF PuriStar® R3-15S*) at circa 70 °C, 2. moisture removal with silica gel, 3. additional drying with phosphorus pentoxide desiccant with indicator (*Merck Sicapent®*) and calcium chloride. Two gloveboxes (*MBraun UNILab LMF*) were used for which the argon atmosphere was purified through a BTS copper catalyst (*vide supra*), 13X molecular sieve and activated carbon for oxygen and water removal below 0.1 ppm. To evacuate the antechambers a rotary vane pump (*Edwards RV12*) was used. Glassware, spatulae, cannulae and filter papers were dried in a compartment dryer at 80 °C or 120 °C for at least one hour before use. Additionally, Schlenk glassware was heated with a heat gun (up to 550 °C) under active vacuum (<0.05 mbar) and filled with argon. Sterile syringes were purged with argon three to five times before use. Solvents were dried and purified by standard procedures¹⁷⁹ by refluxing over appropriate desiccants under an argon atmosphere (*n*-pentane, toluene and petroleum ether 40/65 over sodium wire ($\varnothing = 2$ mm); diethyl ether stabilised with 3,5-di-*t*-butyl-4-hydroxytoluene (BHT) and tetrahydrofuran over benzophenone and sodium wire ($\varnothing = 2$ mm); dichloromethane over calcium hydride) for several days and distilled before use. For use in the glovebox, diethyl ether and toluene were dried using an *MBraun SPS-800* solvent purification system and other solvents were taken from the stills and stored over molecular sieves (pore size 3 Å or 4 Å). For filtration Schlenk frits or stainless steel canulae ($\varnothing = 1$ mm and 2 mm) with *Whatman®* glass microfiber filters (grade GF/A) were used. All reactions were performed with magnetic stirrers and Teflon stir bars. For heating oil (*Marlotherm®*) baths and for cooling ethanol/liquid nitrogen baths were used. After use, stainless steel canulae and Teflon stir bars were cleaned with deionised water and acetone. Glassware was cleaned by storage in a concentrated solution of potassium hydroxide in isopropanol for at least one day and in diluted hydrochloric acid for at least four hours and rinsing with water and soap, deionised water and acetone and drying at 80 °C or 110 °C overnight afterwards. All joints were greased with OKS 1112 grease or with PTFE paste (*Carl Roth*). Vacuum was applied by a rotary vane pump (*Vacuubrand RZ6*) enabling pressures <0.01 mbar.

5.2 Methods and devices

5.2.1 Melting point determination

Melting points were measured using a *MPM-H2* or a *Büchi* melting point device. The samples were grease-sealed in a glass capillary ($\varnothing = 1$ mm) in a glovebox and heated quickly (ca. 10 K min^{-1}) for a rough determination of the melting point or decomposition temperature. Afterwards, a heating rate of approximately 1 K min^{-1} was used until the sample melted or decomposed. No internal or external temperature corrections were performed.

5.2.2 Elemental analysis (EA)

The measurements were performed by the central analytical department of the University of Bonn. Elemental analyses were conducted on an *Elementar Vario Micro* analysis device in quadruplicate or triplicate for each sample. Samples were prepared and weighed in tin or silver sample containers using a micro-analytical balance in a glovebox. For each compound calculated and found mean C, H, N and S values are given.

5.2.3 Mass spectrometry (MS)

The measurements were performed by the central analytical department of the University of Bonn. Mass spectrometry using electron spray ionisation (ESI) or atmospheric-pressure chemical ionisation (APCI) was performed on a *Thermo Fisher Scientific Orbitrap XL* mass spectrometer in acetonitrile or dichloromethane. Only selected data are given for detected ions. The peaks are given in mass-to-charge ratio (m/z). Only the isotopomer with the highest relative abundance is represented and the relative intensities of the peaks are given in parentheses and the proposed fragments in square brackets. Electron impact ionisation (EI) mass spectrometry was performed on a *Thermo Finnigan MAT 95 XL* sector field instrument using an ionisation energy of 70 eV and perfluorokerosene was used for calibration and referencing.

5.2.4 Infrared spectroscopy (IR)

IR spectra of solids were recorded in the spectral range of $4000\text{--}400\text{ cm}^{-1}$ on a *Bruker Alpha* FTIR spectrometer with a single-reflection diamond ATR measurement or a *Shimadzu IRSpirit* FTIR spectrometer with a single-reflection germanium ATR measurement in a glovebox at ambient temperature. All analyses were performed using the program *EZ OMNIC 7.3* of *Fisher Scientific* and *OPUS* of *Bruker*. Only selected wavenumbers of the absorption bands are given using reciprocal centimetres (cm^{-1}). The intensities of the bands are marked as weak (w), medium (m), strong (s) or very strong (vs).

5.2.5 UV/vis spectroscopy

UV/vis spectra were recorded in the spectral range of 200–700 nm on a *Shimadzu UV-1650PC* spectrometer with a double-beam optic photometric system with a maximum wavelength range of 190.0 to 1100 nm, a spectra band width of 2 nm and a wavelength accuracy of ± 0.5 nm with an automatic wavelength correction. An automatic baseline correction with the pure solvent was performed before the analyte solution was measured. The detector is a silicon photodiode with a photometric range of -0.5 to 3.999 absorbance. Quartz glass cuvettes (*Hellma* precision cells *110-QC*) with dimensions of $46\text{ mm} \times 12.5\text{ mm} \times 12.5\text{ mm}$, a light path length of 10 mm and a chamber volume of 3.5 mL were used and closed with PTFE caps before measurement. Measurements were started with a circa 10^{-5} molar solution of the respective compound and diluted until a sufficient spectrum was recorded. All spectra are normed to an absorbance of 1 a.u.; no extinction coefficients were determined. Absorbance wavelengths are given in nanometres (nm) with the relative absorbance (max. 1) and assignment to the associated transition in parentheses.

5.2.6 Nuclear magnetic resonance (NMR) spectroscopy

The measurements were mainly performed by the central analytical department of the University of Bonn. NMR spectra were recorded on a *Bruker Avance I 300 MHz*, *Bruker Avance I 400 MHz*, *Bruker Avance I 500 MHz* or *Bruker Avance III HD Ascend 500 MHz* spectrometer at the NMR department of the University of Bonn. Analyses were performed with the program *MestReNova 14.2*. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were calibrated via the solvent residual signals relative to tetramethylsilane ($\phi = 1\%$ in CDCl_3)(Table 13).

Table 13. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR resonances of solvent residual signals for used deuterated solvents.

solvent	$\delta(^1\text{H})$ / ppm	$\delta(^{13}\text{C}\{^1\text{H}\})$ / ppm
C_6D_6	7.16	128.06
CDCl_3	7.26	77.16
CD_2Cl_2	5.32	53.84
CD_3CN	1.94	1.32, 118.26
THF-d_8	1.73, 3.58	25.37, 67.57

Hetero-nuclei NMR spectra were recorded relative to external references as follows: ^{31}P NMR spectra relative to 85 % H_3PO_4 in water, ^{77}Se NMR spectra relative to neat Me_2Se and ^{11}B NMR spectra relative to $\text{BF}_3\cdot\text{OEt}_2$ in CDCl_3 ($\phi = 15\%$). All lock frequencies were calibrated internally against the ^1H NMR signals of solutions of tetramethylsilane with a volume fraction of $\phi = 1\%$ in the corresponding

deuterated solvent. The deuterated solvents were used without further purification and dried by storing over 3 Å (CD_2Cl_2 , CD_3CN) or 4 Å (C_6D_6 , CDCl_3 , THF-d_8) molecular sieves. The chemical shift (δ) is given in parts per million (ppm) and the coupling constant ($^nJ_{\text{X,Y}}$) (n = number of bonds between the coupling nuclei X and Y) in Hertz (Hz) as absolute values neglecting the sign. The following abbreviations were used to assign the multiplicity of a signal: s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q quartet, m = multiplet, br = broad. Satellite signals are indicated by a “sat”-index (*e.g.* s_{sat}). For ^1H NMR spectra the number of nuclei is given which is determined via integration. If necessary, ^1H and ^{13}C NMR signals of compounds were assigned unambiguously by a combination of 2D-COSY, -HSQC and -HMBC experiments. All experiment were performed at ambient temperature (298 K).

5.2.7 Single crystal X-ray diffraction (SCXRD) analysis

The measurements were performed by the central analytical department of the University of Bonn. SCXRD analyses were performed on a *Bruker D8-Venture* diffractometer at 100 K using monochromated $\text{Cu-K}\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$), a *STOE IPDS-2T* diffractometer at 123 K using monochromated $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) or a *STOE STADIVARI* at 100 K using monochromated $\text{Cu-K}\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$). Intensities were measured by fine-slicing ϕ and ω scans and corrected background, polarisation and Lorentz effects. Following the method by Blessing,¹⁸⁰ a semi-empirical absorption correction was applied. The solution of the structure was performed by direct methods and the refinement was conducted anisotropically by the least-square procedure which is implemented in the *SHELX* program system.¹⁸¹ All non-hydrogen atoms were refined anisotropically; hydrogen atoms were isotropically refined and placed using a riding model. The quality of the crystal structures was evaluated by an in-house grading system consisting of a combination of one or two letters and a number: A = solving and refinement without any (identifiable) errors (excellent structure); B = only marginal problems during refinement (very good structure); C = small problems during refinement (good structure); D = significant problems during refinement (moderate structure) ; E = not for precise discussion, only structural motif confirmed; 1 = found structure was identical to the beforehand proposed one; 2 = found structure was close to the beforehand proposed structure; 3 = found structure contained motifs of the beforehand proposed structure; 4 = found structure was not related to the beforehand proposed structure. For analyses and the ellipsoid representation of the molecular structures the program *Olex2 1.5* of *OlexSys*¹⁸² was used. The appendix (7.4) contains detailed crystallographic data including the refinement parameters as well as bond length and angles.

5.2.8 Cyclic voltammetry (CV)

Cyclovoltammetric measurements were performed in the glovebox with the potentiostat/galvanostat system *WaveNow^{xv}*® of *Pine Research* over scan rates of 50–1600 mV s⁻¹. For all measurements *Pine Research* ceramic screen-printed platinum electrodes containing an Ag/AgCl reference electrode which combine working, counter and reference electrode on one ceramic plate were used. The measurements were carried out in a glass cell with a special PTFE insert at the bottom with a slit to fit the ceramic screen-printed electrode and a slit-volume of circa 1 mL. When using acetonitrile as solvent a 0.1 M solution of the electrolyte *n*-Bu₄PF₆ was prepared. The electrolyte was dried thoroughly *in vacuo* (≤ 0.02 mbar) at 80 °C for at least 24 hours before use. Acetonitrile was purified by drying over CaH₂ and P₂O₅, trap-to-trap recondensation and degassing by three freeze-pump-thaw cycles. The analyte solutions were prepared with concentrations of 1–3 mmol L⁻¹. For each measurements a background scan to determine the anodic and cathodic limits of the electrolyte solution was performed first, followed by analyte addition and the measurement of the open circuit potential and thus, the starting point of the experiments. The oxidation and reduction processes in both anodic and cathodic direction were determined carefully and investigated in isolated form if possible. In the end, cobaltocenium hexafluorophosphate (–1.35 V vs. Fc⁺⁰) or ferrocene were added as internal reference to achieve the IUPAC recommended¹⁸³ referencing to the ferrocene/ferrocenium redox couple (Fc⁺⁰). For the measurement and analysis of the experimental data the software *Aftermath* of *Pine Research* was used.

5.2.9 Theoretical calculations

All quantum chemical calculations were performed with *ORCA 5.0*^{184,185}. Structures were optimised at the TPSS-D4/def2-TZVP/CPCM_{THF} level of theory which combines the TPSS¹⁸⁶ meta-GGA density functional with the charge dependent atom-pairwise DFT-D4 dispersion correction which uses the D4(EEQ)-ATM dispersion model¹⁸⁷ and the def2-TZVP basis set^{188–191} using the conductor-like polarisable continuum model (CPCM)¹⁹² for THF ($\epsilon = 7.25$). The minimum or transition state nature of the compounds has been determined by numerical frequency calculations. All minima have zero imaginary frequencies below –50 cm⁻¹ following the recommendations from the *ORCA 5.0.4* manual¹⁹³. Transition states possess only one major imaginary frequency that describes the transition from starting material to product along the desired bond trajectory. The energetic position of the transition states on the potential hypersurface has been computed with the help of the nudge elastic band optimiser (NEB)^{194,185} as implemented in *ORCA 5.0*. Single point energy calculations were performed at the PW6B95-D4/def2-QZVP/CPCM_{THF} level of theory which combines the higher PW6B95 hybrid-meta-GGA functional¹⁹⁵ including additional SOS-PT2 correlation with the larger def2-QZVP basis set.^{188–191} NICS(1) values were calculated at the B3LYP-D4/def2-TZVPPD level of theory combining the hybrid

functional B3LYP¹⁹⁶ with the highly polarised and diffuse def2-TZVPPD basis set^{188–191} and using the NMR module of *ORCA 5.0* utilising Gauge including atomic orbitals (GIAOs).¹⁹⁷ UV/vis calculations (TD-DFT) were performed at the TPSS-D4/def2-TZVPPD level of theory with 20 excited states (nroots 20) and the CPCM for toluene ($\epsilon = 2.4$) as this combination of functional and basis set produced the most reliable results in a self-conducted study on known systems. The density-fitting RI-JCOSX (def2/J)^{198,188} approach was used to accelerate all calculations.

The graphical representations of the calculated structures and their frontier molecular orbitals (FMOs), taken from the single point energy calculations, were generated with *UCSF Chimera 1.15*.¹⁹⁹ FMOs are depicted with an isovalue of 0.04.

To save computational costs, all structures of new compounds were computed as model compounds with *N*-methyl instead *N*-*n*-butyl substitution. The appendix (7.5) contains the optimised cartesian coordinates (in Å) and electronic energies (in Hartree). Zero-point energies (E_{ZPE}), thermal corrections (E_T) at 298.15 K and entropy corrections (E_S) were taken from the numerical frequency calculations.

5.3 Used chemicals

Chemicals were used without further purification or purified according to standard procedures.¹⁷⁹

Table 14. Sources of the obtained chemicals.

chemical	supplier/company (purity)
[W(CO) ₅ (NCMe)]	Streubel work group
1-hexene	Aldrich (99.9 %), Acros (99.5 %)
1-octene	Aldrich (98 %)
3,3'-bicarbazole	Protasiewicz work group
acetonitrile	VWR (99.9 %)
acetonitrile-d ₃	Aldrich (99.8 %), Deutero (99.8 %)
aluminium oxide 90 active neutral (70–230 mesh ASTM)	Merck
benzene-d ₆	Aldrich (99.9 %), Deutero (99.5 %)
benzophenone	Aldrich (99 %)

borane dimethylsulfide	Aldrich
boron trichloride (1 M in hexane)	Acros, Thermo Scientific
calcium hydride	abcr (92 %), Alfa Aesar (92 %)
carbon dioxide	AirLiquide (99.995 %)
carbon disulfide	Riedel-de-Haën (99.9 %)
Celite® 545	Merck, Acros
chlorodiphenylphosphane	Alfa Aesar (98 %)
chloroform-d	Deutero (99.8–99.95 %)
chromium hexacarbonyl	Merck (98 %), abcr (99 %)
cobaltocenium hexafluorophosphate	Aldrich (98 %)
dichloromethane	Fisher (99.8 %)
dichloromethane-d ₂	Aldrich (99.95 %)
diethyl amine	Alfa Aesar (99 %)
diethyl ether	VWR
diiron nonacarbonyl	Fluka (98 %), abcr (98 %)
di- <i>iso</i> -propyl amine	Acros (99 %)
diphenyl disulfide	Streubel work group
diphenylethyne	Alfa Aesar (99 %)
[Rh(cod)Cl] ₂	Streubel work group, BLD (98 %)
ethanol	Julius Hoesch (99 %)
ethene	Aldrich, Messer® (99.95 %)
ferrocene	Acros (98 %)
formaldehyde (37 wt.% in water)	Acros
glyoxal (40 wt.% in water)	Carl Roth

hydrochloric acid (37 %)	VWR
magnesium sulfate	VWR (99 %)
methanol	Alfa Aesar
methyl trifluoromethanesulfonate	Fluorochem (99 %), abcr (98 %)
molecular sieves 3 Å	Carl Roth
molecular sieves 4 Å	Carl Roth, Alfa Aesar
<i>n</i> -butyl amine	Fluka (99 %)
<i>n</i> -butyl lithium (1.6 M in hexanes)	Acros
<i>n</i> -pentane	Fisher (99 %)
petroleum ether 40/65	Julius Hoesch
phosphorus pentoxide, powder or granular	J. T. Baker (99 %)
phosphorus trichloride	Acros (99 %)
potassium	Riedel-de-Haën (98 %)
potassium graphite	Streubel work group
potassium hexamethyldisilazide	Aldrich (95 %)
potassium <i>tert</i> -butoxide	Alfa Aesar (97 %)
selenium, grey	Acros (99.5 %)
silica gel 60 (63–230 mesh)	Merck Geduran® Si60
silver trifluoromethanesulfonate	TCI (98 %)
sodium	Aldrich
sodium borohydride	Aldrich (99 %)
sodium hydride (60 % in paraffin liquid)	TCI
tetrahydrofuran	Fisher (99.8 %)
tetrahydrofuran- d_8	Carl Roth (99.5 %), Deutero (99.5 %)

tetra- <i>n</i> -butylammonium hexafluorophosphate	Alfa Aesar (98 %)
toluene	VWR (99.9 %)
<i>trans</i> -3-hexene	TCI (99 %), Thermo Scientific (98 %)
<i>trans</i> -diphenylethene	Aldrich (96 %)
triethylammonium chloride	Aldrich
trimethylamine <i>N</i> -oxide dihydrate	Glentham (99 %)
tri- <i>n</i> -butyl phosphane	Alfa Aesar (94.5 %)
tungsten hexacarbonyl	Acros (99 %)

The following compounds were synthesised according to literature-described procedures:

- 1,3-dibutyl-1*H*-imidazolium chloride²⁰⁰
- chlorobis(diethylamino)phosphane²⁰¹
- lithium di-*iso*-propylamide²⁰²
- 1,3,5,7-tetrabutyl-4,8-bis(diethylamino)-1,3,5,7-tetrahydro-2*H*,6*H*-[1,4]diphosphinino[2,3-*d*:5,6-*d'*]diimidazole-2,6-diselone (**XXXIVc**)^{136,137}
- 1,3,5,7-tetrabutyl-1,3,5,7-tetrahydro-2*H*,6*H*-[1,4]diphosphinino[2,3-*d*:5,6-*d'*]diimidazole-2,6-diselone (**1**)^{81,137}
- 1,3,5,7-tetrabutyl-4,8-bis(diethylamino)-1,3,5,7-tetrahydro-2*H*,6*H*-4,8-[1,4]diphosphinino[2,3-*d*:5,6-*d'*]diimidazole-2,6-dium bis(trifluoromethanesulfonate) (**50**)^{136,81}
- 1,3,5,7-tetrabutyl-4,8-bis(diethylamino)-1,3,5,7-tetrahydro-2*H*,6*H*-4,8-[1,4]diphosphinino[2,3-*d*:5,6-*d'*]diimidazole-2,6-diylidene (**31a**)^{136,137}
- 1,3,5,7-tetrabutyl-4,8-bis(diethylamino)-4,8-dioxo-1,3,5,7-tetrahydro-2*H*,6*H*-4,8-[1,4]diphosphinino[2,3-*d*:5,6-*d'*]diimidazole-2,6-diylidene (**31b**)^{136,137}
- [Cr(CO)₅(NCMe)]²⁰³

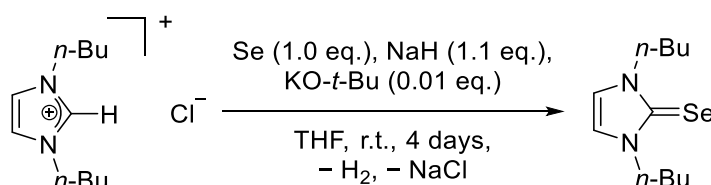
5.4 Waste disposal

All laboratory chemical waste was disposed of according to the *Hazardous Substance Ordinance* (*Gefahrstoffverordnung – GefStoffV*). Solids – including contaminated gloves, syringes, weighing paper and paper towels – organic solvents, inorganic heavy metal waste, filter materials and absorbents as well as canulae were collected separately in designated and labelled containers. Reactive compounds and their residues were neutralised or quenched, respectively, before disposal. The waste was

submitted to the University's Division 4.1 (*Abt. 4.1 – Zentrale Serviceaufgaben, SG – Entsorgung und Gefahrgut*).

5.5 Synthesis and characterisation

5.5.1 Synthesis of 1,3-dibutyl-1,3-dihydro-2*H*-imidazole-2-selone



Synthesis

In a 2 L three-necked round-bottom flask 185 g (0.85 mol, 1.0 eq.) of 1,3-dibutyl-1*H*-imidazolium chloride and 67.4 g (0.85 mol, 1.0 eq.) of grey selenium were suspended in 1 L THF and 22.5 g (0.94 mol, 1.1 eq.) of sodium hydride were added successively to the brown suspension under Argon atmosphere. Afterwards, 1.00 g (0.009 mol, 0.01 eq.) potassium *tert*-butoxide were added and the dark-brown suspension was stirred for four days and after solvent removal *in vacuo* (≤ 0.05 mbar) the brown residue was filtered with 1.2 L dichloromethane. After the solvent was removed *in vacuo* (≤ 0.05 mbar), the residue was purified via column chromatography (SiO₂, h = 10 cm, d = 9 cm, eluent petroleum ether/diethyl ether) and the product was collected in the second fraction with diethyl ether. After removal of the solvent *in vacuo* (≤ 0.05 mbar), the obtained brown oil was washed with five times 100–120 mL *n*-pentane and dried for 3 h.

The obtained NMR spectroscopical values compare well with literature values.²⁰⁴

Reaction code: TT-177, TT-586 (TAT230623p5a014, 25m3a016.22)

Molecular formula: C₂₁H₂₀N₂OSe

Molecular weight: 259.27 g mol⁻¹

Yield: 143 g (0.55 mmol, 65 %)

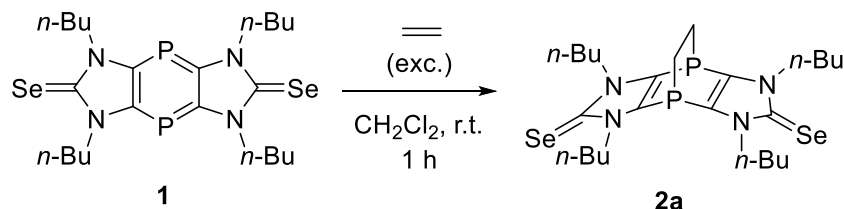
¹H NMR (500.04 MHz, 298.0 K, CDCl₃): δ / ppm = 0.84 (m, 6H, CH₃), 1.27 (m, 4H, CH₂CH₃), 1.67 (m, 4H, NCH₂CH₂), 4.02 (m, 4H, NCH₂), 6.79 (m, 2H, CH).

¹³C{¹H} NMR (125.75 MHz, 298.0 K, CDCl₃): δ / ppm = 13.6 (m, CH₃), 19.6 (m, CH₂CH₃), 31.1 (m, NCH₂CH₂), 49.3 (m, NCH₂), 118.6 (m, CH), 154.5 (m_{sat}, ¹J_{Se,C} = 229 Hz, CSe).

⁷⁷Se NMR (57.24 MHz, 298.0 K, CDCl₃): δ / ppm = -11.8 (s).

5.5.2 Synthesis of 7,8-dihydro-1,4-diphosphabarrelenes **2**

5.5.2.1 Synthesis of 1,3,5,7-tetrabutyl-1,3,5,7-tetrahydro-2*H*,6*H*-4,8-ethano[1,4]diphosphino[2,3-*d*:5,6-*d'*]diimidazole-2,6-diselone **2a**



Synthesis

In a 20 mL Schlenk tube equipped with a stir bar 0.066 g (0.11 mmol, 1.0 eq.) of **1** were dissolved in 6 mL dichloromethane and the Argon atmosphere was exchanged for 1 atm ethene. After stirring for 1 h at ambient temperature the solution had turned orange and the solvent was removed *in vacuo* (≤ 0.05 mbar). The resulting yellow to orange solid was washed four times with 2–4 mL *n*-pentane each and dried for 2 h (≤ 0.02 mbar) yielding a yellow solid.

Reaction code: TT-775 (TAT230421p5a047, TAT230426m3a019)

Molecular formula: C₂₄H₄₀N₄P₂Se₂

Molecular weight: 604.48 g mol⁻¹

Yield: 0.049 g (0.08 mmol, 71 %)

Melting point: 120 °C (dec.)

EA: calculated (%)	C 47.69	H 6.67	N 9.27
found (%)	C 46.85	H 6.66	N 9.20

MS (pos. ESI): m/z (%) = 604.107 (4) [M]⁺, 527.197 (100) [M–Se+H]⁺, 499.165 (25) [M–C₂H₄–Se+H]⁺.

HRMS (pos. ESI): m/z calculated for [C₂₄H₄₀N₄P₂Se₂]⁺: 604.107; found: 604.107.

m/z calculated for [C₂₄H₄₀N₄P₂Se₂H]⁺: 605.1146; found: 605.1145.

IR (ATR): $\tilde{\nu}$ / cm⁻¹ = 2959 (m, $\nu_{\text{as}}(\text{CH}_3)$, $\nu_{\text{s}}(\text{CH}_2)$), 2933 (m, $\nu_{\text{as}}(\text{CH}_3)$, $\nu_{\text{s}}(\text{CH}_2)$), 2871 (m, $\nu_{\text{s}}(\text{CH}_3)$, $\nu_{\text{as}}(\text{CH}_2)$).

¹H NMR (500.04 MHz, 298.0 K, CDCl₃): δ / ppm = 0.96 (t, $^3J_{\text{H,H}} = 7.4$ Hz, 12H, CH₃), 1.38 (qm, $^3J_{\text{H,H}} = 7.4$ Hz, 8H, CH₂CH₃), 1.67–1.82 (m, 12H, PCH₂, NCH₂CH₂), 4.20–4.37 (m, 8H, NCH₂).

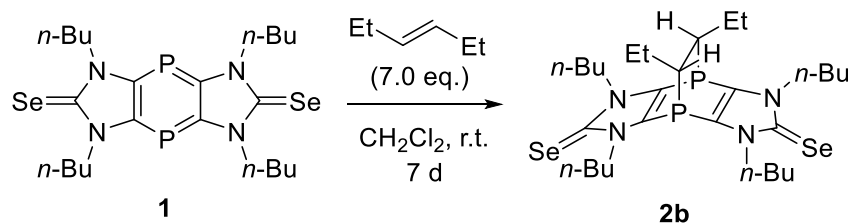
¹³C{¹H} NMR (125.75 MHz, 298.0 K, CDCl₃): δ / ppm = 13.9 (s, CH₃), 19.8 (dd, $J_{\text{P,C}} = 4.6$ Hz, PCH₂), 20.1 (m, CH₂CH₃), 32.0 (m, NCH₂CH₂), 48.9 (m, NCH₂), 137.3 (dd, $J_{\text{P,C}} = 4.6$ Hz, PC), 159.1 (s_{sat} , $^1J_{\text{Se,C}} = 233.4$ Hz, CSe).

^{31}P NMR (202.44 MHz, 298.0 K, CDCl_3): δ / ppm = -94.7 (tm, $^2J_{\text{P,H}} = 5.3$ Hz).

$^{31}\text{P}\{^1\text{H}\}$ NMR (202.44 MHz, 298.0 K, CDCl_3): δ / ppm = -94.7 (s).

^{77}Se NMR (57.24 MHz, 298.0 K, CDCl_3): δ / ppm = 26.4 (s).

5.5.2.2 Synthesis of 1,3,5,7-tetrabutyl-9,10-diethyl-1,3,5,7-tetrahydro-2*H*,6*H*-4,8-ethano[1,4]diphosphinino[2,3-d:5,6-d']diimidazole-2,6-diselone **2b**



Synthesis

In a 150 mL Schlenk tube 3.00 mL (24.1 mmol, 7.0 eq.) *trans*-3-hexene were added dropwise to a solution of 2.000 g (3.47 mmol, 1.0 eq.) of **1** in 60 mL dichloromethane. After stirring for 7 d at ambient temperature the solution had turned red and the solvent was removed *in vacuo* (≤ 0.05 mbar). The resulting slightly pink residue was washed four times with 20 mL *n*-pentane each (until the washing solution is not pink anymore) and the orange solid was dried for 2 h (≤ 0.02 mbar).

Reaction code: TT-500 (04p5a010.22, 04m3a023.22), TT-662 (for EA)

Molecular formula: $\text{C}_{28}\text{H}_{48}\text{N}_4\text{P}_2\text{Se}_2$

Molecular weight: $660.59 \text{ g mol}^{-1}$

Yield: 1.705 g (2.58 mmol, 74 %)

Melting point: 120°C (dec.)

EA: calculated (%) C 50.91 H 7.32 N 8.48

found (%) C 50.20 H 7.22 N 8.58

MS (pos. ESI): m/z (%) = 663.176 (<1) $[\text{M}+\text{H}]^+$, 583.259 (100) $[\text{M}-\text{Se}+\text{H}]^+$, 579.262 (20) $[\text{M}-\text{C}_6\text{H}_{12}]^+$, 499.165 (43) $[\text{M}-\text{C}_6\text{H}_{12}-\text{Se}+\text{H}]^+$.

HRMS (pos. ESI): m/z calculated $[\text{C}_{28}\text{H}_{48}\text{N}_4\text{P}_2\text{Se}_2\text{H}]^+$: 663.1763; found: 663.1756.

IR (ATR): $\tilde{\nu}$ / cm^{-1} = 2957 (m, $\nu_{\text{as}}(\text{CH}_3)$, $\nu_{\text{s}}(\text{CH}_2)$), 2928 (m, $\nu_{\text{as}}(\text{CH}_3)$, $\nu_{\text{s}}(\text{CH}_2)$), 2860 (m, $\nu_{\text{s}}(\text{CH}_3)$, $\nu_{\text{as}}(\text{CH}_2)$).

^1H NMR (500.04 MHz, 298.0 K, CD_2Cl_2): δ / ppm = 0.97 (t, $^3J_{\text{H,H}} = 7.4$ Hz, 12H, $\text{CH}_3(n\text{-Bu})$), 1.10 (t, $^3J_{\text{H,H}} = 7.2$ Hz, 6H, $\text{CH}_3(\text{Et})$), 1.15–1.27 (m, 2H, PCHCH_2), 1.31–1.45 (m, 10H, $\text{NCH}_2\text{CH}_2\text{CH}_2$, PCH), 1.46–1.57 (m, 2H, PCHCH_2), 1.63–1.85 (m, 8H, NCH_2CH_2), 4.15–4.23 (m, 2H, NCH_2), 4.24–4.34 (m, 6H, NCH_2).

$^{13}\text{C}\{^1\text{H}\}$ NMR (125.75 MHz, 298.0 K, CD_2Cl_2): δ / ppm = 11.4 (s, $\text{CH}_3(n\text{-Bu})$), 13.9 (m, $\text{CH}_3(\text{Et})$), 20.3 (m, $\text{NCH}_2\text{CH}_2\text{CH}_2$), 28.3 (m, PCHCH_2), 32.3 (m, NCH_2CH_2), 46.4 (dd, $J_{\text{P,C}} = 5.5$ Hz, PCH), 49.0 (m, NCH_2), 137.1 (dd, $J_{\text{P,C}} = 8.0$ Hz, $J_{\text{P,C}} = 5.5$ Hz, PC), 139.8 (d, $J_{\text{P,C}} = 4.3$ Hz, PC), 159.6 (s_{sat} , $^1J_{\text{Se,C}} = 235.1$ Hz, CSe).

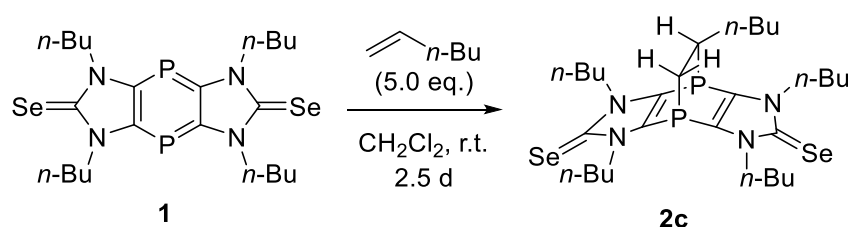
^{31}P NMR (202.44 MHz, 298.0 K, CD_2Cl_2): δ / ppm = -86.3 (m).

$^{31}\text{P}\{^1\text{H}\}$ NMR (202.44 MHz, 298.0 K, CD_2Cl_2): δ / ppm = -86.3 (s).

^{77}Se NMR (57.24 MHz, 298.0 K, CD_2Cl_2): δ / ppm = 31.2 (s).

X-ray diffraction analysis: GXraycu_6823f (GSTR750), good structure (BC1)

5.5.2.3 Synthesis of 1,3,5,7-tetrabutyl-9-butyl-1,3,5,7-tetrahydro-2*H*,6*H*-4,8-ethano[1,4]diphosphinino[2,3-*d*:5,6-*d'*]diimidazole-2,6-diselone **2c**



Synthesis

In a 100 mL Schlenk tube 0.73 mL (8.68 mmol, 5.0 eq.) 1-hexene were added dropwise to a solution of 1.001 g (1.74 mmol, 1.0 eq.) of **1** in 30 mL dichloromethane. After stirring for 3 d at ambient temperature the solution had turned yellow and the solvent was removed *in vacuo* (≤ 0.05 mbar). The resulting yellow residue was washed twice with 10 mL diethyl ether each, four times with 10–20 mL *n*-pentane each, and the beige solid was dried for 2 h (≤ 0.02 mbar).

Reaction code: TT-354 (06p5a016.21, 06m3a024.21), TT-675 (for EA)

Molecular formula: $\text{C}_{28}\text{H}_{48}\text{N}_4\text{P}_2\text{Se}_2$

Molecular weight: 660.59 g mol $^{-1}$

Yield: 0.765 g (1.16 mmol, 67 %)

Melting point: 142 °C (dec.)

EA: calculated (%)	C 50.91	H 7.32	N 8.48
found (%)	C 50.19	H 7.26	N 8.58

MS (pos. ESI): m/z (%) = 663.174 (<1) $[\text{M}+\text{H}]^+$, 583.258 (61) $[\text{M}-\text{Se}+\text{H}]^+$.

HRMS (pos. ESI): m/z calculated $[\text{C}_{28}\text{H}_{48}\text{N}_4\text{P}_2\text{Se}_2\text{H}]^+$: 663.176; found: 663.174.

IR (ATR): $\tilde{\nu}$ / cm^{-1} = 2956 (m, $\nu_{\text{as}}(\text{CH}_3)$, $\nu_{\text{s}}(\text{CH}_2)$), 2927 (m, $\nu_{\text{as}}(\text{CH}_3)$, $\nu_{\text{s}}(\text{CH}_2)$), 2860 (m, $\nu_{\text{s}}(\text{CH}_3)$, $\nu_{\text{as}}(\text{CH}_2)$).

^1H NMR (500.04 MHz, 298.0 K, CD_2Cl_2): δ / ppm = 0.89 (t, $^3J_{\text{H,H}} = 7.3$ Hz, 3H, $\text{CH}_3(\text{PCH}(n\text{-Bu}))$), 0.92–1.92 (m, 12H, $\text{CH}_3(\text{N}(n\text{-Bu}))$), 1.14–1.22 (m, 1H, PCH_2), 1.23–1.32 (m, 4H, $\text{PCHCH}_2\text{CH}_2\text{CH}_2$), 1.32–1.46 (m, 8H, $\text{NCH}_2\text{CH}_2\text{CH}_2$), 1.45–1.55 (m, 2H, PCHCH_2), 1.63–1.86 (m, 8H, NCH_2CH_2), 1.96 (m, 1H, PCH), 2.13 (m, 1H, PCH_2), 4.18–4.37 (m, 8H, NCH_2).

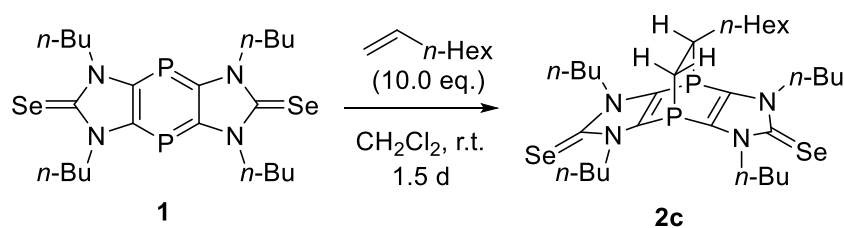
$^{13}\text{C}\{^1\text{H}\}$ NMR (125.75 MHz, 298.0 K, CD_2Cl_2): δ / ppm = 14.0 (m, CH_3), 20.4 (m, $\text{NCH}_2\text{CH}_2\text{CH}_2$), 22.8 (s, $\text{PCHCH}_2\text{CH}_2\text{CH}_2$), 28.2 (dd, $^1J_{\text{P,C}} = 9.5$ Hz, $^2J_{\text{P,C}} = 4.1$ Hz, PCH_2), 31.6 (d, $J_{\text{P,C}} = 15.3$ Hz, $\text{PCHCH}_2\text{CH}_2$), 32.3 (m, NCH_2CH_2), 32.4 (d, $J_{\text{P,C}} = 2.6$ Hz, PCHCH_2), 36.3 (dd, $^1J_{\text{P,C}} = 7.3$ Hz, $^2J_{\text{P,C}} = 2.5$ Hz, PCH), 49.0 (m, NCH_2), 136.2 (dd, $J_{\text{P,C}} = 11.4$ Hz, $J_{\text{P,C}} = 3.2$ Hz, PC), 137.5 (dd, $J_{\text{P,C}} = 6.3$ Hz, $J_{\text{P,C}} = 2.9$ Hz, PC), 138.9 (dd, $J_{\text{P,C}} = 5.7$ Hz, $J_{\text{P,C}} = 2.9$ Hz, PC), 139.9 (dd, $J_{\text{P,C}} = 6.0$ Hz, $J_{\text{P,C}} = 3.7$ Hz, PC), 159.3 (s, CSe), 159.7 (s, CSe).

^{31}P NMR (202.44 MHz, 298.0 K, CD_2Cl_2): δ / ppm = -91.4 (m, PCH_2), -87.0 (m, PCH).

$^{31}\text{P}\{^1\text{H}\}$ NMR (202.44 MHz, 298.0 K, CD_2Cl_2): δ / ppm = -91.4 (d, $^3J_{\text{P,P}} = 17.3$ Hz, PCH_2), -87.0 (d, $^3J_{\text{P,P}} = 17.6$ Hz, PCH).

^{77}Se NMR (57.24 MHz, 298.0 K, CD_2Cl_2): δ / ppm = 27.7 (s), 30.5 (s).

5.5.2.4 Synthesis of 1,3,5,7-tetrabutyl-9-hexyl-1,3,5,7-tetrahydro-2*H*,6*H*-4,8-ethano[1,4]diphosphinino[2,3-*d*:5,6-*d'*]diimidazole-2,6-diselone **2d**



Synthesis

In a 20 mL Schlenk tube 0.22 mL (1.39 mmol, 10.0 eq.) 1-octene were added dropwise to a solution of 0.080 g (0.14 mmol, 1.0 eq.) of **1** in 4 mL dichloromethane. After stirring for 1.5 d at ambient temperature the solution had turned yellow and the solvent was removed *in vacuo* (≤ 0.05 mbar). The resulting yellow residue was washed four times with 5 mL *n*-pentane each, and the beige solid was dried for 3 h (≤ 0.02 mbar).

Reaction code: TT-490 (01p5a008.22, 01m3a009.22)

Molecular formula: $\text{C}_{30}\text{H}_{52}\text{N}_4\text{P}_2\text{Se}_2$

Molecular weight: $688.67 \text{ g mol}^{-1}$

Yield: 0.053 g (0.08 mmol, 55 %)

Melting point: 141 °C (dec.)

MS (pos. ESI): m/z (%) = 691.207 (1) $[M]^+$, 611.291 (41) $[M-Se+H]^+$, 499.165 (12) $[M-Se-C_8H_{16}+H]^+$, 266.191 (85) $[M-2Se+2H]^{2+}$.

HRMS (pos. ESI): m/z calculated $[C_{30}H_{52}N_4P_2Se_2H]^+$: 691.2076; found: 691.2073.

IR (ATR): $\tilde{\nu}$ / cm^{-1} = 2957 (m, $\nu_{as}(CH_3)$, $\nu_s(CH_2)$), 2924 (m, $\nu_{as}(CH_3)$, $\nu_s(CH_2)$), 2854 (m, $\nu_s(CH_3)$, $\nu_{as}(CH_2)$).

^1H NMR (500.04 MHz, 298.0 K, CD_2Cl_2): δ / ppm = 0.86 (t, $^3J_{H,H} = 7.3$ Hz, 3H, $CH_3(n-Hex)$), 0.97 (m, 12H, $CH_3(n-Bu)$), 1.15–1.21 (m, 1H, PCH_2), 1.22–1.33 (m, 6H, $PCHCH_2CH_2CH_2CH_2CH_2$), 1.33–1.44 (m, 10H, $NCH_2CH_2CH_2$, $PCHCH_2CH_2$), 1.44–1.54 (m, 2H, $PCHCH_2$), 1.64–1.85 (m, 8H, NCH_2CH_2), 1.93–2.01 (m, 1H, PCH), 2.08–2.18 (m, 1H, PCH_2), 4.19–4.35 (m, 8H, NCH_2).

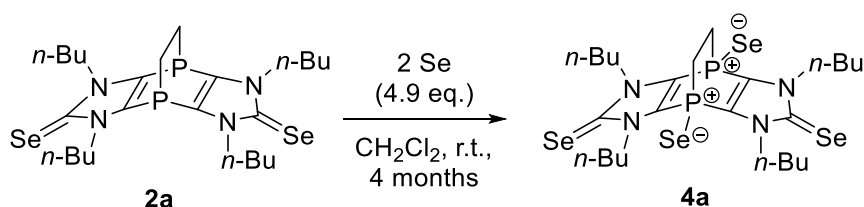
$^{13}C\{^1H\}$ NMR (125.75 MHz, 298.0 K, CD_2Cl_2): δ / ppm = 14.0 (m, $CH_3(n-Bu)$), 14.2 (m, $CH_3(n-Hex)$), 20.4 (m, $NCH_2CH_2CH_2$), 22.9 (s, $PCHCH_2CH_2CH_2CH_2CH_2$), 28.2 (dd, $^1J_{P,C} = 9.4$ Hz, $^2J_{P,C} = 4.1$ Hz, PCH_2), 29.3 (m, $PCHCH_2CH_2CH_2CH_2CH_2$), 32.0 (s, $PCHCH_2CH_2CH_2$), 32.2 (m, NCH_2CH_2), 32.3 (d, $J_{P,C} = 2.6$ Hz, $PCHCH_2$), 35.8 (d, $J_{P,C} = 16.2$ Hz, $PCHCH_2CH_2$), 36.3 (dd, $^1J_{P,C} = 7.3$ Hz, $^2J_{P,C} = 2.5$ Hz, PCH), 49.0 (m, NCH_2), 136.2 (dd, $J_{P,C} = 11.4$ Hz, $J_{P,C} = 3.2$ Hz, PC), 137.5 (dd, $J_{P,C} = 6.3$ Hz, $J_{P,C} = 2.8$ Hz, PC), 138.9 (dd, $J_{P,C} = 5.7$ Hz, $J_{P,C} = 2.9$ Hz, PC), 139.9 (dd, $J_{P,C} = 6.0$ Hz, $J_{P,C} = 3.7$ Hz, PC), 159.3 (s, CSe), 159.7 (s, CSe).

^{31}P NMR (202.44 MHz, 298.0 K, CD_2Cl_2): δ / ppm = -91.4 (m, PCH_2), -87.0 (m, PCH).

$^{31}P\{^1H\}$ NMR (202.44 MHz, 298.0 K, CD_2Cl_2): δ / ppm = -91.4 (d, $^3J_{P,P} = 17.6$ Hz, PCH_2), -87.0 (d, $^3J_{P,P} = 17.6$ Hz, PCH).

^{77}Se NMR (57.24 MHz, 298.0 K, CD_2Cl_2): δ / ppm = 27.7 (s), 30.5 (s).

5.5.3 Generation of 1,3,5,7-tetrabutyl-1,3,5,7-tetrahydro-2*H*,6*H*-4,8-diseleno-4,8-ethano[1,4]diphosphinino[2,3-*d*:5,6-*d'*]diimidazole-2,6-diselone **4a**



Synthesis

In a 20 mL Schlenk tube 0.139 g (0.21 mmol, 1.0 eq.) of **2a** and 0.081 g (1.03 mmol, 4.9 eq.) grey selenium were suspended in 4 mL dichloromethane and stirred at ambient temperature while the reaction course was monitored via $^{31}P\{^1H\}$ NMR spectroscopy. After 4 months no change in the composition of the reaction mixture was observed anymore and the contents were extracted with additional

dichloromethane (twice 4 mL). The solvent was removed *in vacuo* (≤ 0.05 mbar) yielding a yellow solid which was washed with twice 3 mL diethyl ether and three times 3 mL *n*-pentane. After drying for 2 h (≤ 0.02 mbar) the product mixture was obtained as yellow solid and analysed by NMR spectroscopy.

Reaction code: TT-827 (TAT231016p5a002, TAT231006m3a023)

Molecular formula: C₂₄H₄₀N₄P₂Se₂

Molecular weight: 762.44 g mol⁻¹

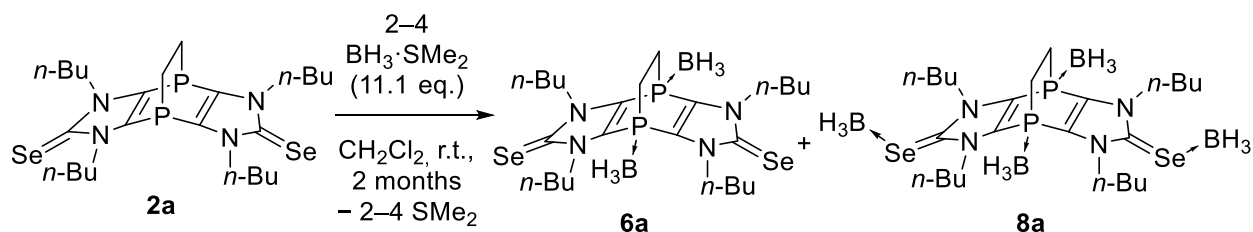
Content in mixture: 12 % (³¹P NMR integration of isolated reaction mixture)

³¹P NMR (202.44 MHz, 298.0 K, CD₂Cl₂): δ / ppm = -22.1 (br *s*_{sat}, ¹*J*_{Se,P} = 856 Hz, ³*J*_{P,P} = 49 Hz).

³¹P{¹H} NMR (202.44 MHz, 298.0 K, CD₂Cl₂): δ / ppm = -21.8 (d, ¹*J*_{Se,P} = 856 Hz).

⁷⁷Se NMR (57.24 MHz, 298.0 K, CD₂Cl₂): δ / ppm = -438.2 (d, ¹*J*_{Se,P} = 856 Hz, PSe), 43.6 (s, CSe).

5.5.4 Generation of (1,3,5,7-tetrabutyl-1,3,5,7-tetrahydro-2*H*,6*H*-4,8-ethano[1,4]diphosphinino[2,3-*d*:5,6-*d'*]diimidazole-2,6-diselone- $\kappa P^1, \kappa P^2$)bis(borane) and (1,3,5,7-tetrabutyl-1,3,5,7-tetrahydro-2*H*,6*H*-4,8-ethano[1,4]diphosphinino[2,3-*d*:5,6-*d'*]diimidazole-2,6-diselone- $\kappa P^1, \kappa P^2, \kappa Se^1, \kappa Se^2$)tetrakis(borane) 6a and 8a



Synthesis

To a solution of 0.112 g (0.19 mmol, 1.0 eq.) of **2a** in 3 mL dichloromethane in a 15 mL Schlenk tube 0.20 mL (2.11 mmol, 11.1 eq.) BH₃·SMe₂ were added and the reaction solution was stirred at ambient temperature while the reaction course was monitored via ³¹P{¹H} NMR spectroscopy. After 2 months no change in the composition of the reaction mixture was observed anymore and the solvent was removed *in vacuo* (≤ 0.05 mbar). The resulting yellow residue was washed with three times 3 mL *n*-pentane and after drying for 2 h (≤ 0.02 mbar) the product mixture was obtained as light yellow solid and analysed by NMR spectroscopy and SCXRD.

Reaction code: TT-893 (TAT231020p5a056, TAT231025m3a036)

Molecular formula: C₂₄H₄₆B₂N₄P₂Se₂ (**6a**), C₂₄H₅₂B₄N₄P₂Se₂ (**8a**)

Molecular weight: 632.17 g mol⁻¹ (**6a**), 659.84 g mol⁻¹ (**8a**)

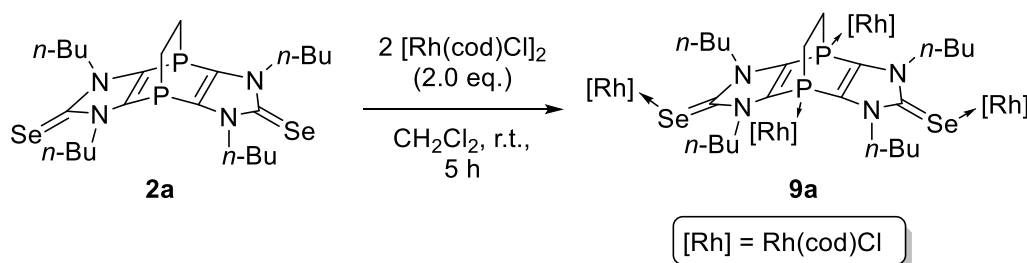
Content in mixture: 60 % (**6a**), 2 % (**8a**) (³¹P NMR integration of isolated reaction mixture)

³¹P NMR (202.44 MHz, 298.0 K, CD₂Cl₂): δ / ppm = -17.8 (br s, **6a**), -17.3 (br s, **8a**).

³¹P{¹H} NMR (202.44 MHz, 298.0 K, CD₂Cl₂): δ / ppm = -17.8 (s, **6a**), -17.3 (s, **8a**).

X-ray diffraction analysis: GXraycu_7878f (GSTR830)(**6a**), very good structure (AB3)

5.5.5 Synthesis of [tetrachlorido(μ-1,3,5,7-tetrabutyl-1,3,5,7-tetrahydro-2*H*,6*H*-4,8-ethano[1,4]diphosphinino[2,3-*d*:5,6-*d'*]diimidazole-2,6-diselone-κ*P*¹,κ*P*²,κ*Se*¹,κ*Se*²)tetrakis(η²,η²-cycloocta-1,5-diene)tetrarhodium(I)] **9a**



Synthesis

In a 20 mL Schlenk tube 0.120 g (0.20 mmol, 1.0 eq.) of **2a** and 0.195 g (0.40 mmol, 2.0 eq.) [Rh(cod)Cl]₂ were dissolved in 6 mL dichloromethane and stirred for 5 h at ambient temperature. The solvent was removed *in vacuo* (≤ 0.05 mbar) and the resulting yellow solid was extracted with three times 2–5 mL toluene. After evaporation of the solvent the oily residue was washed with six times 4–5 mL diethyl ether, three times with 5 mL *n*-pentane, and then dried for 3 h (≤ 0.02 mbar) yielding a yellow solid.

Reaction code: TT-808 (TAT230522p5a004, TAT230522m3a022)

Molecular formula: C₅₆H₈₈Cl₄N₄P₂Rh₄Se₂

Molecular weight: 1590.66 g mol⁻¹

Yield: 0.229 g (0.14 mmol, 73 %)

Melting point: 231 °C (dec.)

EA: calculated (%)	C 42.29	H 5.58	N 3.52
found (%)	C 42.13	H 5.77	N 3.56

MS (pos. ESI): m/z (%) = 1555.009 (25) $[M-Cl]^+$, 1309.041 (86) $[M-[Rh(cod)Cl]-Cl]^+$, 1063.073 (66), $[M-2[Rh(cod)Cl]-Cl]^+$.

HRMS (pos. ESI): m/z calculated for $[C_{56}H_{88}Cl_3N_4P_2Rh_4Se_2]^+$: 1555.0088; found: 1555.0093.

IR (ATR): $\tilde{\nu}$ / cm^{-1} = 2997 (m, $\nu_{as}(CH_3)$, $\nu_s(CH_2)$), 2956 (m, $\nu_{as}(CH_3)$, $\nu_s(CH_2)$), 2872 (m, $\nu_s(CH_3)$, $\nu_{as}(CH_2)$), 2830 (w, $\nu_s(CH_3)$, $\nu_{as}(CH_2)$).

^1H NMR (500.04 MHz, 298.0 K, C_6D_6): δ / ppm = 1.17 (t, $^3J_{H,H} = 7.4$ Hz, 12H, CH_3), 1.45–1.57 (m, $^3J_{H,H} = 7.4$ Hz, 8H, CH_2CH_3), 1.58–1.62 (m, 4H, PCH_2), 1.64–1.79 (m, 16H, CH_2CH_3 , CH_2CH), 2.05–2.15 (m, 4H, CH_2CH), 2.15–2.35 (m, 16H, NCH_2CH_2 , CH_2CH), 2.46–2.59 (m, 4H, CH_2CH), 3.94 (m, 4H, CH), 4.20 (m, 4H, CH), 4.82 (m, 4H, CH), 5.50 (td, $^3J_{H,H} = 12.5$ Hz, $^4J_{P,H} = 5.1$ Hz, 4H, NCH_2), 5.83 (m, 4H, CH), 5.98–6.09 (m, 4H, NCH_2).

$^{13}C\{^1H\}$ NMR (125.75 MHz, 298.0 K, C_6D_6): δ / ppm = 14.3 (s, CH_3), 17.8 (dd, $^1J_{Rh,C} = 19.3$ Hz, $^2J_{P,C} = 9.7$ Hz, PCH_2), 20.9 (br s, CH_2CH_3), 28.8 (s, CH_2CH), 30.8 (s, CH_2CH), 31.4 (m, NCH_2CH_2), 32.3 (s, CH_2CH), 33.3 (m, CH_2CH), 51.6 (br s, NCH_2), 72.7–73.0 (m, CH), 83.1–83.3 (m, CH), 109.7–110.0 (m, CH), 132.3 (d, $^2J_{Rh,C} = 58.2$ Hz, PC), 158.6 (s_{sat} , $^1J_{Se,C} = 209$ Hz, CSe).

^{31}P NMR (202.44 MHz, 298.0 K, C_6D_6): δ / ppm = -21.8 (dm, $^1J_{Rh,P} = 166.7$ Hz).

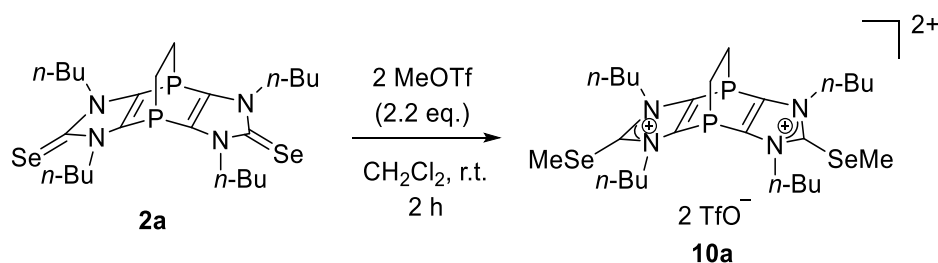
$^{31}P\{^1H\}$ NMR (202.44 MHz, 298.0 K, C_6D_6): δ / ppm = -21.8 (d, $^1J_{Rh,P} = 166.7$ Hz).

^{77}Se NMR (57.24 MHz, 298.0 K, C_6D_6): δ / ppm = 167.8 (d, $^1J_{Rh,Se} = 21.4$ Hz).

X-ray diffraction analysis: Gxray7481 (GSTR816), good structure (BC1)

5.5.6 Synthesis of Se-methylated bis(imidazolium) salts 10

5.5.6.1 Synthesis of 1,3,5,7-tetrabutyl-1,5-dihydro-4,8-ethano[1,4]diphosphinino[2,3-d:5,6-d']di-2,6-bis(methylseleno)imidazolium bis(trifluoromethanesulfonate) **10a**



Synthesis

In a 20 mL Schlenk tube 0.11 mL (1.02 mmol, 2.2 eq.) MeOTf were added dropwise to a solution of 0.281 g (0.47 mmol, 1.0 eq.) of **2a** in 5 mL dichloromethane. After stirring for 2 h at ambient temperature the former orange solution had turned light yellow and the solvent was removed *in vacuo*

(≤ 0.05 mbar). The resulting light yellow, oily residue was washed with twice 5 mL *n*-pentane and dried for 2 h (≤ 0.02 mbar) yielding a colourless solid.

Reaction code: TT-782 (TAT230502p5a006, TAT230502m3a045)

Molecular formula: $C_{28}H_{46}F_6N_4O_6P_2S_2Se_2$

Molecular weight: 932.70 g mol⁻¹

Yield: 0.401 g (0.44 mmol, 95 %)

Melting point: 102 °C

EA: calculated (%)	C 36.06	H 4.97	N 6.01	S 6.87
found (%)	C 35.61	H 5.01	N 5.88	S 7.56

MS (pos. ESI): m/z (%) = 785.106 (100) [M-OTf]⁺, 318.077 (68) [M-2OTf]²⁺.

HRMS (pos. ESI): m/z calculated for $[C_{27}H_{46}F_3N_4O_3P_2S_2Se_2]^+$: 785.1045; found: 785.1041.

IR (ATR): $\tilde{\nu}$ / cm⁻¹ = 2963 (m, $\nu_{as}(CH_3)$, $\nu_s(CH_2)$), 2938 (m, $\nu_{as}(CH_3)$, $\nu_s(CH_2)$), 2878 (m, $\nu_s(CH_3)$, $\nu_{as}(CH_2)$).

¹H NMR (500.04 MHz, 298.0 K, CDCl₃): δ / ppm = 0.93–1.06 (m, 12H, $CH_3(n-Bu)$), 1.40–1.52 (m, 8H, CH_2CH_3), 1.77–1.88 (m, 8H, CH_2CH_3), 2.13–2.18 (m, 4H, PCH_2), 2.45–2.49 (m, 6H, $SeCH_3$), 4.40–4.54 (m, 8H, NCH_2).

¹³C{¹H} NMR (125.75 MHz, 298.0 K, CDCl₃): δ / ppm = 11.2 (s_{sat} , $^1J_{Se,C}$ = 56.9 Hz, $SeCH_3$), 13.7 (s, $CH_3(n-Bu)$), 18.8 (dd, $J_{P,C}$ = 5.6 Hz, PCH_2), 20.3 (m, CH_2CH_3), 33.7 (m, NCH_2CH_2), 51.0 (m, NCH_2), 120.9 (q, $^1J_{F,C}$ = 322 Hz, CF_3), 138.2 (s_{sat} , $^1J_{Se,C}$ = 181 Hz, $CSeCH_3$), 143.2 (dd, $J_{P,C}$ = 9.8 Hz, $J_{P,C}$ = 7.0 Hz, PC).

³¹P NMR (202.44 MHz, 298.0 K, CDCl₃): δ / ppm = -94.5 (m).

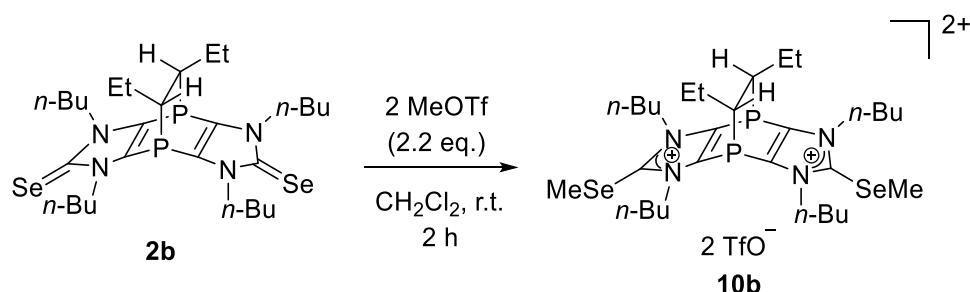
³¹P{¹H} NMR (202.44 MHz, 298.0 K, CDCl₃): δ / ppm = -94.5 (s).

⁷⁷Se NMR (57.24 MHz, 298.0 K, CDCl₃): δ / ppm = 115.8 (s).

X-ray diffraction analysis: Gxray7475 (GSTR829), bad structure (D1)

5.5.6.2 Synthesis of 1,3,5,7-tetrabutyl-9,10-diethyl-1,5-dihydro-4,8-ethano[1,4]diphosphinino[2,3-d:5,6-d']di-2,6-bis(methylseleno)imidazolium bis(trifluoromethanesulfonate)

10b



Synthesis

In a 100 mL Schlenk tube 0.44 mL (4.00 mmol, 2.2 eq.) MeOTf were added dropwise to a solution of 1.202 g (1.82 mmol, 1.0 eq.) of **2b** in 25 mL dichloromethane. After stirring for 2 h at ambient temperature the former light red solution had turned yellow and the solvent was removed *in vacuo* (≤ 0.05 mbar). The resulting oily residue was washed three times with 10–20 mL diethyl ether each and three times 20 mL *n*-pentane at -50 °C. After drying for 3 h (≤ 0.02 mbar) a yellow, sticky solid was obtained.

Reaction code: TT-668 (48p5a023.22, 48m3a017.22)

Molecular formula: C₃₂H₅₄F₆N₄O₆P₂S₂Se₂

Molecular weight: 988.81 g mol⁻¹

Yield: 1.349 g (1.36 mmol, 75 %)

Melting point: ca. -20 °C

MS (pos. ESI): m/z (%) = 841.166 (100) [M-OTf]⁺, 346.107 (41) [M-2OTf]²⁺, 304.060 (45) [M-C₆H₁₂-2OTf]²⁺.

HRMS (pos. ESI): m/z calculated [C₃₁H₅₄F₃N₄O₂P₂SSe₂]⁺: 841.1674; found: 841.1677.

IR (ATR): $\tilde{\nu}$ / cm⁻¹ = 2962 (m, $\nu_{\text{as}}(\text{CH}_3)$, $\nu_{\text{s}}(\text{CH}_2)$), 2935 (m, $\nu_{\text{as}}(\text{CH}_3)$, $\nu_{\text{s}}(\text{CH}_2)$), 2876 (m, $\nu_{\text{s}}(\text{CH}_3)$, $\nu_{\text{as}}(\text{CH}_2)$).

¹H NMR (500.04 MHz, 298.0 K, CD₂Cl₂): δ / ppm = 1.01 (tm, $^3J_{\text{H,H}} = 7.4$ Hz, 12H, CH₃(*n*-Bu)), 1.18 (t, $^3J_{\text{H,H}} = 7.3$ Hz, 6H, CH₃(Et)), 1.30–1.35 (m, 2H, PCHCH₂), 1.40–1.54 (m, 8H, NCH₂CH₂CH₂), 1.63–1.74 (m, 2H, PCHCH₂), 1.76–1.92 (m, 10H, NCH₂CH₂, PCH), 2.48 (s, 6H, SeCH₃), 4.36–4.59 (m, 8H, NCH₂).

¹³C{¹H} NMR (125.75 MHz, 298.0 K, CD₂Cl₂): δ / ppm = 11.2 (s_{sat}, $^1J_{\text{Se,C}} = 56.1$ Hz, SeCH₃), 13.7 (s, CH₃(*n*-Bu)), 13.8 (s, CH₃(*n*-Bu)), 13.9 (dd, $J_{\text{P,C}} = 7.3$ Hz, CH₃(Et)), 20.2 (m, NCH₂CH₂CH₂), 27.9 (dd, $J_{\text{P,C}} = 9.4$ Hz, PCHCH₂), 33.7 (dd, $J_{\text{P,C}} = 2.0$ Hz, NCH₂CH₂), 33.9 (dd, $J_{\text{P,C}} = 2.0$ Hz, NCH₂CH₂), 45.1 (dd, $J_{\text{P,C}} = 5.2$ Hz, PCH),

51.1 (dm, $J_{P,C} = 29.8$ Hz, NCH_2), 121.0 (q, $^1J_{F,C} = 320.8$ Hz, CF_3), 138.9 (s_{sat} , $^1J_{Se,C} = 181$ Hz, $CSeCH_3$), 142.3 (m, PC), 145.6 (dd, $J_{P,C} = 8.9$ Hz, $J_{P,C} = 6.5$ Hz, PC).

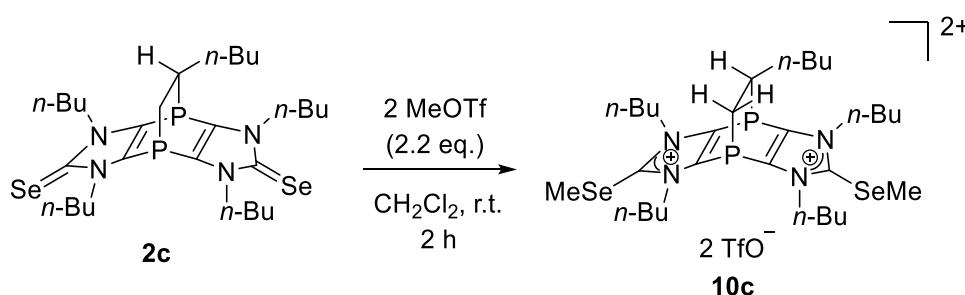
^{31}P NMR (202.44 MHz, 298.0 K, CD_2Cl_2): δ / ppm = -87.0 (m).

$^{31}P\{^1H\}$ NMR (202.44 MHz, 298.0 K, CD_2Cl_2): δ / ppm = -87.0 (s).

^{77}Se NMR (57.24 MHz, 298.0 K, CD_2Cl_2): δ / ppm = 105.8 (s).

5.5.6.3 Synthesis of 1,3,5,7-tetrabutyl-9-butyl-1,5-dihydro-4,8-ethano[1,4]diphosphino[2,3-d:5,6-d']di-2,6-bis(methylseleno)imidazolium bis(trifluoromethanesulfonate)

10c



Synthesis

In a 50 mL Schlenk tube 0.18 mL (1.67 mmol, 2.2 eq.) MeOTf were added dropwise to a solution of 0.500 g (0.76 mmol, 1.0 eq.) of **2c** in 15 mL dichloromethane. After stirring for 2 h at ambient temperature the former dark yellow solution had turned light yellow and the solvent was removed *in vacuo* (≤ 0.05 mbar). The resulting oily residue was washed three times with 5 mL diethyl ether each and three times with 5 mL *n*-pentane each. After drying for 3 h (≤ 0.02 mbar) a light yellow, sticky solid was obtained.

Reaction code: TT-430 (30m3c024.21), TT-689

Molecular formula: $C_{32}H_{54}F_6N_4O_6P_2S_2Se_2$

Molecular weight: $988.81 \text{ g mol}^{-1}$

Yield: 0.141 g (0.14 mmol, 62 %)

Melting point: ca. $-20^\circ C$

MS (pos. ESI): m/z (%) = 841.172 (100) $[M-OTf]^+$, 346.110 (88) $[M-2OTf]^{2+}$, 304.062 (92) $[M-C_6H_{12}-2OTf]^{2+}$.

MS (neg. ESI): m/z (%) = 149.0 (100) $[OTf]^-$.

HRMS (pos. ESI): m/z calculated $[\text{C}_{31}\text{H}_{54}\text{F}_3\text{N}_4\text{O}_2\text{P}_2\text{SSe}_2]^+$: 841.1674; found: 841.1673.

IR (ATR): $\tilde{\nu} / \text{cm}^{-1}$ = 2961 (m, $\nu_{\text{as}}(\text{CH}_3)$, $\nu_{\text{s}}(\text{CH}_2)$), 2934 (m, $\nu_{\text{as}}(\text{CH}_3)$, $\nu_{\text{s}}(\text{CH}_2)$), 2874 (m, $\nu_{\text{s}}(\text{CH}_3)$, $\nu_{\text{as}}(\text{CH}_2)$).

^1H NMR (300.13 MHz, 298.0 K, CD_2Cl_2): δ / ppm = 0.90 (t, $^3J_{\text{H,H}} = 7.3$ Hz, 3H, $\text{CH}_3(\text{PCH}(n\text{-Bu}))$), 0.96–1.07 (m, 12H, $\text{CH}_3(\text{N}(n\text{-Bu}))$), 1.24–1.40 (m, 5H, PCH_2 , $\text{PCHCH}_2\text{CH}_2\text{CH}_2$), 1.40–1.60 (m, 10H, PCHCH_2 , $\text{NCH}_2\text{CH}_2\text{CH}_2$), 1.75–1.93 (m, 8H, NCH_2CH_2), 2.33–2.46 (m, 1H, PCH), 2.55–2.74 (m, 1H, PCH_2), 2.47 (s, 3H, SeCH_3), 2.49 (s, 3H, SeCH_3), 4.36–4.60 (m, 8H, NCH_2).

$^{13}\text{C}\{^1\text{H}\}$ NMR (75.48 MHz, 298.0 K, CD_2Cl_2): δ / ppm = 11.1 (s, SeCH_3), 11.3 (s, SeCH_3), 13.7 (br s, $\text{CH}_3(\text{N}(n\text{-Bu}))$), 14.0 (s, $\text{CH}_3(\text{PCH}(n\text{-Bu}))$), 20.3 (m, $\text{NCH}_2\text{CH}_2\text{CH}_2$), 22.7 (s, $\text{PCHCH}_2\text{CH}_2\text{CH}_2$), 26.4 (m, PCH_2), 31.5 (d, $J_{\text{P,C}} = 15.3$ Hz, $\text{PCHCH}_2\text{CH}_2$), 33.7 (m, NCH_2CH_2), 34.1 (d, $J_{\text{P,C}} = 2.6$ Hz, PCHCH_2), 35.3 (m, PCH), 50.9–51.2 (m, NCH_2), 120.9 (q, $^1J_{\text{F,C}} = 320.8$ Hz, CF_3), 138.3 (m, CSeCH_3), 138.4 (m, CSeCH_3), 141.9 (dd, $J_{\text{P,C}} = 19.4$ Hz, $J_{\text{P,C}} = 3.5$ Hz, PC), 142.1 (dd, $J_{\text{P,C}} = 13.2$ Hz, $J_{\text{P,C}} = 3.5$ Hz, PC), 144.9–145.2 (m, PC).

^{31}P NMR (121.51 MHz, 298.0 K, CD_2Cl_2): δ / ppm = -91.2 (m, PCH_2), -87.0 (m, PCH).

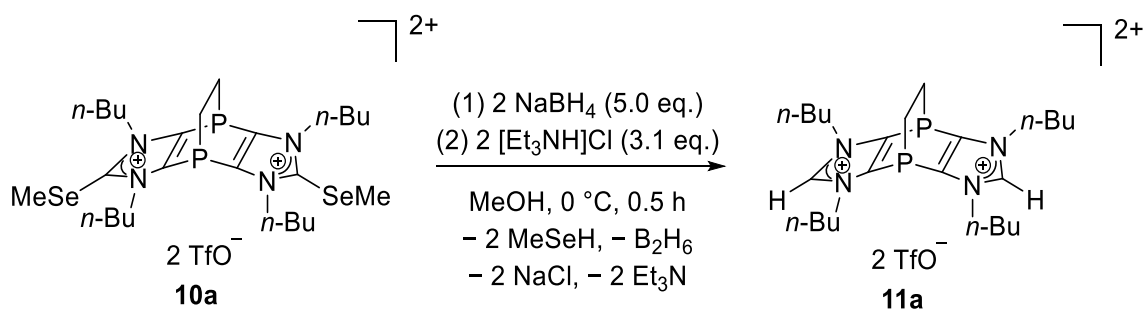
$^{31}\text{P}\{^1\text{H}\}$ NMR (121.51 MHz, 298.0 K, CD_2Cl_2): δ / ppm = -91.2 (d, $^3J_{\text{P,P}} = 16.7$ Hz, PCH_2), -87.0 (d, $^3J_{\text{P,P}} = 16.7$ Hz, PCH).

^{77}Se NMR (57.24 MHz, 298.0 K, CD_2Cl_2): δ / ppm = 102.8 (s), 103.5 (s).

X-ray diffraction analysis: Gxray6752 (GSTR472), very bad structure (E1)

5.5.7 Synthesis of bis(imidazolium) salts 11

5.5.7.1 Synthesis of 1,3,5,7-tetrabutyl-1,5-dihydro-4,8-ethano[1,4]diphosphinino[2,3-d:5,6-d']diimidazolium bis(trifluoromethanesulfonate) **11a**



Synthesis

In a 50 mL Schlenk tube 0.315 g (8.10 mmol, 5.0 eq.) NaBH_4 were added to a solution of 1.511 g (1.62 mmol, 1.0 eq.) of **10a** in 16 mL methanol at -20°C which resulted in a darkening of the yellow solution and gas formation (MeSeH). After stirring for 20 min the gas evolution had stopped and 0.691 g (5.02 mmol, 3.1 eq.) $[\text{Et}_3\text{NH}]\text{Cl}$ were added. The suspension was let warm up to ambient

temperature and the solvent was removed *in vacuo* (≤ 0.05 mbar). The resulting yellow, oily residue was filtered over a bed of celite® and silica (d = 2 cm, h = 1 cm each) with 120 mL tetrahydrofuran. After solvent removal *in vacuo* (≤ 0.05 mbar), extraction with three times 5–10 mL dichloromethane, followed by solvent evaporation, the light-yellow residue was washed with three times 10 mL *n*-pentane at -40 °C and dried for 3 h (≤ 0.02 mbar) yielding a sticky, beige solid.

Reaction code: TT-809 (TAT230517p5a034)

Molecular formula: C₂₆H₄₂F₆N₄O₆P₂S₂

Molecular weight: 746.70 g mol⁻¹

Yield: 0.805 g (1.08 mmol, 67 %)

Melting point: 121 °C

MS (pos. ESI): m/z (%) = 597.239 (100) [M-OTf]⁺, 210.128 (17) [M-2OTf-C₂H₄]²⁺,

HRMS (pos. ESI): m/z calculated for [C₂₇H₄₆F₃N₄O₃P₂S]⁺: 597.2399; found: 597.2396.

IR (ATR): $\tilde{\nu}$ / cm⁻¹ = 3110 (w, ν (CH)), 3040 (w, ν (CH)), 2966 (w, ν_{as} (CH₃), ν_s (CH₂)), 2936 (w, ν_{as} (CH₃), ν_s (CH₂)).

¹H NMR (500.04 MHz, 298.0 K, CD₂Cl₂): δ / ppm = 0.97 (t, ³ $J_{H,H}$ = 7.4 Hz, 12H, CH₃), 1.35–1.44 (m, 8H, CH₂CH₃), 1.87 (tt, ³ $J_{H,H}$ = 8.8 Hz, ³ $J_{H,H}$ = 6.8 Hz, 8H, CH₂CH₃), 2.10 (t, $J_{P,H}$ = 5.4 Hz, 4H, PCH₂), 4.33 (t, ³ $J_{H,H}$ = 7.5 Hz, 8H, NCH₂), 8.93 (t, ⁴ $J_{P,H}$ = 3.0 Hz, CH).

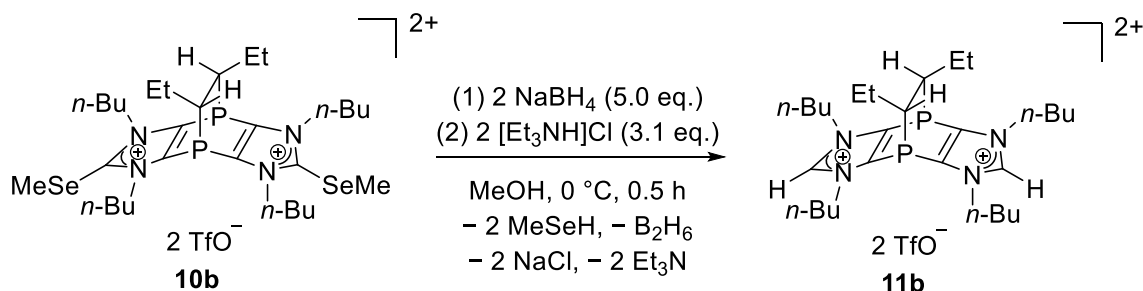
¹³C{¹H} NMR (125.75 MHz, 298.0 K, CD₂Cl₂): δ / ppm = 13.4 (s, CH₃), 18.8 (dd, $J_{P,C}$ = 5.6 Hz, PCH₂), 20.0 (m, CH₂CH₃), 33.0 (m, NCH₂CH₂), 49.9 (m, NCH₂), 121.0 (q, ¹ $J_{F,C}$ = 320.5 Hz, CF₃), 138.8 (s, CH), 141.9 (dd, $J_{P,C}$ = 9.5 Hz, $J_{P,C}$ = 7.0 Hz, PC).

³¹P NMR (202.44 MHz, 298.0 K, CD₂Cl₂): δ / ppm = -97.4 (m).

³¹P{¹H} NMR (202.44 MHz, 298.0 K, CD₂Cl₂): δ / ppm = -97.4 (s).

X-ray diffraction analysis: Gxray7479 (GSTR817), structural motif confirmed (E1)

5.5.7.2 Synthesis of 1,3,5,7-tetrabutyl-9,10-diethyl-1,5-dihydro-4,8-ethano[1,4]diphosphinino[2,3-d:5,6-d']diimidazolium bis(trifluoromethanesulfonate) **11b**



Synthesis

In a 100 mL Schlenk tube 0.194 g (5.13 mmol, 5.0 eq.) NaBH_4 were added to a solution of 1.016 g (1.03 mmol, 1.0 eq.) of **10b** in 20 mL methanol at $-20\text{ }^{\circ}\text{C}$ which resulted in a darkening of the yellow solution and gas formation (MeSeH). After stirring for 20 min the gas evolution had stopped and 0.438 g (3.18 mmol, 3.1 eq.) $[\text{Et}_3\text{NH}]\text{Cl}$ were added. The suspension was let warm up to ambient temperature and the solvent was removed *in vacuo* (≤ 0.05 mbar). The resulting yellow, oily residue was filtered over a bed of celite® and silica ($d = 4$ cm, $h = 1$ cm each) with 250 mL tetrahydrofuran. After solvent removal *in vacuo* (≤ 0.05 mbar), extraction with three times 5–10 mL dichloromethane, followed by solvent evaporation, the yellow residue was washed with three times 10 mL *n*-pentane at $-20\text{ }^{\circ}\text{C}$ and dried for 3 h (≤ 0.02 mbar) yielding a waxy, yellow solid.

Reaction code: TT-537 (10p5a029.22)

Molecular formula: $\text{C}_{30}\text{H}_{50}\text{F}_6\text{N}_4\text{O}_6\text{P}_2\text{S}_2$

Molecular weight: 802.81 g mol^{-1}

Yield: 0.540 g (0.673 mmol, 66 %)

Melting point: ca. $0\text{ }^{\circ}\text{C}$

MS (pos. ESI): m/z (%) = 53.304 (100) $[\text{M}-\text{OTf}]^+$, 252.176 (15) $[\text{M}-2\text{OTf}]^{2+}$, 210.129 (35) $[\text{M}-2\text{OTf}-\text{C}_6\text{H}_{12}]^{2+}$.

MS (neg. ESI): m/z (%) = 149.0 (100) $[\text{OTf}]^-$.

HRMS (pos. ESI): m/z calculated $[\text{C}_{29}\text{H}_{50}\text{F}_3\text{N}_4\text{O}_3\text{P}_2\text{S}]^+$: 653.3025; found: 653.3027.

IR (ATR): $\tilde{\nu} / \text{cm}^{-1}$ = 3113 (w, $\nu(\text{CH})$), 3043 (w, $\nu(\text{CH})$), 2963 (w, $\nu_{\text{as}}(\text{CH}_3)$, $\nu_{\text{s}}(\text{CH}_2)$), 2934 (w, $\nu_{\text{as}}(\text{CH}_3)$, $\nu_{\text{s}}(\text{CH}_2)$), 2874 (w, $\nu_{\text{s}}(\text{CH}_3)$, $\nu_{\text{as}}(\text{CH}_2)$).

^1H NMR (500.04 MHz, 298.0 K, CD_2Cl_2): δ / ppm = 0.93–1.01 (m, 12H, $\text{CH}_3(n\text{-Bu})$), 1.15 (t, $^3J_{\text{H,H}} = 7.2$ Hz, 6H, $\text{CH}_3(\text{Et})$), 1.24–1.33 (m, 2H, PCHCH_2), 1.30–1.46 (m, 8H, $\text{NCH}_2\text{CH}_2\text{CH}_2$), 1.57–1.66 (m, 2H, PCHCH_2),

1.66–1.73 (m, 2H, PCH), 1.81–1.91 (m, 8H, NCH₂CH₂), 4.24–4.32 (m, 4H, NCH₂), 4.32–4.42 (m, 4H, NCH₂), 9.03 (t, ⁴J_{P,H} = 2.9 Hz, CH).

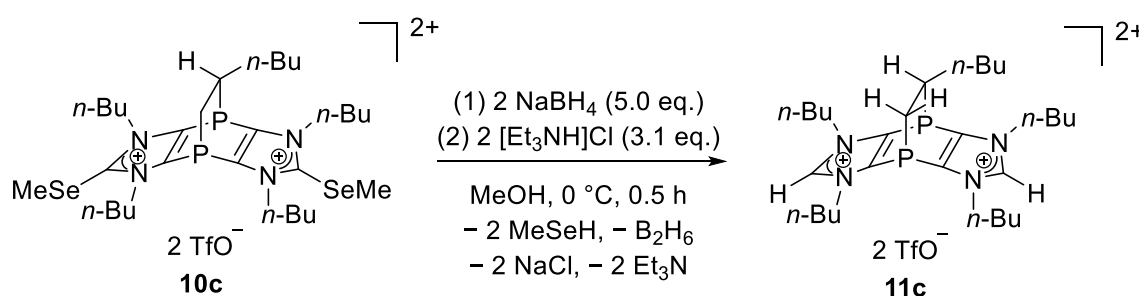
¹³C{¹H} NMR (125.75 MHz, 298.0 K, CD₂Cl₂): δ / ppm = 13.5 (s, CH₃(*n*-Bu)), 13.6 (s, CH₃(*n*-Bu)), 13.8 (m, CH₃(Et)), 19.9 (m, NCH₂CH₂CH₂), 20.0 (m, NCH₂CH₂CH₂), 28.0 (m, PCHCH₂), 33.0 (m, NCH₂CH₂), 33.2 (m, NCH₂CH₂), 45.1 (dd, J_{P,C} = 5.4 Hz, PCH), 50.0 (tm, J_{P,C} = 4.1 Hz, NCH₂), 121.0 (q, ¹J_{F,C} = 320.2 Hz, CF₃), 139.6 (s, CH), 141.1 (dd, J_{P,C} = 12.8 Hz, J_{P,C} = 8.1, PC), 143.9 (dd, J_{P,C} = 8.8 Hz, J_{P,C} = 6.6 Hz, PC).

³¹P NMR (202.44 MHz, 298.0 K, CD₂Cl₂): δ / ppm = -90.4 (m).

³¹P{¹H} NMR (202.44 MHz, 298.0 K, CD₂Cl₂): δ / ppm = -90.4 (s).

X-ray diffraction analysis: Gxray6856 (GSTR757), moderate structure (CD1)

5.5.7.3 Synthesis of 1,3,5,7-tetrabutyl-9-butyl-1,5-dihydro-4,8-ethano[1,4]diphosphinino[2,3-d:5,6-d']diimidazolium bis(trifluoromethanesulfonate) **11c**



Synthesis

In a 50 mL Schlenk tube 0.108 g (2.84 mmol, 5.0 eq.) NaBH₄ were added to a solution of 0.563 g (0.57 mmol, 1.0 eq.) of **10c** in 9 mL methanol at -20 °C which resulted in a darkening of the yellow solution and gas formation (MeSeH). After stirring for 20 min the gas evolution had stopped and 0.243 g (1.76 mmol, 3.1 eq.) [Et₃NH]Cl were added. The suspension was let warm up to ambient temperature and the solvent was removed *in vacuo* (≤ 0.05 mbar). The resulting light yellow, oily residue was filtered over a bed of celite® and silica (d = 2 cm, h = 1 cm each) with 100 mL tetrahydrofuran. After solvent removal *in vacuo* (≤ 0.05 mbar), extraction with three times 5–10 mL dichloromethane, followed by solvent evaporation, the light-yellow residue was washed with five times 8 mL *n*-pentane at -20 °C and dried for 2 h (≤ 0.02 mbar) yielding a sticky, beige solid.

Reaction code: TT-498 (03p5a024.22), TT-691

Molecular formula: C₃₀H₅₀F₆N₄O₆P₂S₂

Molecular weight: 802.81 g mol⁻¹

Yield: 0.207 g (0.26 mmol, 46 %)

Melting point: 50 °C

MS (pos. ESI): m/z (%) = 653.301 (100) $[M-OTf]^+$, 252.174 (55) $[M-2OTf]^{2+}$, 210.128 (39) $[M-2OTf-C_6H_{12}]^{2+}$.

MS (neg. ESI): m/z (%) = 149.0 (100) $[OTf]^-$.

HRMS (pos. ESI): m/z calculated $[C_{29}H_{50}F_3N_4O_2P_2S]^+$: 653.3025; found: 653.3029.

IR (ATR): $\tilde{\nu}$ / cm^{-1} = 3117 (w, $\nu(CH)$), 3042 (w, $\nu(CH)$), 2962 (w, $\nu_{as}(CH_3)$, $\nu_s(CH_2)$), 2934 (w, $\nu_{as}(CH_3)$, $\nu_s(CH_2)$), 2875 (w, $\nu_s(CH_3)$, $\nu_{as}(CH_2)$).

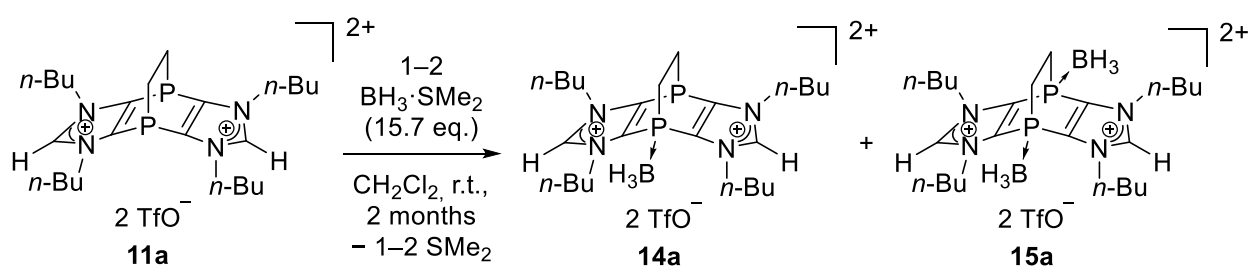
^1H NMR (500.04 MHz, 298.0 K, CD_2Cl_2): δ / ppm = 0.90 (t, $^3J_{H,H} = 7.3$ Hz, 3H, $CH_3(PCH(n-Bu))$), 0.93–1.01 (m, 12H, $CH_3(N(n-Bu))$), 1.26–1.34 (m, 4H, $PCHCH_2CH_2CH_2$), 1.34–1.42 (m, 8H, $NCH_2CH_2CH_2$), 1.42–1.56 (m, 3H, $PCHCH_2$, PCH_2), 1.79–1.92 (m, 8H, NCH_2CH_2), 2.27–2.37 (m, 1H, PCH), 2.45–2.56 (m, 1H, PCH_2), 4.26–4.42 (m, 8H, NCH_2), 8.88 (dd, $^4J_{P,H} = 3.0$ Hz, CH), 9.06 (dd, $^4J_{P,H} = 2.9$ Hz).

$^{13}C\{^1H\}$ NMR (125.75 MHz, 298.0 K, CD_2Cl_2): δ / ppm = 13.5 (s, $CH_3(N(n-Bu))$), 13.9 (s, $CH_3(PCH(n-Bu))$), 20.0 (m, $NCH_2CH_2CH_2$), 22.7 (s, $PCHCH_2CH_2CH_2$), 26.5 (dd, $J_{P,C} = 10.1$ Hz, $J_{P,C} = 3.5$ Hz, PCH_2), 31.5 (d, $J_{P,C} = 15.6$ Hz, $PCHCH_2CH_2$), 33.1 (m, NCH_2CH_2), 35.1 (d, $J_{P,C} = 16.3$ Hz, $PCHCH_2$), 35.4 (dd, $J_{P,C} = 7.2$ Hz, $J_{P,C} = 1.9$ Hz, PCH), 50.0 (m, NCH_2), 120.8 (q, $^1J_{F,C} = 320.1$ Hz, CF_3), 138.8 (s, CH), 139.4 (s, CH), 140.4 (dd, $J_{P,C} = 17.8$ Hz, $J_{P,C} = 4.3$ Hz, PC), 141.6 (dd, $J_{P,C} = 12.4$ Hz, $J_{P,C} = 4.0$ Hz, PC), 143.3 (dd, $J_{P,C} = 12.2$ Hz, $J_{P,C} = 4.0$ Hz, PC), 143.7 (dd, $J_{P,C} = 11.4$ Hz, $J_{P,C} = 4.7$ Hz, PC).

^{31}P NMR (202.44 MHz, 298.0 K, CD_2Cl_2): δ / ppm = -94.4 (m, PCH_2), -91.0 (m, PCH).

$^{31}P\{^1H\}$ NMR (202.44 MHz, 298.0 K, CD_2Cl_2): δ / ppm = -94.4 (d, $^3J_{P,P} = 16.0$ Hz, PCH_2), -91.0 (d, $^3J_{P,P} = 16.0$ Hz, PCH).

5.5.8 Generation of (1,3,5,7-tetrabutyl-1,5-dihydro-4,8-ethano[1,4]diphosphinino[2,3-d:5,6-d']diimidazolium- κP^1)borane bis(trifluoromethanesulfonate) and (1,3,5,7-tetrabutyl-1,5-dihydro-4,8-ethano[1,4]diphosphinino[2,3-d:5,6-d']diimidazolium- $\kappa P^1, \kappa P^2$)bis(borane) bis(trifluoromethanesulfonate) 14a and 15a



Synthesis

In a 20 mL Schlenk tube 0.20 mL (2.11 mmol, 15.7 eq.) $\text{BH}_3\cdot\text{SMe}_2$ were added to a solution of 0.100 g (0.13 mmol, 1.0 eq.) of **11a** in 2.5 mL dichloromethane and the reaction solution was stirred at ambient temperature while the reaction course was monitored via $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. After 2 months no change in the composition of the reaction mixture was observed anymore and the solvent was removed *in vacuo* (≤ 0.05 mbar). The resulting colourless residue was washed with three times 3 mL *n*-pentane and after drying for 2 h (≤ 0.02 mbar) the product mixture was obtained as slightly sticky, colourless solid and analysed by NMR spectroscopy and SCXRD.

Reaction code: TT-894 (TAT231020p5a055)

Molecular formula: $\text{C}_{26}\text{H}_{45}\text{BF}_6\text{N}_4\text{O}_6\text{P}_2\text{S}_2$ (**14a**), $\text{C}_{26}\text{H}_{48}\text{B}_2\text{F}_6\text{N}_4\text{O}_6\text{P}_2\text{S}_2$ (**15a**)

Molecular weight: 760.54 g mol⁻¹ (**14a**), 774.37 g mol⁻¹ (**15a**)

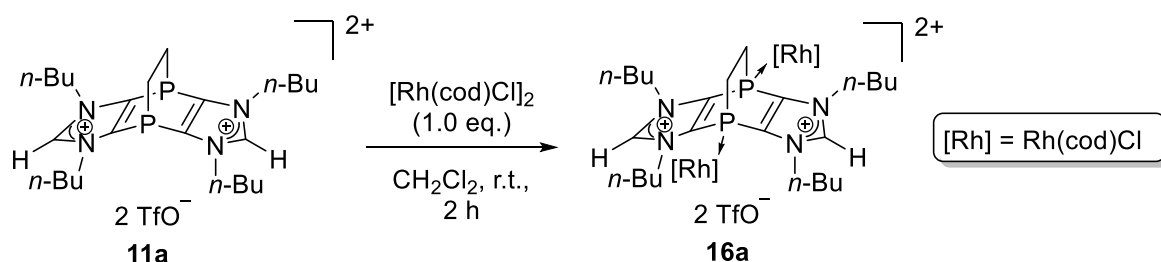
Content in mixture: 68 % (**14a**), 3 % (**15a**) (^{31}P NMR integration of isolated reaction mixture)

^{31}P NMR (202.50 MHz, 298.0 K, CD_2Cl_2): δ / ppm = -98.1 (br s, **14a**), -13.3 (br s, **14a**), -14.7 (br s, **15a**).

$^{31}\text{P}\{^1\text{H}\}$ NMR (202.50 MHz, 298.0 K, CD_2Cl_2): δ / ppm = -98.1 (d, $^3J_{\text{P,P}} = 5.8$ Hz, **14a**), -13.3 (br s, **14a**), -14.7 (br s, **15a**).

X-ray diffraction analysis: Gxray7904 (GSTR832)(**14a**), moderate structure (CD1)

5.5.9 Synthesis of [dichlorido(μ -1,3,5,7-tetrabutyl-1,5-dihydro-4,8-ethano[1,4]diphosphinino[2,3-d:5,6-d']diimidazolium- $\kappa\text{P}^1, \kappa\text{P}^2$)bis(η^2, η^2 -cycloocta-1,5-diene)dirhodium(I)] bis(trifluoromethanesulfonate) **16a**



Synthesis

In a 20 mL Schlenk tube 0.079 g (0.11 mmol, 1.0 eq.) of **11a** and 0.052 g (0.11 mmol, 1.0 eq.) $[\text{Rh}(\text{cod})\text{Cl}]_2$ were dissolved in 4 mL dichloromethane and stirred for 2 h at ambient temperature yielding a yellow suspension. The solvent was removed *in vacuo* (≤ 0.05 mbar) and the resulting yellow solid was washed with three times a mixture of 2 mL toluene and 2 mL *n*-pentane each, twice 2 mL diethyl ether and three times 3–4 mL *n*-pentane and dried for 2 h (≤ 0.02 mbar) yielding a yellow solid.

Reaction code: TT-808 (TAT230802p5a041)

Molecular formula: C₄₂H₆₆Cl₂F₆N₄O₆P₂Rh₂S₂

Molecular weight: 1239.78 g mol⁻¹

Yield: 0.092 g (0.07 mmol, 67 %)

Melting point: > 250 °C

EA: calculated (%)	C 40.69	H 5.37	N 4.52	S 5.17
found (%)	C 40.76	H 5.37	N 4.37	S 5.32

MS (pos. ESI): m/z (%) = 1089.1775 (4) [M-OTf]⁺, 843.2086 (21) [M-[Rh(cod)Cl]-OTf]⁺, 597.2401 (100) [M-2[Rh(cod)Cl]-OTf]⁺.

MS (neg. ESI): m/z (%) = 149.1 (100) [OTf]⁻.

HRMS (pos. ESI): m/z calculated for [C₄₁H₆₆Cl₂F₃N₄O₃P₂Rh₂S]⁺: 1089.1765; found: 1089.1775.

IR (ATR): $\tilde{\nu}$ / cm⁻¹ = 3112 (w, ν (CH)), 3042 (w, ν (CH)), 2964 (m, ν_{as} (CH₃), ν_s (CH₂)), 2878 (m, ν_s (CH₃)).

¹H NMR (499.96 MHz, 298.0 K, CD₂Cl₂): δ / ppm = 1.09 (t, ³J_{H,H} = 7.4 Hz, 12H, CH₃), 1.57–1.67 (m, 8H, CH₂CH₃), 2.05–2.16 (m, 12H, NCH₂CH₂, PCH₂), 2.30–2.39 (m, 8H, CH₂CH), 2.42–2.52 (m, 4H, CH₂CH), 2.53–2.63 (m, 4H, CH₂CH), 4.30–4.36 (m, 4H, CH₂CH), 4.93–5.01 (m, 4H, NCH₂), 5.61–5.69 (m, 4H, NCH₂), 5.84–5.89 (m, 4H, CH₂CH), 8.55 (t, ⁴J_{P,H} = 3.3 Hz, 2H, CH).

¹³C{¹H} NMR (125.73 MHz, 298.0 K, CD₂Cl₂): δ / ppm = 13.9 (s, CH₃), 17.8 (dd, ¹J_{Rh,C} = 20.3 Hz, ²J_{P,C} = 9.9 Hz, PCH₂), 20.5 (s, CH₂CH₃), 29.2 (s, CH₂CH), 32.1 (m, NCH₂CH₂), 33.3 (m, CH₂CH), 51.6 (d, ³J_{P,C} = 2.8 Hz, NCH₂), 74.5–74.7 (m, CH₂CH), 112.6–112.8 (m, CH₂CH), 121.0 (q, ¹J_{F,C} = 320.8 Hz, CF₃), 134.8 (d, ²J_{Rh,C} = 55.0 Hz, PC), 140.1 (t, ³J_{P,C} = 3.5 Hz, CH).

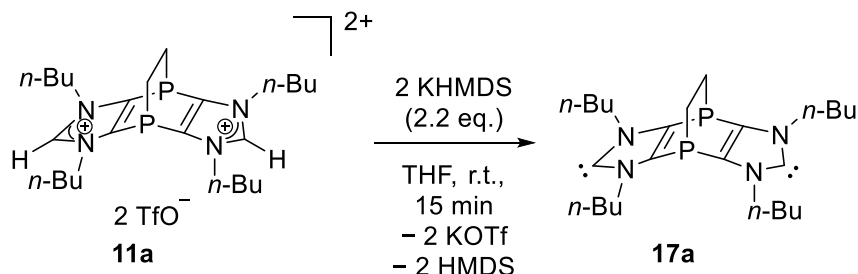
³¹P NMR (202.41 MHz, 298.0 K, CD₂Cl₂): δ / ppm = -24.7 (br d, ¹J_{Rh,P} = 167.8 Hz).

³¹P{¹H} NMR (202.41 MHz, 298.0 K, CD₂Cl₂): δ / ppm = -24.7 (dd, ¹J_{Rh,P} = 172 Hz, ⁴J_{Rh,P} = 3 Hz), -24.7 (dd, ¹J_{Rh,P} = 163 Hz, ⁴J_{Rh,P} = 4 Hz).

X-ray diffraction analysis: Gxraymo_7738_0m_4g (GSTR827), moderate structure (CD1)

5.5.10 Synthesis of bis(NHCs) **17**

5.5.10.1 Synthesis of 1,3,5,7-tetrabutyl-1,3,5,7-tetrahydro-2*H*,6*H*-4,8-ethano[1,4]diphosphino[2,3-*d*:5,6-*d'*]diimidazole-2,6-ylidene **17a**



Synthesis

In a 50 mL Schlenk tube 0.397 g (1.99 mmol, 2.2 eq.) KHMDS in 5 mL THF were added to a suspension of 0.675 g (0.90 mmol, 1.0 eq.) of **11a** in 15 mL THF via a transfer canula, resulting in an orange, slightly turbid solution. After stirring for 15 min at ambient temperature the solvent was removed *in vacuo* (≤ 0.05 mbar) at the same temperature. The resulting yellow solid mixed with an orange, oily residue was extracted with three times 5–7 mL toluene. After removal of the solvent *in vacuo* (≤ 0.05 mbar) at ambient temperature, washing with twice 10 mL *n*-pentane and drying for 4 h (≤ 0.02 mbar) a beige solid was obtained.

Reaction code: TT-810 (TAT230523p5a022)

Molecular formula: C₂₄H₄₀N₄P₂

Molecular weight: 446.56 g mol^{−1}

Yield: 0.141 g (0.32 mmol, 36 %)

Melting point: 104 °C (dec.)

EA: calculated (%) C 64.55 H 9.03 N 12.55

 found (%) C 63.44 H 8.96 N 12.37

MS (pos. APCI): m/z (%) = 483.300 (100) [M+2H₂O+H]⁺, 465.289 (31) [M+H₂O+H]⁺.

HRMS (pos. APCI): m/z calculated for [C₂₄H₄₃N₄P₂O]⁺: 465.2907; found: 465.2897.

IR (ATR): $\tilde{\nu}$ / cm^{−1} = 2957 (w, $\nu_{\text{as}}(\text{CH}_3)$, $\nu_{\text{s}}(\text{CH}_2)$), 2931 (w, $\nu_{\text{as}}(\text{CH}_3)$, $\nu_{\text{s}}(\text{CH}_2)$), 2871 (m, $\nu_{\text{s}}(\text{CH}_3)$, $\nu_{\text{as}}(\text{CH}_2)$).

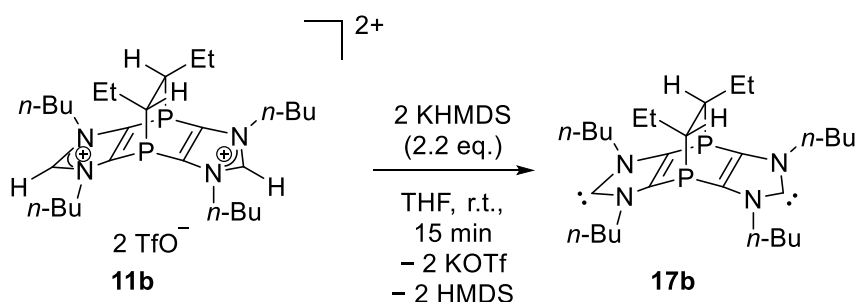
¹H NMR (500.04 MHz, 298.0 K, THF-*d*₈): δ / ppm = 0.93 (t, $^3J_{\text{H,H}} = 7.4$ Hz, 12H, CH₃), 1.27–1.38 (m, 8H, CH₂CH₃), 1.60 (t, $J_{\text{P,H}} = 5.3$ Hz, 4H, PCH₂), 1.70–1.82 (m, 8H, NCH₂CH₂), 4.03–4.15 (m, 8H, NCH₂).

$^{13}\text{C}\{^1\text{H}\}$ NMR (125.75 MHz, 298.0 K, THF- d_8): δ / ppm = 14.3 (s, CH_3), 19.8 (dd, $J_{\text{P,C}} = 6.4$ Hz, PCH_2), 20.8 (m, CH_2CH_3), 35.7 (m, NCH_2CH_2), 50.1 (m, NCH_2), 140.4 (dd, $J_{\text{P,C}} = 6.1$ Hz, $J_{\text{P,C}} = 4.1$ Hz, PC), 220.0 (br s, C^2).

^{31}P NMR (202.44 MHz, 298.0 K, THF- d_8): δ / ppm = -94.8 (m).

$^{31}\text{P}\{^1\text{H}\}$ NMR (202.44 MHz, 298.0 K, THF- d_8): δ / ppm = -94.8 (s).

5.5.10.2 Synthesis of 1,3,5,7-tetrabutyl-9,10-diethyl-1,3,5,7-tetrahydro-2*H*,6*H*-4,8-ethano[1,4]diphosphinino[2,3-*d*:5,6-*d'*]diimidazole-2,6-ylidene **17b**



Synthesis

In a 50 mL Schlenk tube 0.338 g (1.69 mmol, 2.2 eq.) KHMDS were added to a solution of 0.561 g (0.70 mmol, 1.0 eq.) of **11b** in 7.5 mL THF via a syringe in two portions of 1–1.5 mL THF each, resulting in an orange, slightly turbid solution. After stirring for 15 min at ambient temperature the solvent was removed *in vacuo* (≤ 0.05 mbar) at the same temperature. The resulting yellow solid mixed with an orange, oily residue was extracted with three times 3–6 mL *n*-pentane. After removal of the solvent *in vacuo* (≤ 0.05 mbar) at ambient temperature and drying for 6 h (≤ 0.02 mbar) an orange oil was obtained.

Reaction code: TT-643 (44p5a045.22), TT-681

Molecular formula: $\text{C}_{28}\text{H}_{48}\text{N}_4\text{P}_2$

Molecular weight: $502.67 \text{ g mol}^{-1}$

Yield: 0.150 g (0.298 mmol, 43 %)

Melting point: ca. 0°C

MS (pos. ESI): m/z (%) = 539.364 (60) $[\text{M}+2\text{H}_2\text{O}+\text{H}]^+$, 521.353 (100) $[\text{M}+\text{H}_2\text{O}+\text{H}]^+$, 503.343 (1) $[\text{M}+\text{H}]^+$, 419.249 (4) $[\text{M}-\text{C}_6\text{H}_{12}+\text{H}]^+$, 437.259 (36) $[\text{M}-\text{C}_6\text{H}_{12}+\text{H}_2\text{O}+\text{H}]^+$.

HRMS (pos. APCI): m/z calculated $[\text{C}_{28}\text{H}_{48}\text{N}_4\text{P}_2\text{H}]^+$: 503.3427; found: 503.3425.

IR (ATR): $\tilde{\nu}$ / cm^{-1} = 2957 (w, $\nu_{\text{as}}(\text{CH}_3)$, $\nu_{\text{s}}(\text{CH}_2)$), 2931 (w, $\nu_{\text{as}}(\text{CH}_3)$, $\nu_{\text{s}}(\text{CH}_2)$), 2872 (w, $\nu_{\text{s}}(\text{CH}_3)$, $\nu_{\text{as}}(\text{CH}_2)$).

^1H NMR (500.04 MHz, 298.0 K, C_6D_6): δ / ppm = 0.84 (t, $^3J_{\text{H,H}} = 7.3$ Hz, 12H, $\text{CH}_3(n\text{-Bu})$), 0.96 (t, $^3J_{\text{H,H}} = 7.2$ Hz, 6H, $\text{CH}_3(\text{Et})$), 1.05–1.11 (m, 2H, PCHCH_2), 1.14–1.21 (m, 2H, PCHCH_2), 1.21–1.37 (m, 10H, $\text{NCH}_2\text{CH}_2\text{CH}_2$, PCHCH_2), 1.79–1.95 (m, 8H, NCH_2CH_2), 4.19–4.31 (m, 8H, NCH_2).

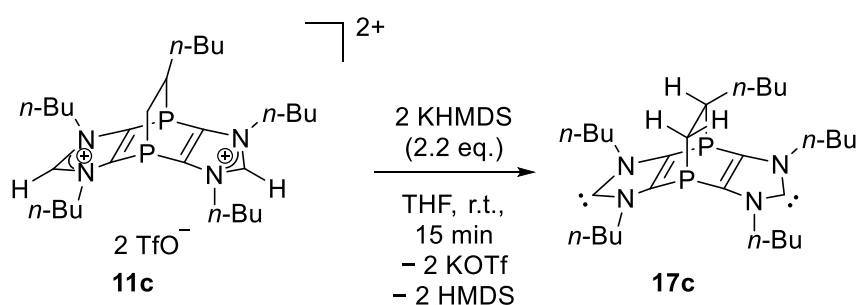
$^{13}\text{C}\{^1\text{H}\}$ NMR (125.75 MHz, 298.0 K, C_6D_6): δ / ppm = 13.9–14.1 (m, $\text{CH}_3(n\text{-Bu})$, $\text{CH}_3(\text{Et})$), 20.1 (s, $\text{NCH}_2\text{CH}_2\text{CH}_2$), 28.4 (m, PCHCH_2), 35.1 (br s, NCH_2CH_2), 35.2 (br s, NCH_2CH_2), 46.2 (dd, $J_{\text{P,C}} = 6.0$ Hz, PCH), 50.0 (s, NCH_2), 50.1 (s, NCH_2), 139.3 (m, PC), 141.7 (m, PC), 218.4 (br s, C^2).

^{31}P NMR (202.44 MHz, 298.0 K, C_6D_6): δ / ppm = –86.2 (m).

$^{31}\text{P}\{^1\text{H}\}$ NMR (202.44 MHz, 298.0 K, C_6D_6): δ / ppm = –86.2 (s).

X-ray diffraction analysis: Gxray6966 (GSTR778), good structure (BC1)

5.5.10.3 Synthesis of 1,3,5,7-tetrabutyl-9-butyl-1,3,5,7-tetrahydro-2*H*,6*H*-4,8-ethano[1,4]diphosphinino[2,3-*d*:5,6-*d'*]diimidazole-2,6-ylidene **17c**



Synthesis

In a 20 mL Schlenk tube 0.147 g (0.18 mmol, 1.0 eq.) of **11c** and 0.080 g (0.40 mmol, 2.2 eq.) KHMDS were dissolved in 3 mL THF, resulting in an orange, slightly turbid solution. After stirring for 15 min at ambient temperature the solvent was removed *in vacuo* (≤ 0.05 mbar) at the same temperature. The resulting colourless solid mixed with a yellow, oily residue was extracted with three times 5 mL diethyl ether. After removal of the solvent *in vacuo* (≤ 0.05 mbar) at ambient temperature and drying for 5 h (≤ 0.02 mbar) a yellow-orange oil was obtained.

Reaction code: TT-730 (TAT230201p5a041)

Molecular formula: $\text{C}_{28}\text{H}_{48}\text{N}_4\text{P}_2$

Molecular weight: 502.67 g mol $^{-1}$

Yield: 0.050 g (0.10 mmol, 54 %)

Melting point: ca. 0 °C

MS (pos. APCI): m/z (%) = 539.364 (100) $[M+2H_2O+H]^+$, 521.353 (77) $[M+H_2O+H]^+$, 503.343 (<1) $[M+H]^+$, 419.249 (1) $[M-C_6H_{12}+H]^+$.

HRMS (pos. APCI): m/z calculated $[C_{28}H_{48}N_4P_2H]^+$: 503.3427; found: 503.3429.

IR (ATR): $\tilde{\nu}$ / cm^{-1} = 2956 (w, $\nu_{as}(CH_3)$, $\nu_s(CH_2)$), 2928 (w, $\nu_{as}(CH_3)$, $\nu_s(CH_2)$), 2872 (w, $\nu_s(CH_3)$, $\nu_{as}(CH_2)$).

^1H NMR (500.04 MHz, 298.0 K, C_6D_6): δ / ppm = 0.78–0.86 (m, 15H, $CH_3(PCH(n-Bu))$, $CH_3(N(n-Bu))$), 0.87–0.91 (m, 1H, PCH_2), 0.92–0.99 (m, 2H, $PCHCH_2CH_2CH_2$), 1.21–1.32 (m, 10H, $NCH_2CH_2CH_2$, $PCHCH_2CH_2$), 1.33–1.39 (m, 8H, $NCH_2CH_2CH_2$, $PCHCH_2$), 1.59–1.66 (m, 1H, PCH), 1.66–1.75 (m, 1H, PCH_2), 1.79–1.98 (m, 8H, NCH_2CH_2), 4.22–4.31 (m, 8H, NCH_2).

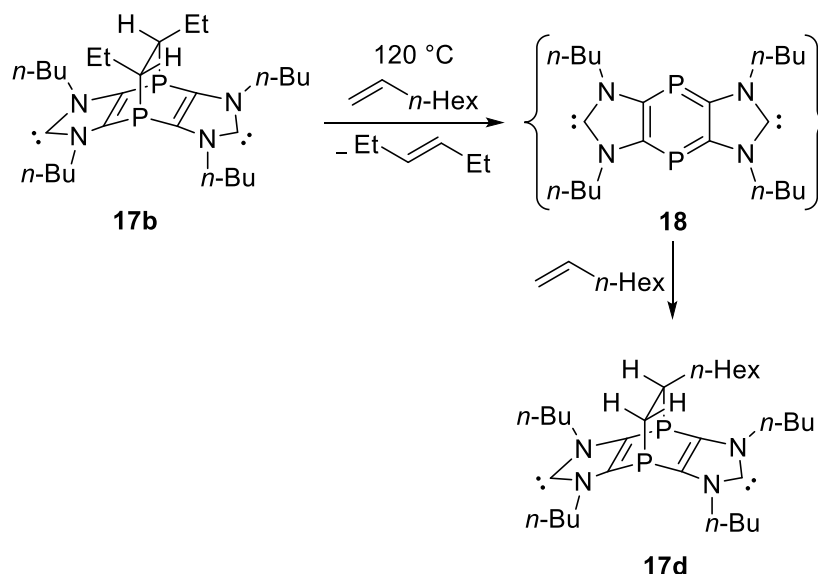
$^{13}C\{^1H\}$ NMR (125.75 MHz, 298.0 K, C_6D_6): δ / ppm = 13.9–14.0 (m, CH_3), 20.1–20.2 (m, $NCH_2CH_2CH_2$), 22.8 (s, $PCHCH_2CH_2CH_2$), 28.2 (dd, $^1J_{P,C} = 9.1$ Hz, $^2J_{P,C} = 4.8$ Hz, PCH_2), 31.7 (d, $J_{P,C} = 14.9$ Hz, $PCHCH_2$), 34.9–35.3 (m, NCH_2CH_2), 35.7–35.8 (m, PCH), 35.9 (br s, $PCHCH_2CH_2$), 49.8–50.0 (m, NCH_2), 138.7 (d, $J_{P,C} = 13.7$ Hz, PC), 139.7 (d, $J_{P,C} = 9.0$ Hz, PC), 140.7 (d, $J_{P,C} = 8.6$ Hz, PC), 142.0 (d, $J_{P,C} = 8.3$ Hz, PC), 219.9 (t, $^3J_{P,C} = 2.7$ Hz, C^2), 220.5 (t, $^3J_{P,C} = 3.0$ Hz, C^2).

^{31}P NMR (202.44 MHz, 298.0 K, C_6D_6): δ / ppm = –92.0 (m, PCH_2), –86.4 (m, PCH).

$^{31}P\{^1H\}$ NMR (202.44 MHz, 298.0 K, C_6D_6): δ / ppm = –92.0 (d, $^3J_{P,P} = 19.7$ Hz, PCH_2), –86.4 (d, $^3J_{P,P} = 19.4$ Hz, PCH).

X-ray diffraction analysis: Gxray7213 (GSTR803), moderate structure (D1)

5.5.10.4 Generation of 1,3,5,7-tetrabutyl-9-hexyl-1,3,5,7-tetrahydro-2*H*,6*H*-4,8-ethano[1,4]diphosphinino[2,3-*d*:5,6-*d'*]diimidazole-2,6-ylidene **17d**



Synthesis

A solution of 0.008 g (0.015 mmol, 1.0 eq.) of **17b** in 0.45 mL 1-octene was heated to 120 °C for 2 h in a *J Young*® NMR tube. The solvent was removed *in vacuo* (≤ 0.05 mbar) and the brown solid was redissolved in 0.45 mL THF and analysed via $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy.

Reaction code: TT-694 (TAT230113m3a026)

Molecular formula: $\text{C}_{30}\text{H}_{52}\text{N}_4\text{P}_2$

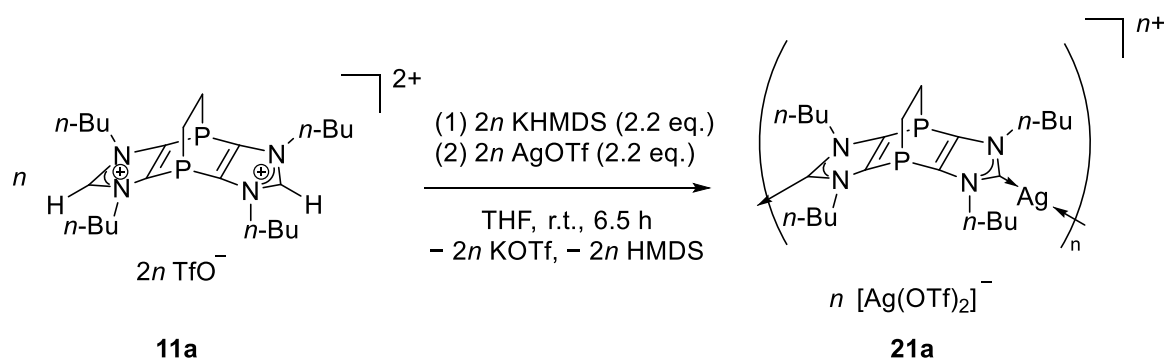
Molecular weight: $530.72 \text{ g mol}^{-1}$

Content in mixture: 96 % ($^{31}\text{P}\{^1\text{H}\}$ NMR integration of reaction mixture)

$^{31}\text{P}\{^1\text{H}\}$ NMR (121.51 MHz, 298.0 K, THF): $\delta / \text{ppm} = -91.6$ (d, $^3J_{\text{P,P}} = 19.6 \text{ Hz}$, PCH_2), -86.2 (d, $^3J_{\text{P,P}} = 19.6 \text{ Hz}$, PCH).

5.5.11 Synthesis of bis(NHC) Ag(I) complexes **21**

5.5.11.1 Synthesis of $[(\mu\text{-}1,3,5,7\text{-tetrabutyl-}1,3,5,7\text{-tetrahydro-}2H,6H\text{-}4,8\text{-ethano}[1,4]\text{diphosphinino}[2,3\text{-}d:5,6\text{-}d']\text{diimidazole-}2,6\text{-ylidene-}2\kappa\text{C},6\kappa\text{C})\text{bis}(\text{trifluoromethanesulfonato})\text{disilver(I)}]$ **21a**



Synthesis

In a 50 mL Schlenk tube 0.060 g (0.30 mmol, 2.2 eq.) KHMDs were added to a solution of 0.102 g (0.14 mmol, 1.0 eq.) of **11a** in 3 mL THF via a transfer canula in two portions of 1–3 mL THF each. After stirring for 15 min at ambient temperature 0.077 g (0.30 mmol, 2.2 eq.) AgOTf were added and the brown suspension was stirred for another 6.5 h. The solvent was removed *in vacuo* (≤ 0.05 mbar) and the residue was extracted with 8 mL acetonitrile. After removal of the solvent *in vacuo* (≤ 0.05 mbar) the brown solid was washed with three times 3–4 mL THF and three times 4 mL *n*-pentane. After drying for 2 h (≤ 0.02 mbar) a brown solid in 87 % purity was obtained.

Reaction code: TT-878 (TAT230803p5a057)

Molecular formula: C₂₆H₄₀Ag₂F₆N₄O₆P₂S₂

Molecular weight: 960.42 g mol⁻¹

Yield: not determined due to remaining impurities

Melting point: not determined due to remaining impurities

MS (pos. ESI): m/z (%) = 419.247 (100) [M-2AgOTf+H]⁺, 597.238 (47) [M-2Ag-OTf+2H]⁺, 852.058 (<1) [M-OTf+CH₃CN]⁺.

HRMS (pos. APCI): m/z calculated [C₂₅H₄₀Ag₂N₄P₂O₃S₁F₃]⁺: 811.0343; found: 811.0316.

m/z calculated [C₂₄H₄₀Ag₂N₄P₂O₃S₁F₃(CH₃CN)]⁺: 852.0610; found: 852.0587.

IR (ATR): $\tilde{\nu}$ / cm⁻¹ = 2961 (w, $\nu_{as}(\text{CH}_3)$, $\nu_s(\text{CH}_2)$), 2933 (w, $\nu_{as}(\text{CH}_3)$, $\nu_s(\text{CH}_2)$), 2876 (w, $\nu_s(\text{CH}_3)$, $\nu_{as}(\text{CH}_2)$).

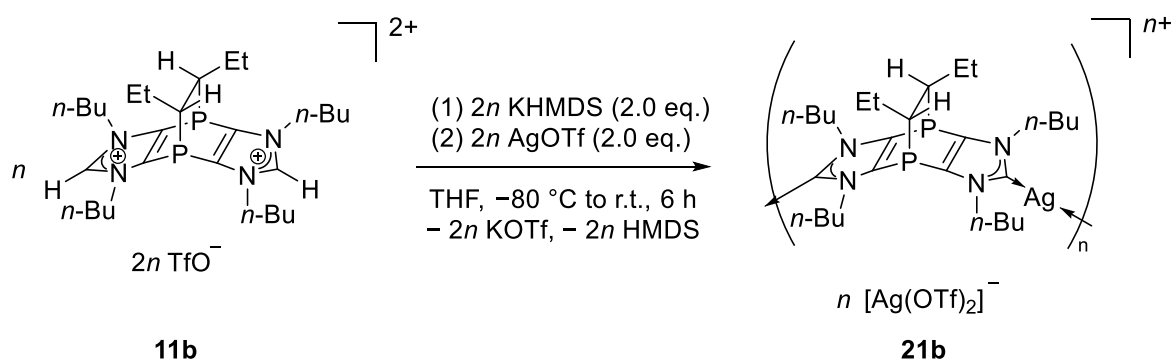
¹H NMR (499.96 MHz, 298.0 K, CH₃CN-d₃): δ / ppm = 0.92 (t, ³J_{H,H} = 7.5 Hz, 12H, CH₃), 1.27–1.38 (m, 8H, CH₂CH₃), 1.75–1.88 (m, 8H, NCH₂CH₂), 1.95–2.00 (m, 4H, PCH₂), 4.24–4.40 (m, 8H, NCH₂).

¹³C{¹H} NMR (125.73 MHz, 298.0 K, CH₃CN-d₃): δ / ppm = 14.1 (s, CH₃), 19.5 (m, PCH₂), 20.7 (s, CH₂CH₃), 35.4 (s, NCH₂CH₂), 51.6 (s, NCH₂), 122.1 (q, ¹J_{F,C} = 320.9 Hz, CF₃), 141.1 (s, PC), 184.7 (br s, CAg).

³¹P NMR (202.41 MHz, 298.0 K, CH₃CN-d₃): δ / ppm = -88.9 (m, FWHM = 44.0 Hz).

³¹P{¹H} NMR (202.41 MHz, 298.0 K, CH₃CN-d₃): δ / ppm = -88.9 (br s, FWHM = 40.9 Hz).

5.5.11.2 Synthesis of [(μ-1,3,5,7-tetrabutyl-9,10-diethyl-1,3,5,7-tetrahydro-2*H*,6*H*-4,8-ethano[1,4]diphosphinino[2,3-d:5,6-d']diimidazole-2,6-ylidene-2κC,6κC)bis(trifluoromethanesulfonato)disilver(I)] **21b**



Synthesis

In a 20 mL Schlenk tube 0.034 g (0.17 mmol, 2.0 eq.) KHMDS were added to a solution of 0.069 g (0.09 mmol, 1.0 eq.) of **11b** in 4 mL THF at -80 °C via a transfer canula in two portions of 1 mL THF each. Afterwards 0.049 g (0.17 mmol, 2.0 eq.) AgOTf were added and the brown suspension was stirred for 6 h. The solvent was removed *in vacuo* (≤ 0.05 mbar) and the residue extracted with 5 mL

acetonitrile. After solvent removal *in vacuo* (≤ 0.05 mbar) the residual solid was washed with three times 2 mL THF, with twice 3 mL diethyl ether and with three times 3 mL *n*-pentane. After drying for 3 h (≤ 0.02 mbar) a brown solid was obtained.

Reaction code: TT-554 (14p5b003.22)

Molecular formula: C₃₀H₄₈Ag₂F₆N₄O₆P₂S₂

Molecular weight: 1016.53 g mol⁻¹

Yield: 0.051 g (0.05 mmol, 58 %)

Melting point: 187 °C

MS (pos. ESI): m/z (%) = 400.100 (9) [M-2OTf+2CH₃CN]²⁺, 358.053 (21) [M-2OTf+2CH₃CN-C₆H₁₂]²⁺, 210.129 (54) [M-2AgOTf-C₆H₁₂+2H]²⁺, 252.175 (53) [M-2AgOTf+2H]²⁺, 188.959 (100) [Ag(CH₃CN)₂]²⁺, 147.932 (72) [Ag(CH₃CN)]²⁺.

MS (neg. ESI): m/z (%) = 148.9 (100) [OTf]⁻.

IR (ATR): $\tilde{\nu}$ / cm⁻¹ = 2961 (w, $\nu_{as}(\text{CH}_3)$, $\nu_s(\text{CH}_2)$), 2932 (w, $\nu_{as}(\text{CH}_3)$, $\nu_s(\text{CH}_2)$), 2874 (w, $\nu_s(\text{CH}_3)$, $\nu_{as}(\text{CH}_2)$).

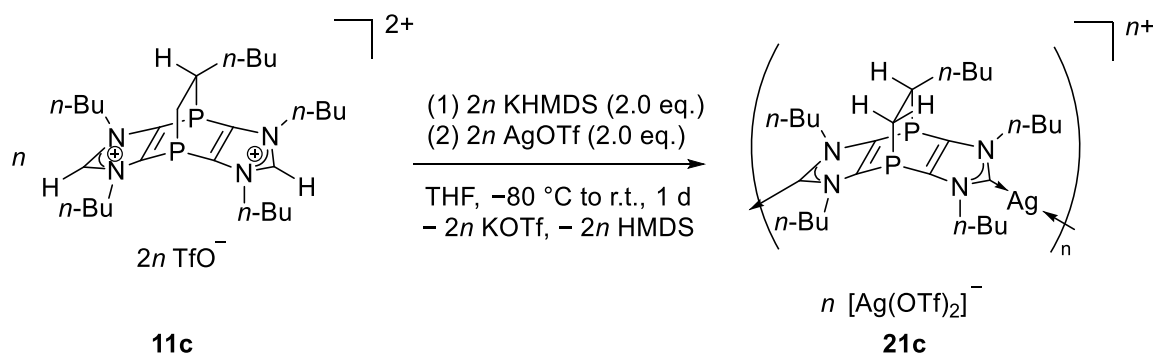
¹H NMR (500.04 MHz, 298.0 K, CH₃CN-d₃): δ / ppm = 0.92 (t, ³J_{H,H} = 7.4 Hz, 12H, CH₃(*n*-Bu)), 1.06 (t, ³J_{H,H} = 7.3 Hz, 6H, CH₃(Et)), 1.25–1.37 (m, 8H, NCH₂CH₂CH₂), 1.37–1.49 (m, 4H, PCHCH₂), 1.76–1.80 (m, 2H, PCH), 1.80–1.88 (m, 8H, NCH₂CH₂), 4.25–4.42 (m, 8H, NCH₂).

¹³C{¹H} NMR (125.75 MHz, 298.0 K, CH₃CN-d₃): δ / ppm = 13.6 (d, J_{P,C} = 15.3 Hz, CH₃(Et)), 14.0 (s, CH₃(*n*-Bu)), 14.1 (m, CH₃(*n*-Bu)), 20.6 (m, NCH₂CH₂CH₂), 28.4 (d, J_{P,C} = 17.6 Hz, PCHCH₂), 35.4 (m, NCH₂CH₂), 44.5 (m, PCH), 51.7 (dm, J_{P,C} = 8.7 Hz, NCH₂), 122.0 (q, ¹J_{F,C} = 320.9 Hz, CF₃), 140.4 (s, PC), 142.5 (s, PC), 186.0 (br s, CAg).

³¹P NMR (202.44 MHz, 298.0 K, CH₃CN-d₃): δ / ppm = -79.6 (br s, FWHM = 85.6 Hz).

³¹P{¹H} NMR (202.44 MHz, 298.0 K, CH₃CN-d₃): δ / ppm = -79.6 (br s, FWHM = 78.9 Hz).

5.5.11.3 Synthesis of [(μ-1,3,5,7-tetrabutyl-9-butyl-1,3,5,7-tetrahydro-2*H*,6*H*-4,8-ethano[1,4]diphosphinino[2,3-*d*:5,6-*d'*]diimidazole-2,6-ylidene-2κC,6κC)bis(trifluoromethanesulfonato)disilver(I)] **21c**



Synthesis

In a 50 mL Schlenk tube 0.052 g (0.26 mmol, 2.0 eq.) KHMDS were added to a solution of 0.105 g (0.13 mmol, 1.0 eq.) of **11c** in 5 mL THF at -80°C via a transfer canula in two portions of 1–3 mL THF each. Afterwards 0.068 g (0.26 mmol, 2.0 eq.) AgOTf were added and the brown suspension was stirred for 1 d. The solvent was removed *in vacuo* (≤ 0.05 mbar) and the residue extracted with 6 mL acetonitrile. After solvent removal *in vacuo* (≤ 0.05 mbar) the residual solid was washed with twice 3 mL diethyl ether and with three times 3 mL *n*-pentane. After drying for 3 h (≤ 0.02 mbar) a brown solid was obtained.

Reaction code: TT-543 (12p54022.22)

Molecular formula: $\text{C}_{30}\text{H}_{48}\text{Ag}_2\text{F}_6\text{N}_4\text{O}_6\text{P}_2\text{S}_2$

Molecular weight: $1016.53 \text{ g mol}^{-1}$

Yield: 0.081 g (0.08 mmol, 61 %)

Melting point: 185°C

EA: calculated (%)	C 35.38	H 4.95	N 5.50
found (%)	C 33.22	H 4.70	N 4.99

MS (pos. ESI): m/z (%) = 469.812 (4) $[\text{2M-4OTf-Ag}+2\text{CH}_3\text{CN}]^{3+}$, 400.098 (11) $[\text{M-2OTf}+2\text{CH}_3\text{CN}]^{2+}$, 358.051 (17) $[\text{M-2OTf}+2\text{CH}_3\text{CN-C}_6\text{H}_{12}]^{2+}$, 210.129 (2) $[\text{M-2AgOTf-C}_6\text{H}_{12}+2\text{H}]^{2+}$, 252.175 (4) $[\text{M-2AgOTf}+2\text{H}]^{2+}$, 188.957 (100) $[\text{Ag}(\text{CH}_3\text{CN})_2]^{2+}$, 147.931 (66) $[\text{Ag}(\text{CH}_3\text{CN})]^{2+}$.

MS (neg. ESI): m/z (%) = 149.0 (100) $[\text{OTf}]^-$.

HRMS (pos. ESI): m/z calculated $[\text{C}_{30}\text{H}_{48}\text{Ag}_2\text{N}_4\text{P}_2(\text{CH}_3\text{CN})_2]^+$: 400.099; found: 400.098.

IR (ATR): $\tilde{\nu} / \text{cm}^{-1}$ = 2959 (w, $\nu_{\text{as}}(\text{CH}_3)$, $\nu_{\text{s}}(\text{CH}_2)$), 2930 (w, $\nu_{\text{as}}(\text{CH}_3)$, $\nu_{\text{s}}(\text{CH}_2)$), 2874 (w, $\nu_{\text{s}}(\text{CH}_3)$, $\nu_{\text{as}}(\text{CH}_2)$).

^1H NMR (500.04 MHz, 298.0 K, $\text{CH}_3\text{CN}-d_3$): δ / ppm = 0.88 (t, $^3J_{\text{H,H}} = 7.3 \text{ Hz}$, 3H, $\text{CH}_3(\text{PCH}(n\text{-Bu}))$), 0.90–0.95 (m, 12H, $\text{CH}_3(\text{N}(n\text{-Bu}))$), 1.25–1.38 (m, 10H, $\text{NCH}_2\text{CH}_2\text{CH}_2$, $\text{PCHCH}_2\text{CH}_2\text{CH}_2$), 1.39–1.48 (m, 4H, $\text{PCHCH}_2\text{CH}_2$), 1.48–1.51 (m, 1H, PCH_2), 1.77–1.88 (m, 8H, NCH_2CH_2), 2.21–2.28 (m, 1H, PCH), 2.28–2.37 (m, 1H, PCH_2), 4.25–4.40 (m, 8H, NCH_2).

$^{13}\text{C}\{^1\text{H}\}$ NMR (125.75 MHz, 298.0 K, $\text{CH}_3\text{CN}-d_3$): δ / ppm = 14.0 (s, $\text{CH}_3(\text{PCH}(n\text{-Bu}))$), 14.1 (s, $\text{CH}_3(\text{N}(n\text{-Bu}))$), 20.6 (m, $\text{NCH}_2\text{CH}_2\text{CH}_2$), 20.7 (m, $\text{NCH}_2\text{CH}_2\text{CH}_2$), 23.1 (s, $\text{PCHCH}_2\text{CH}_2\text{CH}_2$), 26.9 (m, PCH_2), 31.6 (d, $J_{\text{P,C}} = 15.9 \text{ Hz}$, $\text{PCHCH}_2\text{CH}_2$), 35.5 (m, NCH_2CH_2), 35.5 (m, PCHCH_2), 35.6 (m, PCH), 51.7 (m, NCH_2), 122.2 (q, $^1J_{\text{F,C}} = 320.9 \text{ Hz}$, CF_3), 139.7 (m, PC), 141.1 (m, PC), 142.1 (m, PC), 143.0 (m, PC), 185.0 (br s, CAg).

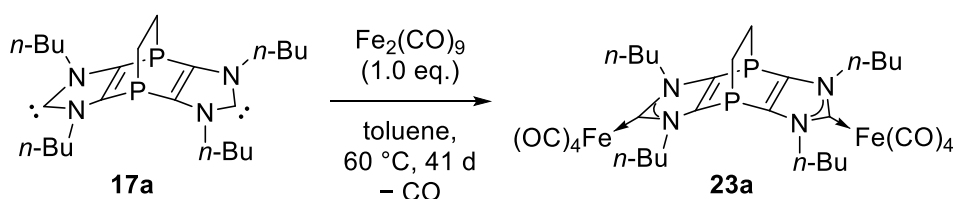
^{31}P NMR (202.44 MHz, 298.0 K, $\text{CH}_3\text{CN}-d_3$): δ / ppm = –86.8 (m, FWHM = 49.9 Hz PCH_2), –81.7 (m, FWHM = 98.1 Hz, PCH).

$^{31}\text{P}\{^1\text{H}\}$ NMR (202.44 MHz, 298.0 K, $\text{CH}_3\text{CN}-d_3$): δ / ppm = –86.8 (br s, FWHM = 49.6 Hz, PCH_2), –81.7 (br s, FWHM = 90.6 Hz, PCH).

5.5.12 Synthesis of bis(NHC) Fe(0) complexes 23

5.5.12.1 Synthesis of [octacarbonyl(μ -1,3,5,7-tetrabutyl-1,3,5,7-tetrahydro-2*H*,6*H*-4,8-ethano[1,4]diphosphinino[2,3-*d*:5,6-*d'*]diimidazole-2,6-ylidene-2 κC ,6 κC)diiron(0)]

23a



Synthesis

In a 25 mL Schlenk tube 0.077 g (0.17 mmol, 1.0 eq.) of **17a** were added to a solution of 0.063 g (0.17 mmol, 1.0 eq.) $\text{Fe}_2(\text{CO})_9$ in 3 mL toluene via a transfer canula in two portions of 3 and 1 mL toluene. The orange suspension was stirred for 41 d at 60°C until completion of the reaction as determined via $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopic monitoring. The reaction solution was extracted with additionally twice 3 mL toluene and after the solvent was removed *in vacuo* ($\leq 0.05 \text{ mbar}$) the oily residue was washed with three times 2–4 mL *n*-pentane. After drying for 3 h ($\leq 0.02 \text{ mbar}$) an orange solid was obtained.

Reaction code: TT-881 (TAT230914p5a055)

Molecular formula: C₃₂H₄₀Fe₂N₄O₈P₂

Molecular weight: 782.33 g mol⁻¹

Yield: 0.052 mg (0.07 mmol, 39 %)

Melting point: 125 °C (dec.)

MS (pos. ESI): *m/z* (%) = 615.194 (100) [M-Fe(CO)₄+H]⁺, 785.124 (2) [M+3H]⁺.

HRMS (pos. ESI): *m/z* calculated [C₃₂H₄₀Fe₂N₄O₈P₂H]⁺: 783.1084; found: 783.1094.

IR (ATR): $\tilde{\nu}$ / cm⁻¹ = 2962 (w, $\nu_{as}(\text{CH}_3)$, $\nu_s(\text{CH}_2)$), 2934 (w, $\nu_{as}(\text{CH}_3)$, $\nu_s(\text{CH}_2)$), 2876 (w, $\nu_s(\text{CH}_3)$, $\nu_{as}(\text{CH}_2)$), 2037 (s, $\nu(\text{CO})$), 1907 (vs, $\nu(\text{CO})$).

¹H NMR (499.96 MHz, 298.0 K, C₆D₆): δ / ppm = 0.74 (t, $J_{\text{P,H}} = 5.6$ Hz, 4H, PCH₂), 0.85 (t, $^3J_{\text{H,H}} = 7.4$ Hz, 12H, CH₃), 1.20–1.30 (m, 8H, CH₂CH₃), 1.63–1.77 (m, 8H, NCH₂CH₂), 4.23–4.37 (m, 8H, NCH₂).

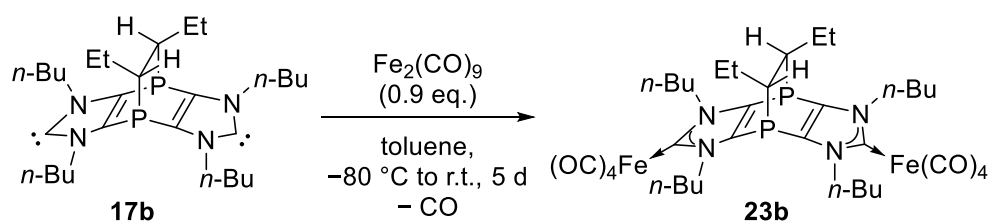
¹³C{¹H} NMR (125.73 MHz, 298.0 K, C₆D₆): δ / ppm = 13.8 (s, CH₃), 19.0 (dd, $J_{\text{P,C}} = 6.3$ Hz, PCH₂), 20.1 (s, CH₂CH₃), 33.9 (dd, $J_{\text{P,C}} = 2.4$ Hz, NCH₂CH₂), 50.8 (dd, $J_{\text{P,C}} = 2.7$ Hz, NCH₂), 141.6 (m, PC), 187.1 (t, $^3J_{\text{P,C}} = 2.8$ Hz, CFe), 218.6 (s, CO).

³¹P NMR (202.41 MHz, 298.0 K, C₆D₆): δ / ppm = -92.2 (m).

³¹P{¹H} NMR (202.41 MHz, 298.0 K, C₆D₆): δ / ppm = -92.2 (s).

5.5.12.2 Synthesis of [octacarbonyl(μ-1,3,5,7-tetrabutyl-9-butyl-1,3,5,7-tetrahydro-2*H*,6*H*-4,8-ethano[1,4]diphosphinino[2,3-*d*:5,6-*d'*]diimidazole-2,6-ylidene-2κC,6κC)diiron(0)]

23b



Synthesis

In a 50 mL Schlenk tube 0.412 g (0.82 mmol, 1.0 eq.) of **17b** were added to a solution of 0.268 g (0.74 mmol, 0.9 eq.) Fe₂(CO)₉ in 10 mL toluene via a transfer canula in two portions of 10 and 5 mL toluene at -80 °C. The orange suspension was stirred for 5 d until completion of the reaction as determined via ³¹P{¹H} NMR spectroscopic monitoring. After the solvent was removed *in vacuo* (≤ 0.05 mbar) the orange, oily residue filtered over a bed of silica and celite® (d = 2 cm, h = 1 cm each)

with 150 mL THF. After evaporation of the solvent *in vacuo* (≤ 0.05 mbar) the residue was extracted with three times 10–20 mL *n*-pentane. After solvent removal *in vacuo* (≤ 0.05 mbar) and drying for 2 h (≤ 0.02 mbar) an orange solid was obtained.

Reaction code: TT-710 (TAT230124p5a030)

Molecular formula: $\text{C}_{36}\text{H}_{48}\text{Fe}_2\text{N}_4\text{O}_8\text{P}_2$

Molecular weight: $838.44 \text{ g mol}^{-1}$

Yield: 0.314 g (0.38 mmol, 46 %)

Melting point: 121 °C (dec.)

MS (pos. ESI): m/z (%) = 671.255 (100) $[\text{M}-\text{Fe}(\text{CO})_4+\text{H}]^+$, 643.261 (6) $[\text{M}-\text{Fe}(\text{CO})_4-\text{CO}+\text{H}]^+$, 587.162 (2) $[\text{M}-\text{Fe}(\text{CO})_4-\text{C}_6\text{H}_{12}+\text{H}]^+$.

HRMS (pos. ESI): m/z calculated $[\text{C}_{32}\text{H}_{48}\text{FeN}_4\text{O}_4\text{P}_2\text{H}]^+$: 671.2577; found: 671.2575.

IR (ATR): $\tilde{\nu} / \text{cm}^{-1}$ = 2961 (w, $\nu_{\text{as}}(\text{CH}_3)$, $\nu_{\text{s}}(\text{CH}_2)$), 2932 (w, $\nu_{\text{as}}(\text{CH}_3)$, $\nu_{\text{s}}(\text{CH}_2)$), 2874 (w, $\nu_{\text{s}}(\text{CH}_3)$, $\nu_{\text{as}}(\text{CH}_2)$), 2037 (s, $\nu(\text{CO})$), 1909 (vs, $\nu(\text{CO})$).

^1H NMR (500.04 MHz, 298.0 K, C_6D_6): δ / ppm = 0.75 (t, $^3J_{\text{H,H}} = 6.8$ Hz, 6H, $\text{CH}_3(\text{Et})$), 0.85 (t, $^3J_{\text{H,H}} = 7.4$ Hz, 12H, $\text{CH}_3(n\text{-Bu})$), 0.89 (m, 2H, PCH), 0.94–1.00 (m, 4H, PCHCH₂), 1.21–1.38 (m, 8H, NCH₂CH₂CH₂), 1.67–1.84 (m, 8H, NCH₂CH₂), 4.15–4.29 (m, 4H, NCH₂), 4.38–4.54 (m, 4H, NCH₂).

$^{13}\text{C}\{^1\text{H}\}$ NMR (125.75 MHz, 298.0 K, C_6D_6): δ / ppm = 13.4 (m, $\text{CH}_3(\text{Et})$), 13.8 (s, $\text{CH}_3(n\text{-Bu})$), 13.8 (s, $\text{CH}_3(n\text{-Bu})$), 20.2 (m, NCH₂CH₂CH₂), 27.1 (m, PCHCH₂), 34.0 (m, NCH₂CH₂), 45.7 (dd, $J_{\text{P,C}} = 6.3$ Hz, PCH), 51.0 (dm, $J_{\text{P,C}} = 11.4$ Hz, $J_{\text{P,C}} = 2.7$ Hz, NCH₂), 141.0 (m, $J_{\text{P,C}} = 8.0$, $J_{\text{P,C}} = 5.3$, PC), 143.6 (m, $J_{\text{P,C}} = 4.3$, PC), 187.8 (dd, $J_{\text{P,C}} = 2.7$ Hz, CFe), 218.7 (s, CO).

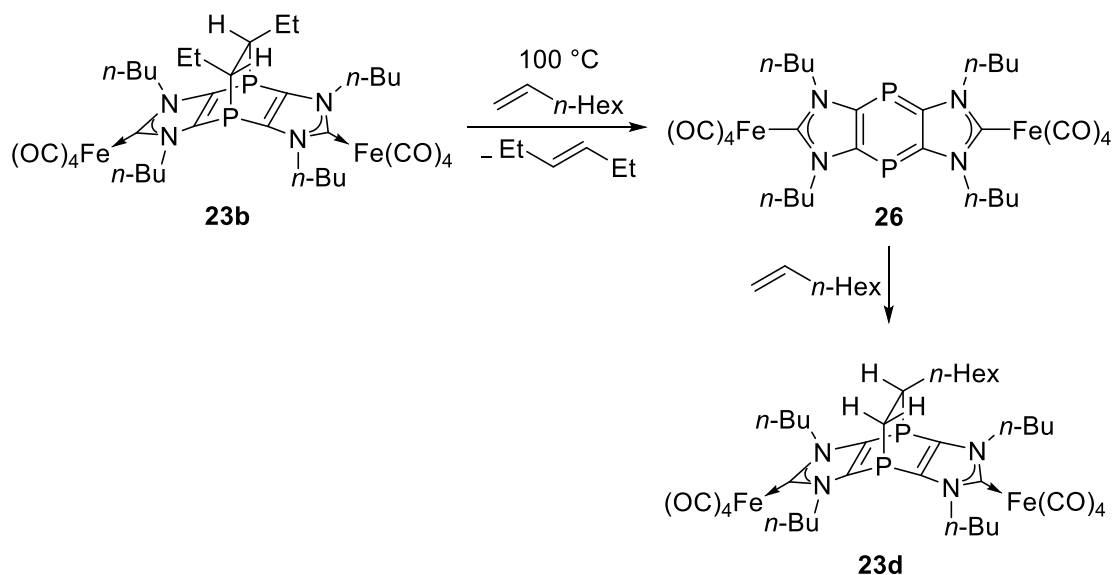
^{31}P NMR (202.44 MHz, 298.0 K, C_6D_6): δ / ppm = –82.2 (m).

$^{31}\text{P}\{^1\text{H}\}$ NMR (202.44 MHz, 298.0 K, C_6D_6): δ / ppm = –82.2 (s).

X-ray diffraction analysis: Gxray7393 (GSTR810), moderate structure (CD1)

5.5.12.3 Generation of [octacarbonyl(μ -1,3,5,7-tetrabutyl-9-hexyl-1,3,5,7-tetrahydro-2*H*,6*H*-4,8-ethano[1,4]diphosphinino[2,3-*d*:5,6-*d'*]diimidazole-2,6-ylidene-2 κ C,6 κ C)diiron(I)]

23d



Synthesis

A solution of 0.015 g (0.018 mmol, 1.0 eq.) of **23b** in 0.45 mL 1-octene was heated to 100 °C for 7 h in a *J Young*® NMR tube. The brown reaction solution was analysed via $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy.

Reaction code: TT-968 (TAT231117m3a015)

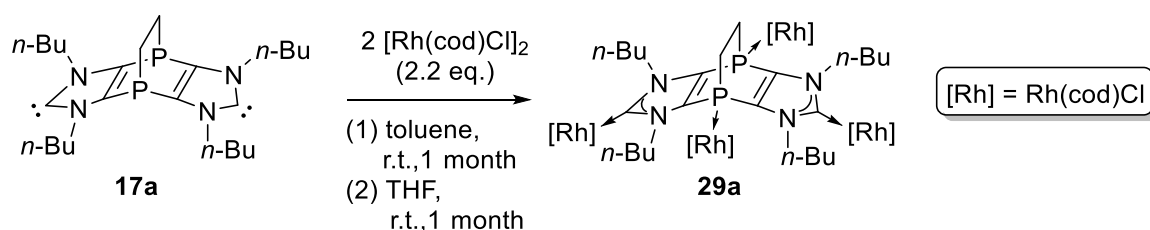
Molecular formula: $\text{C}_{38}\text{H}_{52}\text{Fe}_2\text{N}_4\text{O}_8\text{P}_2$

Molecular weight: 866.49 g mol $^{-1}$

Content in mixture: 99 % ($^{31}\text{P}\{^1\text{H}\}$ NMR integration of reaction mixture)

$^{31}\text{P}\{^1\text{H}\}$ NMR (121.51 MHz, 298.0 K, 1-octene): δ / ppm = -89.1 (d, $^3J_{\text{P,P}} = 18.2$ Hz, PCH_2), -83.7 (d, $^3J_{\text{P,P}} = 18.2$ Hz, PCH).

5.5.13 Synthesis of [tetrachlorido(μ -1,3,5,7-tetrabutyl-1,3,5,7-tetrahydro-2*H*,6*H*-4,8-ethano[1,4]diphosphinino[2,3-*d*:5,6-*d'*]diimidazole-2,6-ylidene-2 κ C,6 κ C, κ P ^{1} , κ P ^{2})tetrakis(η^2 , η^2 -cycloocta-1,5-diene)tetrarhodium(I)] 29a



Synthesis

In a 20 mL Schlenk tube 0.050 g (0.11 mmol, 1.0 eq.) of **17a** and 0.121 g (0.25 mmol, 2.2 eq.) $[\text{Rh}(\text{cod})\text{Cl}]_2$ were dissolved in 3 mL toluene and stirred for 1 month at ambient temperature yielding an orange suspension. The solvent was evaporated *in vacuo* (≤ 0.05 mbar) and the solids were redissolved in 5 mL THF and stirred for 1 month. After removal of the solvent *in vacuo* (≤ 0.05 mbar) the yellow-brown residue was washed with eight times 5 mL *n*-pentane. After drying for 3 h (≤ 0.02 mbar) a yellow-brown solid was obtained.

Reaction code: TT-898 (TAT231017p5a017)

Molecular formula: $\text{C}_{56}\text{H}_{88}\text{Cl}_4\text{N}_4\text{P}_2\text{Rh}_4$

Molecular weight: $1432.72 \text{ g mol}^{-1}$

Yield: *not determined due to remaining impurities*

Melting point: *not determined due to remaining impurities*

MS (pos. ESI): m/z (%) = 693.2484 (100) $[\text{M}-3(\text{Rh}(\text{cod})\text{Cl})+\text{H}]^+$, 939.2165 (72) $[\text{M}-2(\text{Rh}(\text{cod})\text{Cl})+\text{H}]^+$:

HRMS (pos. ESI): m/z calculated $[\text{C}_{56}\text{H}_{88}\text{Cl}_4\text{N}_4\text{P}_2\text{Rh}_4\text{H}]^+$: 1433.1510; found: 1433.1508.

IR (ATR): $\tilde{\nu} / \text{cm}^{-1}$ = 2982 (w, $\nu_{\text{as}}(\text{CH}_3)$, $\nu_s(\text{CH}_2)$, $\nu(\text{CH})$), 2964 (w, $\nu_{\text{as}}(\text{CH}_3)$, $\nu_s(\text{CH}_2)$), 2871 (w, $\nu_s(\text{CH}_3)$).

^1H NMR (500.18 MHz, 298.0 K, CD_2Cl_2): δ / ppm = 1.19 (t, $^3J_{\text{H,H}} = 7.2 \text{ Hz}$, 12H, CH_3), 1.62–1.74 (m, 8H, CH_2CH_3), 1.49–1.58 (m, 4H, PCH_2), 1.85–1.99 (m, 16H, CH_2CH), 2.19–3.30 (m, 8H, CH_2CH), 2.39 (m, 12H, NCH_2CH_2), 2.49 (m, 4H, CH_2CH), 2.62 (m, 4H, CH_2CH), 3.11–3.20 (m, 4H, CH_2CH), 3.92–4.02 (m, 4H, CH_2CH), 4.87–5.05 (m, 4H, CH_2CH), 5.33–5.43 (m, 4H, NCH_2), 5.68–5.79 (m, 4H, NCH_2), 5.80–5.91 (m, 4H, CH_2CH).

$^{13}\text{C}\{^1\text{H}\}$ NMR (125.78 MHz, 298.0 K, CD_2Cl_2): δ / ppm = 14.2 (s, CH_3), 18.0 (dd, $^1J_{\text{Rh,C}} = 23.1 \text{ Hz}$, $^2J_{\text{P,C}} = 8.8 \text{ Hz}$, PCH_2), 21.2 (s, CH_2CH_3), 28.9 (s, CH_2CH), 29.2 (s, CH_2CH), 33.5 (m, NCH_2CH_2), 33.1 (m, CH_2CH), 34.0 (m, CH_2CH), 52.1 (m, NCH_2), 70.2 (m, CH_2CH), 72.7 (m, CH_2CH), 98.3 (m, CH_2CH), 111.0 (m, CH_2CH , 2nd isomer), 110.2 (m, CH_2CH , 1st isomer), 134.2 (dd, $J_{\text{Rh,C}} = 53.0 \text{ Hz}$, $J_{\text{P,C}} = 3.2 \text{ Hz}$, PC), 191.7 (t, $^1J_{\text{Rh,P}} = 52.4 \text{ Hz}$, CRh).

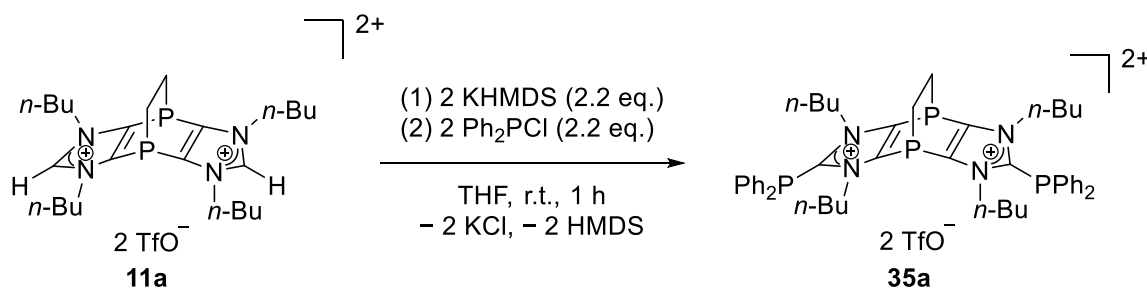
^{31}P NMR (202.50 MHz, 298.0 K, CD_2Cl_2): δ / ppm = -33.8 (d, $^1J_{\text{Rh,P}} = 160.8 \text{ Hz}$, 1st isomer), -29.5 (d, $^1J_{\text{Rh,P}} = 163.5 \text{ Hz}$, 2nd isomer)(ratio 2.8:1).

$^{31}\text{P}\{^1\text{H}\}$ NMR (202.50 MHz, 298.0 K, CD_2Cl_2): δ / ppm = -33.8 (d, $^1J_{\text{Rh,P}} = 160.8 \text{ Hz}$, 1st isomer), -29.5 (d, $^1J_{\text{Rh,P}} = 163.7 \text{ Hz}$, 2nd isomer)(ratio 2.9:1).

X-ray diffraction analysis: Gxraymo_7837f (GSTR828), moderate structure (D1)

5.5.14 Synthesis of Ph₂P-substituted bis(imidazolium) salts 35

5.5.14.1 Synthesis of 1,3,5,7-tetrabutyl-9,10-diethyl-1,5-dihydro-4,8-ethano[1,4]diphosphino[2,3-d:5,6-d']di-2,6-bis(diphenylphosphino)imidazolium bis(trifluoromethanesulfonate) **35a**



Synthesis

In a 20 mL Schlenk tube 0.063 g (0.32 mmol, 2.2 eq.) KHMDs were added to a solution of 0.107 g (0.14 mmol, 1.0 eq.) of **11a** in 4 mL THF via a transfer canula in two portions of 1–3 mL THF each. After stirring for 5 min at ambient temperature, 0.06 mL (0.069 g, 0.32 mmol, 2.2 eq.) Ph₂PCl were added and the light yellow, slightly turbid solution was stirred for another 50 min. The solvent was removed *in vacuo* (≤ 0.05 mbar) and the residue was extracted with three times 2–5 mL toluene. After removal of the solvent *in vacuo* (≤ 0.05 mbar) the yellow, oily residue was washed with three times 3 mL diethyl ether and four times 2–3 mL *n*-pentane. After drying for 2 h (≤ 0.02 mbar) a light-yellow solid in 88 % purity was obtained.

Reaction code: TT-869 (TAT230720p5a038)

Molecular formula: C₅₀H₆₀F₆N₄O₆P₄S

Molecular weight: 1115.06 g mol⁻¹

Yield: not determined due to remaining impurities

Melting point: not determined due to remaining impurities

MS (pos. ESI): m/z (%) = 408.187 (100) [M–2OTf]²⁺, 316.165 (52) [M–2OTf–Ph₂P+H]²⁺.

MS (neg. ESI): m/z (%) = 149.0 (100) [OTf]⁻.

HRMS (pos. ESI): m/z calculated [C₄₈H₆₀N₄P₄]²⁺: 408.1879; found: 408.1866.

IR (ATR): $\tilde{\nu}$ / cm⁻¹ = 2982 (w, $\nu_{\text{as}}(\text{CH}_3)$, $\nu_{\text{s}}(\text{CH}_2)$), 2964 (w, $\nu_{\text{as}}(\text{CH}_3)$, $\nu_{\text{s}}(\text{CH}_2)$), 2869 (w, $\nu_{\text{s}}(\text{CH}_3)$, $\nu_{\text{as}}(\text{CH}_2)$).

¹H NMR (499.96 MHz, 298.0 K, C₆D₆): δ / ppm = 0.60 (t, $^3J_{\text{H,H}} = 7.3$ Hz, 12H, CH₃), 0.75–0.89 (m, 8H, CH₂CH₃), 1.23–1.41 (m, 8H, NCH₂CH₂), 2.62 (dd, $J_{\text{P,H}} = 5.4$ Hz, 4H, PCH₂), 4.54–4.69 (m, 8H, NCH₂), 7.03

(tm, $^3J_{\text{H,H}} = 7.4$ Hz, 4H, *para*-CH), 7.32 (tm, $^3J_{\text{H,H}} = 7.9$ Hz, 8H, *meta*-CH), 7.65 (tm, $^3J_{\text{H,H}} = 8.4$ Hz, 8H, *ortho*-CH).

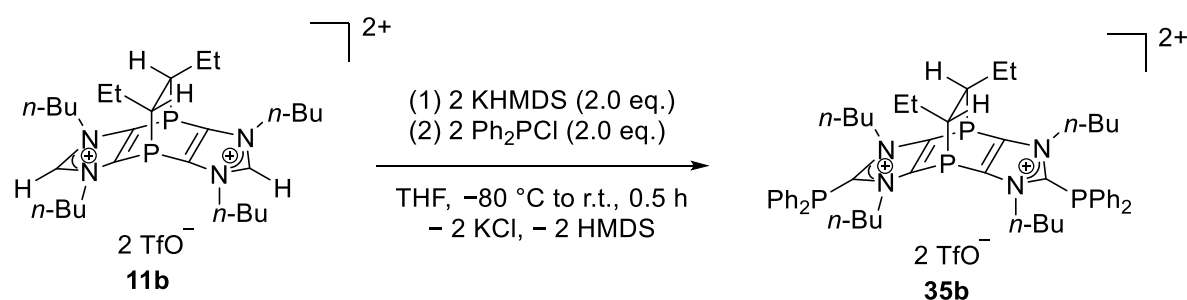
$^{13}\text{C}\{^1\text{H}\}$ NMR (125.73 MHz, 298.0 K, C_6D_6): δ / ppm = 13.5 (s, CH_3), 19.1 (m, PCH_2), 19.9 (s, CH_2CH_3), 33.3 (s, NCH_2CH_2), 50.4 (d, $^2J_{\text{P,C}} = 9.5$ Hz, NCH_2), 122.1 (q, $^1J_{\text{F,C}} = 321.9$ Hz, CF_3), 130.1 (d, $^4J_{\text{P,C}} = 7.4$ Hz, *para*-C), 130.5 (s, *meta*-C), 134.0 (d, $^2J_{\text{P,C}} = 20.6$ Hz, *ortho*-C), 144.3 (m, PC), 146.2 (d, $^1J_{\text{P,C}} = 58.5$ Hz, CPh_2).

^{31}P NMR (202.41 MHz, 298.0 K, C_6D_6): δ / ppm = -92.2 (m, bridgehead P), -25.1 (m, PPh_2).

$^{31}\text{P}\{^1\text{H}\}$ NMR (202.41 MHz, 298.0 K, C_6D_6): δ / ppm = -92.2 (s, bridgehead P), -25.1 (s, PPh_2).

X-ray diffraction analysis: Gxraycu_7656f_pl (GSTR821), moderate structure (D1)

5.5.14.2 Synthesis of 1,3,5,7-tetrabutyl-9,10-diethyl-1,5-dihydro-4,8-ethano[1,4]diphosphinino[2,3-d:5,6-d']di-2,6-bis(diphenylphosphino)imidazolium bis(trifluoromethanesulfonate) **35b**



Synthesis

In a 25 mL Schlenk tube 0.053 g (0.27 mmol, 2.0 eq.) KHMDS were added to a solution of 0.097 g (0.12 mmol, 1.0 eq.) of **11b** in 5 mL THF via a transfer canula in 4 mL THF at -80°C . After stirring for 5 min, 0.05 mL (0.059 g, 0.27 mmol, 2.0 eq.) Ph_2PCl were added and the colourless solution was stirred for 0.5 h. The solvent was removed *in vacuo* (≤ 0.05 mbar) and the colourless, oily residue was extracted with three times 4–10 mL toluene. After removal of the solvent *in vacuo* (≤ 0.05 mbar) the residue was washed with three times 5–10 mL *n*-pentane. After drying for 4 h (≤ 0.02 mbar) a yellow solid was obtained.

Reaction code: TT-574 (20t4a119.22)

Molecular formula: $\text{C}_{54}\text{H}_{68}\text{F}_6\text{N}_4\text{O}_6\text{P}_4\text{S}_2$

Molecular weight: $1171.17 \text{ g mol}^{-1}$

Yield: 0.084 g (0.07 mmol, 59 %)

Melting point: 108°C

MS (pos. ESI): m/z (%) = 436.219 (100) $[M-2OTf]^{2+}$, 394.172 (80) $[M-2OTf-C_6H_{12}]^{2+}$, 344.198 (60) $[M-2OTf-PPh_2+H]^{2+}$, 302.151 (51) $[M-2OTf-PPh_2-C_6H_{12}+H]^{2+}$, 185.052 (16) $[PPh_2]^+$.

MS (neg. ESI): m/z (%) = 149.0 (100) $[OTf]^-$.

HRMS (pos. ESI): m/z calculated $[C_{52}H_{68}N_4P_4]^{2+}$: 436.2192; found: 436.2197.

IR (ATR): $\tilde{\nu}$ / cm^{-1} = 2961 (w, $\nu_{as}(CH_3)$, $\nu_s(CH_2)$), 2932 (w, $\nu_{as}(CH_3)$, $\nu_s(CH_2)$), 2874 (w, $\nu_s(CH_3)$, $\nu_{as}(CH_2)$).

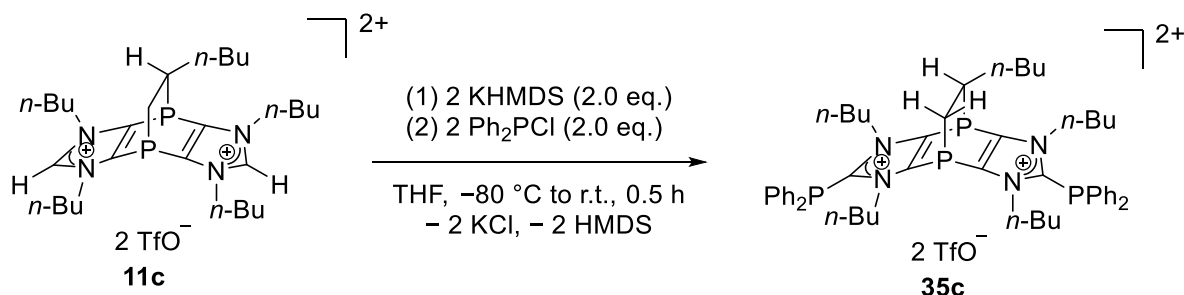
^1H NMR (400.13 MHz, 298.0 K, C_6D_6): δ / ppm = 0.56–0.66 (m, 12H, $CH_3(n-Bu)$), 0.71–0.96 (m, 8H, $NCH_2CH_2CH_2$), 1.22–1.29 (t, $^3J_{H,H} = 7.3$ Hz, 6H, $CH_3(Et)$), 1.34–1.47 (m, 4H, NCH_2CH_2), 1.27–1.34 (m, 4H, NCH_2CH_2), 1.50–1.66 (m, 2H, $PCHCH_2$), 1.78–1.97 (m, 2H, $PCHCH_2$), 2.43–2.53 (m, 2H, PCH), 4.37–4.57 (m, 4H, NCH_2), 4.65–4.75 (m, 2H, NCH_2), 4.79–4.90 (m, 2H, NCH_2), 6.98–7.08 (m, 4H, *para*-CH), 7.13–7.22 (m, 4H, *meta*-CH), 7.29–7.39 (m, 4H, *meta*-CH), 7.51–7.64 (m, 8H, *ortho*-CH).

$^{13}C\{^1H\}$ NMR (100.63 MHz, 298.0 K, C_6D_6): δ / ppm = 13.5 (s, $CH_3(n-Bu)$), 13.6 (s, $CH_3(n-Bu)$), 13.9 (m, $CH_3(Et)$), 19.9 (s, $NCH_2CH_2CH_2$), 20.0 (s, $NCH_2CH_2CH_2$), 28.1 (dd, $J_{P,C} = 9.2$ Hz, $PCHCH_2$), 33.4 (s, NCH_2CH_2), 44.4 (dd, $J_{P,C} = 5.9$ Hz, PCH), 50.5 (dm, $J_{P,C} = 9.8$ Hz, NCH_2), 50.8 (dm, $J_{P,C} = 10.2$ Hz, NCH_2), 122.2 (q, $^1J_{F,C} = 322.0$ Hz, CF_3), 130.0 (d, $^3J_{P,C} = 7.3$ Hz, *meta*-C), 130.3 (d, $^3J_{P,C} = 7.5$ Hz, *meta*-C), 130.7 (d, $^4J_{P,C} = 9.1$ Hz, *para*-C), 133.8 (d, $^2J_{P,C} = 20.5$ Hz, *ortho*-C), 143.7 (m, PC), 146.2 (m, PC), 147.1 (d, $^1J_{P,C} = 59.1$ Hz, CPhPh₂).

^{31}P NMR (162.00 MHz, 298.0 K, C_6D_6): δ / ppm = –84.3 (m, bridgehead P), –25.3 (m, Ph₂P).

$^{31}P\{^1H\}$ NMR (162.00 MHz, 298.0 K, C_6D_6): δ / ppm = –84.3 (s, bridgehead P), –25.3 (s, Ph₂P).

5.5.14.3 Synthesis of 1,3,5,7-tetrabutyl-9-butyl-1,5-dihydro-4,8-ethano[1,4]diphosphinino[2,3-d:5,6-d']di-2,6-bis(diphenylphosphino)imidazolium bis(trifluoromethanesulfonate) **35c**



Synthesis

In a 25 mL Schlenk tube 0.054 g (0.27 mmol, 2.0 eq.) KHMDs were added to a solution of 0.108 g (0.14 mmol, 1.0 eq.) of **11c** in 5 mL THF via a transfer canula in 4 mL THF at –80 °C. After stirring for

5 min, 0.05 mL (0.059 g, 0.27 mmol, 2.0 eq.) Ph_2PCI were added and the colourless solution was stirred for 0.5 h. The solvent was removed *in vacuo* (≤ 0.05 mbar) and the colourless, oily residue was extracted with three times 2–4 mL toluene. After removal of the solvent *in vacuo* (≤ 0.05 mbar) the residue was washed with three times 3–4 mL *n*-pentane. After drying for 4 h (≤ 0.02 mbar) a colourless solid was obtained.

Reaction code: TT-556 (15p5a014.22)

Molecular formula: $\text{C}_{54}\text{H}_{68}\text{F}_6\text{N}_4\text{O}_6\text{P}_4\text{S}_2$

Molecular weight: 1171.17 g mol⁻¹

Yield: 0.082 g (0.07 mmol, 52 %)

Melting point: 217 °C

MS (pos. ESI): m/z (%) = 4436.219 (24) $[\text{M}-2\text{OTf}]^{2+}$, 394.173 (12) $[\text{M}-2\text{OTf}-\text{C}_6\text{H}_{12}]^{2+}$, 344.198 (100) $[\text{M}-2\text{OTf}-\text{PPh}_2+\text{H}]^{2+}$, 302.151 (59) $[\text{M}-2\text{OTf}-\text{PPh}_2-\text{C}_6\text{H}_{12}+\text{H}]^{2+}$, 252.176 (14) $[\text{M}-2\text{OTf}-2\text{PPh}_2+2\text{H}]^{2+}$, 210.129 (12) $[\text{M}-2\text{OTf}-2\text{PPh}_2-\text{C}_6\text{H}_{12}+2\text{H}]^{2+}$, 185.052 (9) $[\text{PPh}_2]^+$.

HRMS (pos. ESI): m/z calculated $[\text{C}_{52}\text{H}_{68}\text{N}_4\text{P}_4]^{2+}$: 436.2192; found: 436.2193.

IR (ATR): $\tilde{\nu}$ / cm⁻¹ = 3054 (w, $\nu_{\text{as}}(\text{CH})$), 2959 (w, $\nu_{\text{as}}(\text{CH}_3)$, $\nu_{\text{s}}(\text{CH}_2)$), 2931 (w, $\nu_{\text{as}}(\text{CH}_3)$, $\nu_{\text{s}}(\text{CH}_2)$), 2873 (w, $\nu_{\text{s}}(\text{CH}_3)$, $\nu_{\text{as}}(\text{CH}_2)$).

¹H NMR (500.04 MHz, 298.0 K, C_6D_6): δ / ppm = 0.53–0.60 (m, 6H, $\text{CH}_3(\text{N}(n\text{-Bu}))$), 0.62–0.69 (m, 6H, $\text{CH}_3(\text{N}(n\text{-Bu}))$), 0.72–0.89 (m, 4H, $\text{NCH}_2\text{CH}_2\text{CH}_2$), 0.89–1.05 (m, 4H, $\text{NCH}_2\text{CH}_2\text{CH}_2$), 0.95 (t, $^3J_{\text{H,H}} = 7.4$ Hz, $\text{CH}_3(\text{PCH}(n\text{-Bu}))$), 1.13–1.24 (m, 2H, NCH_2CH_2), 1.32–1.53 (m, 4H, NCH_2CH_2 , $\text{PCHCH}_2\text{CH}_2\text{CH}_2$), 1.52–1.65 (m, 2H, $\text{PCHCH}_2\text{CH}_2$), 1.67–1.87 (m, 6H, NCH_2CH_2 , $\text{PCHCH}_2\text{CH}_2$), 2.47–2.57 (m, 1H, PCH), 2.55–2.68 (m, 1H, PCH_2), 3.46–3.55 (m, 1H, PCH_2), 4.51–5.00 (m, 8H, NCH_2), 6.98–6.95 (m, 2H, *para*-CH), 7.01–7.06 (m, 2H, *para*-CH), 7.06–7.14 (m, 4H, *meta*-CH), 7.54–7.60 (m, 4H, *meta*-CH), 7.60–7.66 (m, 4H, *ortho*-CH), 7.70–7.80 (m, 4H, *ortho*-CH).

¹³C{¹H} NMR (125.75 MHz, 298.0 K, C_6D_6): δ / ppm = 13.5–13.7 (s, $\text{CH}_3(\text{N}(n\text{-Bu}))$), 14.1 (s, $\text{CH}_3(\text{PCH}(n\text{-Bu}))$), 19.8 (s, $\text{NCH}_2\text{CH}_2\text{CH}_2$), 19.9 (s, $\text{NCH}_2\text{CH}_2\text{CH}_2$), 20.1 (m, $\text{NCH}_2\text{CH}_2\text{CH}_2$), 22.9 (s, $\text{PCHCH}_2\text{CH}_2\text{CH}_2$), 26.2 (d, $J_{\text{P,C}} = 12.4$ Hz, PCH_2), 31.8 (d, $J_{\text{P,C}} = 14.0$ Hz, $\text{PCHCH}_2\text{CH}_2$), 33.2 (m, NCH_2CH_2), 33.8 (m, NCH_2CH_2), 35.1 (d, $J_{\text{P,C}} = 15.4$ Hz, PCHCH_2), 36.8–37.0 (m, PCH), 50.3–50.8 (m, NCH_2), 122.1 (q, $^1J_{\text{F,C}} = 322.2$ Hz, CF_3), 129.5–129.7 (m, *para*-C), 130.1–130.4 (m, *para*-C, *meta*-C), 130.5–130.8 (m, *meta*-C), 133.7–134.8 (m, *ortho*-C), 142.5 (m, $J_{\text{P,C}} = 15.6$ Hz, $J_{\text{P,C}} = 4.0$ Hz, PC), 144.0 (dd, $J_{\text{P,C}} = 15.1$ Hz, $J_{\text{P,C}} = 3.1$ Hz, PC), 145.9–146.1 (m, PC), 146.1 (d, $^1J_{\text{P,C}} = 58.7$ Hz, CPh_2), 143.6–146.7 (m, PC), 146.8 (d, $^1J_{\text{P,C}} = 57.9$ Hz, CPh_2).

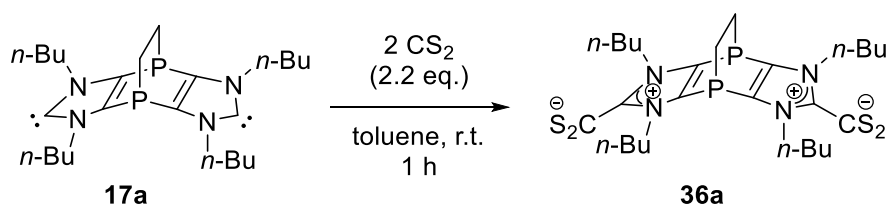
^{31}P NMR (202.44 MHz, 298.0 K, C_6D_6): δ / ppm = -87.1 (m, PCH_2), -86.8 (m, PCH), -25.5 (m, PPh_2), 25.1 (m, PPh_2).

$^{31}\text{P}\{^1\text{H}\}$ NMR (202.44 MHz, 298.0 K, C_6D_6): δ / ppm = -87.1 (d, $^3J_{\text{P,P}} = 15.7$ Hz, PCH_2), -86.8 (d, $^3J_{\text{P,P}} = 15.7$ Hz, PCH), -25.5 (s, PPh_2), 25.1 (s, PPh_2).

X-ray diffraction analysis: Gxraymo_6889f (GSTR764), moderate structure (D1)

5.5.15 Synthesis of bis(NHC) CS_2 adducts **36**

5.5.15.1 Synthesis of 1,3,5,7-tetrabutyl-9,10-diethyl-1,5-dihydro-4,8-ethano[1,4]diphosphino[2,3-d:5,6-d']di-2,6-bis(dithiocarboxy)imidazolium **36a**



Synthesis

In a 15 mL Schlenk tube 0.02 mL (0.019 g, 0.25 mmol, 2.2 eq.) CS_2 were added dropwise to a solution of 0.051 g (0.11 mmol, 1.0 eq.) of **17a** in 2 mL toluene. After stirring for 40 min the red reaction solution was filtered through a syringe equipped with filtering paper and the reaction mixture extracted with additional 2.5 mL toluene and 2.75 mL THF. The solvent was removed *in vacuo* (≤ 0.05 mbar) and the red, oily residue was washed with twice 2 mL diethyl ether and five times 2 mL *n*-pentane. After drying for 2 h (≤ 0.02 mbar) a red solid was obtained.

Reaction code: TT-851 (TAT230706p5a057)

Molecular formula: $\text{C}_{26}\text{H}_{40}\text{N}_4\text{P}_2\text{S}_4$

Molecular weight: $598.82 \text{ g mol}^{-1}$

Yield: 0.026 g (0.04 mmol, 39 %)

Melting point: 210°C

EA: calculated (%)	C 52.15	H 6.73	N 9.36	S 21.42
found (%)	C 51.93	H 6.63	N 9.29	S 20.56

MS (pos. ESI): m/z (%) = 599.169 (24) $[\text{M}+\text{H}]^+$, 523.224 (100) $[\text{M}-\text{CS}_2+2\text{H}]^+$.

HRMS (pos. ESI): m/z calculated $[\text{C}_{30}\text{H}_{48}\text{N}_4\text{P}_2\text{S}_4\text{H}]^+$: 599.1684; found: 599.1688.

IR (ATR): $\tilde{\nu} / \text{cm}^{-1} = 2956$ (w, $\nu_{\text{as}}(\text{CH}_3)$, $\nu_{\text{s}}(\text{CH}_2)$, $\nu(\text{CH})$), 2929 (w, $\nu_{\text{as}}(\text{CH}_3)$, $\nu_{\text{s}}(\text{CH}_2)$), 2869 (w, $\nu_{\text{s}}(\text{CH}_3)$, $\nu_{\text{as}}(\text{CH}_2)$), 1468 (m, $\nu_{\text{as}}(\text{NCN})$), 1052 (s, $\nu_{\text{as}}(\text{CS}_2)$).

UV/vis: λ / nm (abs.) = 288 (0.62, NCN), 361 (1, CS_2).

^1H NMR (500.04 MHz, 298.0 K, THF-d_8): $\delta / \text{ppm} = 0.94$ (t, $^3J_{\text{H,H}} = 7.4$ Hz, 12H, CH_3), 1.35–1.43 (m, 8H, $\text{NCH}_2\text{CH}_2\text{CH}_2$), 1.87–1.95 (m, 8H, NCH_2CH_2), 2.16 (t, $J_{\text{P,C}} = 5.3$ Hz, 4H, PCH_2), 4.22–4.36 (m, 8H, NCH_2).

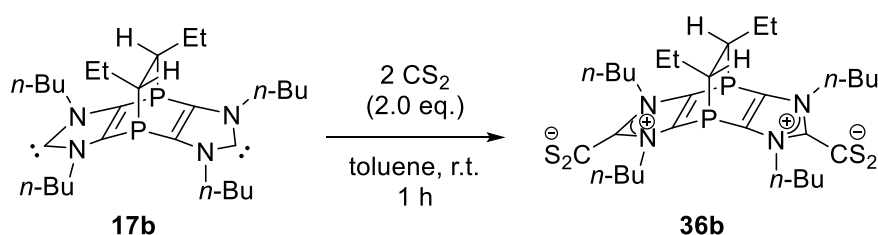
$^{13}\text{C}\{^1\text{H}\}$ NMR (125.75 MHz, 298.0 K, THF-d_8): $\delta / \text{ppm} = 14.2$ (s, CH_3), 20.0 (dd, $J_{\text{P,C}} = 6.0$ Hz, PCH_2), 21.0 (s, CH_2CH_3), 33.9 (m, NCH_2CH_2), 48.3 (m, NCH_2), 138.5 (dd, $J_{\text{P,C}} = 8.1$ Hz, $J_{\text{P,C}} = 6.3$ Hz, PC), 152.4 (s, CCS_2), 224.9 (s, CS_2).

^{31}P NMR (202.41 MHz, 298.0 K, THF-d_8): $\delta / \text{ppm} = -95.4$ (m).

$^{31}\text{P}\{^1\text{H}\}$ NMR (202.41 MHz, 298.0 K, THF-d_8): $\delta / \text{ppm} = -95.4$ (s).

X-ray diffraction analysis: Gxray7591 (GSTR825), moderate structure (D1)

5.5.15.2 Synthesis of 1,3,5,7-tetrabutyl-9,10-diethyl-1,5-dihydro-4,8-ethano[1,4]diphosphinino[2,3-d:5,6-d']di-2,6-bis(dithiocarboxy)imidazolium **36b**



Synthesis

In a 15 mL Schlenk tube 0.02 mL (0.029 g, 0.37 mmol, 2.0 eq.) CS_2 were added dropwise to a solution of 0.094 g (0.19 mmol, 1.0 eq.) of **17b** in 3 mL toluene. After stirring for 1 h the solvent was removed *in vacuo* (≤ 0.05 mbar) and the red, oily residue was extracted with three times 2–5 mL toluene. After removal of the solvent *in vacuo* (≤ 0.05 mbar) the residue was washed with three times 3–5 mL *n*-pentane at -60 °C. After drying for 4 h (≤ 0.02 mbar) a red solid was obtained.

Reaction code: TT-790 (TAT230504p5a056)

Molecular formula: $\text{C}_{30}\text{H}_{48}\text{N}_4\text{P}_2\text{S}_4$

Molecular weight: $654.93 \text{ g mol}^{-1}$

Yield: 0.075 g (0.12 mmol, 61 %)

Melting point: 96 °C

EA: calculated (%) C 55.02 H 7.39 N 8.55 S 19.58

found (%) C 54.56 H 7.11 N 8.45 S 18.40

MS (pos. ESI): m/z (%) = 655.230 (47) $[M+H]^+$.

HRMS (pos. ESI): m/z calculated $[C_{30}H_{48}N_4P_2S_4H]^+$: 655.2310; found: 655.2312.

IR (ATR): $\tilde{\nu}$ / cm^{-1} = 2956 (w, $\nu_{\text{as}}(\text{CH}_3)$, $\nu_{\text{s}}(\text{CH}_2)$), 2930 (w, $\nu_{\text{as}}(\text{CH}_3)$, $\nu_{\text{s}}(\text{CH}_2)$), 2870 (w, $\nu_{\text{s}}(\text{CH}_3)$, $\nu_{\text{as}}(\text{CH}_2)$), 1469 (m, $\nu_{\text{as}}(\text{NCN})$), 1054 (s, $\nu_{\text{as}}(\text{CS}_2)$).

UV/vis: λ / nm (abs.) = 287 (0.65, NCN), 363 (1, CS_2).

^1H NMR (500.04 MHz, 298.0 K, C_6D_6): δ / ppm = 0.79 (tm, $^3J_{\text{H,H}} = 7.3$ Hz, 12H, $\text{CH}_3(n\text{-Bu})$), 0.86–0.93 (m, 8H, PCHCH_2 , $\text{CH}_3(\text{Et})$), 1.12–1.26 (m, 12H, $\text{NCH}_2\text{CH}_2\text{CH}_2$, PCHCH_2 , PCH), 1.75–1.86 (m, 2H, NCH_2CH_2), 1.88–1.96 (m, 4H, NCH_2CH_2), 1.97–2.05 (m, 2H, NCH_2CH_2), 4.23–4.43 (m, 8H, NCH_2).

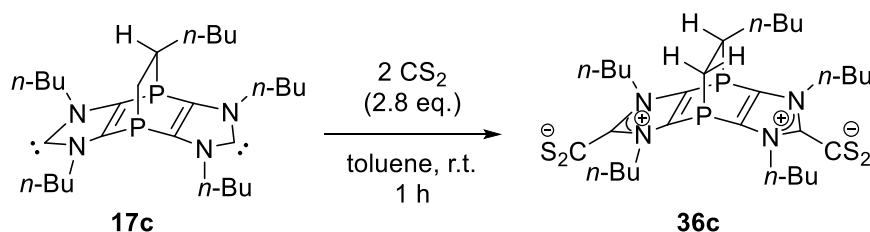
$^{13}\text{C}\{^1\text{H}\}$ NMR (125.75 MHz, 298.0 K, C_6D_6): δ / ppm = 13.8 (m, $\text{CH}_3(n\text{-Bu})$, $\text{CH}_3(\text{Et})$), 20.3 (m, $\text{NCH}_2\text{CH}_2\text{CH}_2$), 27.7 (dd, $J_{\text{P,C}} = 9.1$ Hz, PCHCH_2), 33.3 (s, NCH_2CH_2), 33.4 (s, NCH_2CH_2), 46.2 (dd, $J_{\text{P,C}} = 6.0$ Hz, PCH), 48.4 (dm, $J_{\text{P,C}} = 11.8$ Hz, NCH_2), 135.9 (dd, $J_{\text{P,C}} = 10.6$ Hz, $J_{\text{P,C}} = 7.0$ Hz, PC), 138.9 (m, PC), 152.7 (s, CCS_2), 223.8 (s, CS_2).

^{31}P NMR (202.41 MHz, 298.0 K, C_6D_6): δ / ppm = -87.1 (m).

$^{31}\text{P}\{^1\text{H}\}$ NMR (202.41 MHz, 298.0 K, C_6D_6): δ / ppm = -87.1 (s).

X-ray diffraction analysis: Gxray7570 (GSTR838), moderate structure (D1)

5.5.15.3 Synthesis of 1,3,5,7-tetrabutyl-9-butyl-1,5-dihydro-4,8-ethano[1,4]diphosphinino[2,3-d:5,6-d']di-2,6-bis(dithiocarboxy)imidazolium **36c**



Synthesis

In a 15 mL Schlenk tube 0.02 mL (0.025 g, 0.33 mmol, 2.8 eq.) CS_2 were added dropwise to a solution of 0.058 g (0.12 mmol, 1.0 eq.) of **17c** in 2 mL toluene. After stirring for 1 h the red reaction solution was filtered through a syringe equipped with filtering paper and the reaction mixture extracted with additional 2 mL toluene. After removal of the solvent *in vacuo* (≤ 0.05 mbar) the residue was washed with twice 2 mL diethyl ether and five times 2 mL *n*-pentane. After drying for 2 h (≤ 0.02 mbar) a red solid was obtained.

Reaction code: TT-850 (TAT230706p5a058)

Molecular formula: C₃₀H₄₈N₄P₂S₄

Molecular weight: 654.93 g mol⁻¹

Yield: 0.022 g (0.03 mmol, 29 %)

Melting point: 138 °C

EA: calculated (%)	C 55.02	H 7.39	N 8.55	S 19.58
found (%)	C 55.02	H 7.46	N 8.44	S 17.94

MS (pos. ESI): m/z (%) = 655.230 (33) [M+H]⁺, 181.170 (100) [C₁₁H₂₁N₂]⁺.

HRMS (pos. ESI): m/z calculated [C₃₀H₄₈N₄P₂S₄H]⁺: 655.2310; found: 655.2314.

IR (ATR): $\tilde{\nu}$ / cm⁻¹ = 2957 (w, $\nu_{as}(\text{CH}_3)$, $\nu_s(\text{CH}_2)$), 2927 (w, $\nu_{as}(\text{CH}_3)$, $\nu_s(\text{CH}_2)$), 2870 (w, $\nu_s(\text{CH}_3)$, $\nu_{as}(\text{CH}_2)$), 1467 (m, $\nu_{as}(\text{NCN})$), 1054 (s, $\nu_{as}(\text{CS}_2)$).

UV/vis: λ / nm (abs.) = 287 (0.66, NCN), 364 (1, CS₂).

¹H NMR (499.96 MHz, 298.0 K, THF-d₈): δ / ppm = 0.89–0.98 (m, 15H, CH₃(N(*n*-Bu)), CH₃(PCH(*n*-Bu))), 1.31–1.45 (m, 12H, NCH₂CH₂CH₂, PCHCH₂CH₂CH₂), 1.48–1.58 (m, 2H, PCHCH₂CH₂), 1.59–1.66 (m, 1H, PCH₂), 1.80–2.20 (m, 8H, NCH₂CH₂), 2.38–2.47 (m, 1H, PCH), 2.50–2.59 (m, 1H, PCH₂), 4.20–4.37 (m, 8H, NCH₂).

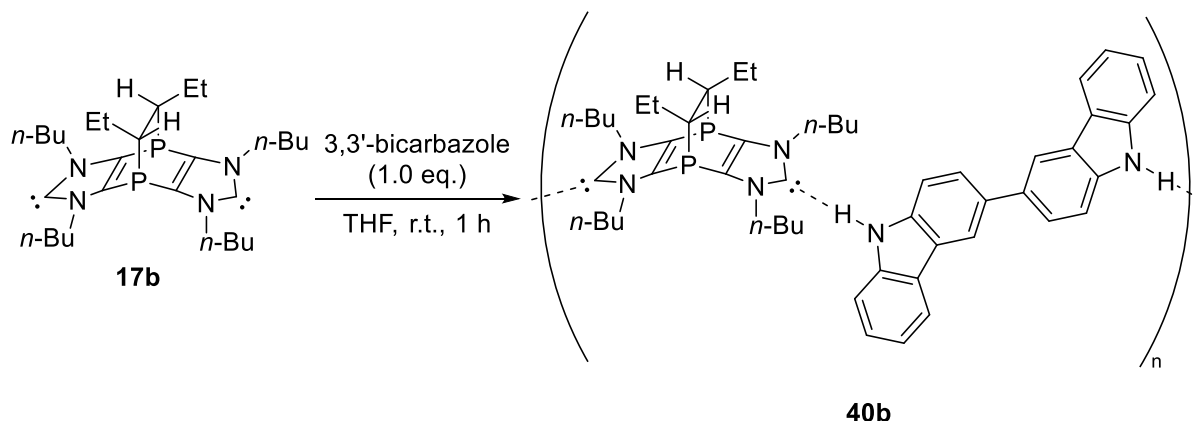
¹³C{¹H} NMR (125.73 MHz, 298.0 K, THF-d₈): δ / ppm = 14.1–14.2 (m, CH₃(N(*n*-Bu)), CH₃(PCH(*n*-Bu))), 14.4 (m, CH₃(N(*n*-Bu)), CH₃(PCH(*n*-Bu))), 20.9–21.0 (s, NCH₂CH₂CH₂), 23.5 (s, PCHCH₂CH₂CH₂), 27.6 (d, $J_{P,C}$ = 10.1 Hz, $J_{P,C}$ = 3.9 Hz, PCH₂), 32.3 (d, $J_{P,C}$ = 15.3 Hz, PCHCH₂CH₂), 33.8–34.0 (m, NCH₂CH₂), 34.1 (m, NCH₂CH₂), 36.1 (dm, $J_{P,C}$ = 16.7 Hz, PCHCH₂), 36.8 (dd, $J_{P,C}$ = 7.3 Hz, $J_{P,C}$ = 2.4 Hz, PCH), 48.3–48.5 (m, NCH₂), 136.8 (dd, $J_{P,C}$ = 15.5 Hz, $J_{P,C}$ = 3.9 Hz, PC), 138.2 (dd, $J_{P,C}$ = 10.8 Hz, $J_{P,C}$ = 3.6 Hz, PC), 139.8 (dd, $J_{P,C}$ = 10.2 Hz, $J_{P,C}$ = 3.6 Hz, PC), 140.4 (dd, $J_{P,C}$ = 9.1 Hz, $J_{P,C}$ = 4.4 Hz, PC), 152.4 (s, CCS₂), 152.8 (s, CCS₂), 224.8 (s, CS₂).

³¹P NMR (202.41 MHz, 298.0 K, THF-d₈): δ / ppm = -92.0 (m, PCH₂), -88.6 (m, PCH).

³¹P{¹H} NMR (202.41 MHz, 298.0 K, THF-d₈): δ / ppm = -92.0 (d, $^3J_{P,P}$ = 17.0 Hz, PCH₂), -88.6 (d, $^3J_{P,P}$ = 17.0 Hz, PCH).

X-ray diffraction analysis: Gxray7592 (GSTR839), bad structure (F)

5.5.16 Synthesis of 1,3,5,7-tetrabutyl-9,10-diethyl-1,3,5,7-tetrahydro-2*H*,6*H*-4,8-ethano[1,4]diphosphinino[2,3-*d*:5,6-*d'*]diimidazole-2,6-ylidene—3,3'-Bi-9*H*-carbazole (1/1) **40b**



Synthesis

In a 10 mL vial in the glovebox 0.057 g (0.17 mmol, 1.0 eq.) 3,3'-bicarbazole in 3.5 mL THF were added in two portions to a solution of 0.086 g (0.17 mmol, 1.0 eq.) of **17b** in 4 mL THF. The yellow solution was shaken and let stand for 1 h. After solvent removal *in vacuo* (≤ 0.05 mbar) and drying for 2 h (≤ 0.05 mbar) an intensive yellow solid was obtained.

Reaction code: TT-620 (TT-620-2)

Molecular formula: C₅₂H₆₄N₆P₂

Molecular weight: 835.07 g mol⁻¹

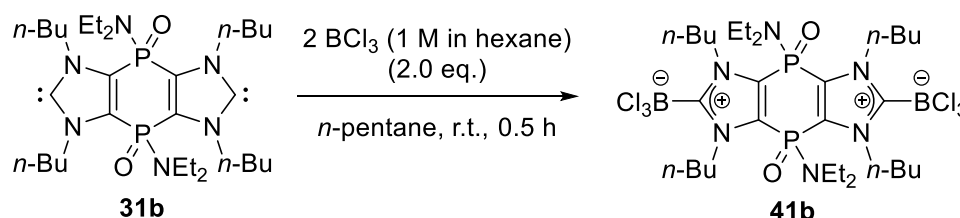
Yield: 0.140 g (0.17 mmol, 98 %)

¹H NMR (500.24 MHz, 298.0 K, THF-*d*₈): δ / ppm = 0.79 (tm, $^3J_{\text{H,H}} = 7.4$ Hz, 12H, CH₃(*n*-Bu)), 1.07 (t, 6H, $^3J_{\text{H,H}} = 7.1$ Hz, CH₃(Et)), 1.11–1.20 (m, 2H, PCHCH₂, PCH), 1.22–1.36 (m, 10H, NCH₂CH₂CH₂, PCHCH₂, PCH), 1.36–1.47 (m, 2H, PCHCH₂, PCH), 1.68–1.81 (m, 8H, NCH₂CH₂), 4.00–4.16 (m, 8H, NCH₂), 7.09 (dd, $^3J_{\text{H,H}} = 7.5$ Hz, 2H, CH), 7.29 (dd, $^3J_{\text{H,H}} = 7.6$ Hz, 2H, CH), 7.45 (d, $^3J_{\text{H,H}} = 8.1$ Hz, 2H, CH), 7.51 (d, $^3J_{\text{H,H}} = 8.3$ Hz, 2H, CH), 7.72 (dd, $^3J_{\text{H,H}} = 8.4$ Hz, $^4J_{\text{H,H}} = 1.9$ Hz, 2H, CH), 8.13 (d, $^3J_{\text{H,H}} = 7.7$ Hz, 2H, CH), 7.09 (d, $^4J_{\text{H,H}} = 1.8$ Hz, 2H, CH), 10.76–11.21 (br s, 2H, NH).

¹³C{¹H} NMR (125.80 MHz, 298.0 K, THF-*d*₈): δ / ppm = 14.2–14.4 (m, CH₃(*n*-Bu), CH₃(Et)), 20.7 (m, NCH₂CH₂CH₂), 29.1 (m, PCHCH₂), 33.5 (s, NCH₂CH₂), 33.6 (s, NCH₂CH₂), 46.7 (dd, $J_{\text{P,C}} = 6.0$ Hz, PCH), 50.2 (dm, $J_{\text{P,C}} = 15.8$ Hz, NCH₂), 112.1 (s, CH), 118.9 (s, CH), 119.1 (s, CH), 120.9 (s, CH), 124.9 (s, C), 125.1 (s, C), 125.9 (s, CH), 126.0 (s, CH), 134.2 (s, C), 139.9 (m, PC), 141.4 (m, CNH), 142.3 (m, PC), 143.0 (m, CNH), 214.8 (br s, C²).

$^{31}\text{P}\{^1\text{H}\}$ NMR (202.49 MHz, 298.0 K, THF- d_8): δ / ppm = -86.9 (s).

5.5.17 Synthesis of 1,3,5,7-tetrabutyl-4,8-bis(diethylamino)-4,8-dioxo-1,5-dihydro-4,8-[1,4]diphosphinino[2,3-d:5,6-d']di-2,6-bis(trichloroborato)imidazolium 41b



Synthesis

In a 50 mL Schlenk tube 0.44 mL (0.44 mmol, 2.0 eq.) BCl_3 (1 M in hexane) were added dropwise to a solution of 0.131 g (0.22 mmol, 1.0 eq.) of **31b** in 10 mL *n*-pentane. After stirring for 0.5 h the solvent was removed *in vacuo* (≤ 0.05 mbar) yielding a beige solid which was purified via column chromatography at -20°C (Al_2O_3 , $h = 7$ cm, $d = 1$ cm, eluent diethyl ether/dichloromethane) collecting the second fraction in dichloromethane. After solvent removal *in vacuo* (≤ 0.05 mbar) the residue was washed with three times 1–1.5 mL *n*-pentane and dried for 3 h (≤ 0.02 mbar) yielding a colourless solid.

Reaction code: TT-274 (35p5a032.20)

Molecular formula: $\text{C}_{30}\text{H}_{56}\text{B}_2\text{Cl}_2\text{N}_6\text{O}_2\text{P}_2$

Molecular weight: 829.09 g mol^{-1}

Yield: 0.004 g (0.005 mmol, 2 %)

Melting point: $> 220^\circ\text{C}$

MS (EI, 70 eV): m/z (%) = 675.3 (100) $[\text{M}-\text{BCl}_4]^+$, 594.3 (54) $[\text{M}-2\text{BCl}_3]^+$, 522.2 (35) $[\text{M}-2\text{BCl}_3-\text{NEt}_2]^+$, 466.1 (41) $[\text{M}-2\text{BCl}_3-\text{NEt}_2-\text{C}_4\text{H}_8]^+$, 72.0 (35) $[\text{NEt}_2]^+$.

IR (ATR): $\tilde{\nu}$ / cm^{-1} = 2962 (w, $\nu_{\text{as}}(\text{CH}_3)$, $\nu_{\text{s}}(\text{CH}_2)$, $\nu(\text{CH})$), 2873 (w, $\nu_{\text{s}}(\text{CH}_3)$, $\nu_{\text{as}}(\text{CH}_2)$).

^1H NMR (500.14 MHz, 298.0 K, CD_2Cl_2): δ / ppm = 1.00 (m, $^3J_{\text{H,H}} = 8.7$ Hz, $^3J_{\text{H,H}} = 7.2$ Hz, 24H, CH_3), 1.39–1.52 (m, 8, $\text{NCH}_2\text{CH}_2\text{CH}_2$), 1.94–2.06 (m, 4H, NCH_2CH_2), 2.13–2.25 (m, 4H, NCH_2CH_2), 3.13–3.21 (m, 8H, PNCH_2), 4.12–4.43 (br m, 4H, NCH_2), 5.18–5.30 (br m, 4H, NCH_2).

$^{13}\text{C}\{^1\text{H}\}$ NMR (125.78 MHz, 298.0 K, CD_2Cl_2): δ / ppm = 13.7 (s, CH_3), 20.1 (s, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 34.2 (s, NCH_2CH_2), 38.2 (d, $J_{\text{P,C}} = 5.0$ Hz, NCH_2CH_3), 51.7 (s, NCH_2), 131.1 (d, $J_{\text{P,C}} = 20.1$ Hz, PC), 132.3 (d, $J_{\text{P,C}} = 20.2$ Hz, PC).

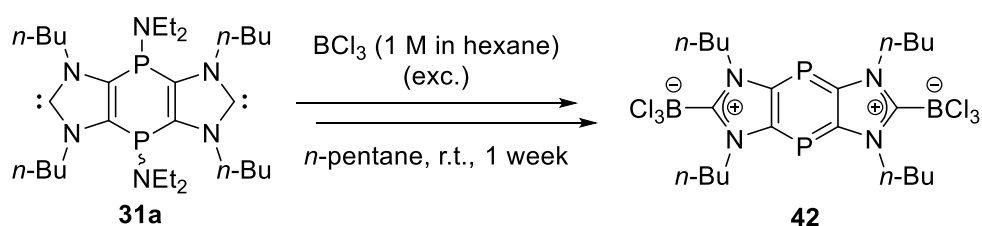
^{31}P NMR (202.48 MHz, 298.0 K, CD_2Cl_2): δ / ppm = -4.7 (m).

$^{31}\text{P}\{^1\text{H}\}$ NMR (202.48 MHz, 298.0 K, CD_2Cl_2): δ / ppm = -4.7 (s).

$^{11}\text{B}\{^1\text{H}\}$ NMR (160.46 MHz, 298.0 K, CD_2Cl_2): δ / ppm = 1.8 (s).

X-ray diffraction analysis: Gxraycu_6489f, average structure (C1)

5.5.18 Generation of 1,3,5,7-tetrabutyl-1,5-dihydro-[1,4]diphosphinino[2,3-d:5,6-d']di-2,6-bis(trichloroborato)imidazolium 42



Synthesis

In a 15 mL Schlenk tube 0.46 mL (0.46 mmol, 6.0 eq.) BCl_3 (1 M in hexane) were added dropwise to a solution of 0.043 g (0.08 mmol, 1.0 eq.) of **31a** in 3 mL *n*-pentane. After stirring for 4 h at ambient temperature the solvent was removed *in vacuo* (≤ 0.05 mbar) yielding a light-yellow solid. After washing with three times 3–6 mL *n*-pentane and drying for 1 h (≤ 0.02 mbar) a light-yellow solid was obtained.

Reaction code: TT-369 (09t4a101.21), TT-933 (TAT231020p5a054)

Molecular formula: $\text{C}_{22}\text{H}_{36}\text{B}_2\text{Cl}_6\text{N}_4\text{P}_2$

Molecular weight: $652.83 \text{ g mol}^{-1}$

Yield: not determined due to remaining impurities

Melting point not determined due to remaining impurities

Content in mixture: up to 94 % ($^{31}\text{P}\{^1\text{H}\}$ NMR integration of isolated reaction mixture)

MS (pos. ESI): m/z (%) = 569.170 (10) $[\text{M}-\text{BCl}_3+\text{O}_2+3\text{H}]^+$, 533.193 (27) $[\text{M}-\text{BCl}_4+\text{O}_2+2\text{H}]^+$, 453.254 (100) $[\text{M}-2\text{BCl}_3+\text{O}_2+3\text{H}]^+$, 437.259 (80) $[\text{M}-2\text{BCl}_3+\text{OH}+2\text{H}]^+$, 227.131 (80) $[\text{M}-2\text{BCl}_3+\text{O}_2+4\text{H}]^{2+}$.

MS (neg. ESI): m/z (%) = 669.074 (41) $[\text{M}+\text{OH}]^-$, 685.0685 (14) $[\text{M}+\text{O}_2+\text{H}]^-$.

HRMS (neg. ESI): m/z calculated $[\text{C}_{22}\text{H}_{36}\text{B}_2\text{Cl}_6\text{N}_4\text{P}_2\text{OH}]^-$: 669.0746; found: 669.0743.

IR (ATR): $\tilde{\nu}$ / cm^{-1} = 2963 (w, $\nu_{\text{as}}(\text{CH}_3)$, $\nu_{\text{s}}(\text{CH}_2)$, $\nu(\text{CH})$), 2934 (w, $\nu_{\text{as}}(\text{CH}_3)$, $\nu_{\text{s}}(\text{CH}_2)$, $\nu(\text{CH})$), 2876 (w, $\nu_{\text{s}}(\text{CH}_3)$, $\nu_{\text{as}}(\text{CH}_2)$).

^1H NMR (500.14 MHz, 298.0 K, CD_2Cl_2): δ / ppm = 1.07 (t, $^3J_{\text{H,H}} = 7.4$ Hz, 12H, CH_3), 1.52–1.65 (m, 8H, $\text{NCH}_2\text{CH}_2\text{CH}_2$), 2.16–2.27 (m, 8H, NCH_2CH_2), 4.83–4.90 (m, 4H, NCH_2), 5.19–5.26 (m, 4H, NCH_2).

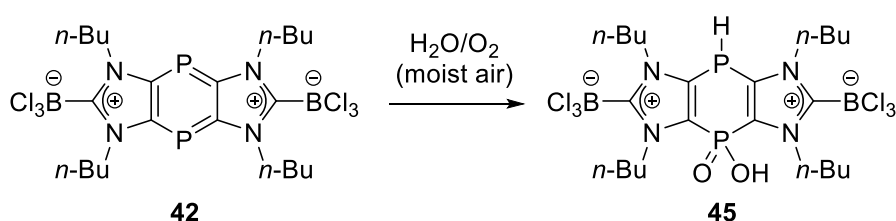
$^{13}\text{C}\{^1\text{H}\}$ NMR (125.78 MHz, 298.0 K, CD_2Cl_2): δ / ppm = 13.7 (m, CH_3), 20.4 (m, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 31.2 (m, NCH_2CH_2), 50.5–50.9 (m, NCH_2), 155.7 (d, $J_{\text{P,C}} = 24.7$ Hz, PC), 162.7 (br m, $\text{C}(\text{BCl}_3)$).

^{31}P NMR (162.00 MHz, 298.0 K, CD_2Cl_2): δ / ppm = 118.6 (s).

$^{31}\text{P}\{^1\text{H}\}$ NMR (162.00 MHz, 298.0 K, CD_2Cl_2): δ / ppm = 118.6 (s).

$^{11}\text{B}\{^1\text{H}\}$ NMR (128.38 MHz, 298.0 K, CD_2Cl_2): δ / ppm = 2.1 (br s).

5.5.19 Generation of 1,3,5,7-tetrabutyl-4-hydrido-8-hydroxy-8-oxo-1,5-dihydro-4,8-[1,4]diphosphinino[2,3-d:5,6-d']di-2,6-bis(trichloroborato)imidazolium **45**



Synthesis

In a 10 mL vial 0.005 g (<0.01 mmol, 1.0 eq.) of **42** in 94 % purity were exposed to moist air for 1.5 h leading to fading of the yellow colour. The beige solid was analysed via NMR spectroscopy.

Reaction code: TT-369-4 (10m3a041.21)

Molecular formula: $\text{C}_{22}\text{H}_{38}\text{B}_2\text{Cl}_6\text{N}_4\text{O}_2\text{P}_2$

Molecular weight: 686.84 g mol^{-1}

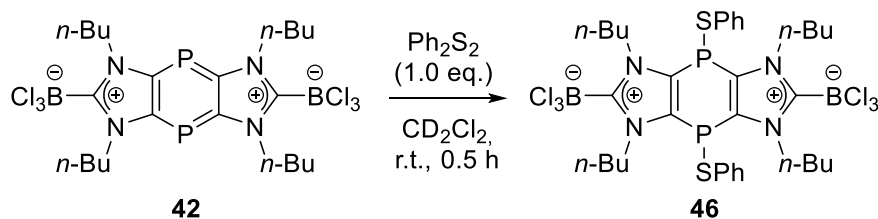
Content in mixture: 91 % ($^{31}\text{P}\{^1\text{H}\}$ NMR integration of reaction mixture)

^{31}P NMR (121.51 MHz, 298.0 K, CH_2Cl_2): δ / ppm = -127.5 (d, $^1J_{\text{P,H}} = 234.4$ Hz, PH), 14.2 (s, $\text{P}(\text{O})\text{OH}$).

$^{31}\text{P}\{^1\text{H}\}$ NMR (121.51 MHz, 298.0 K, CH_2Cl_2): δ / ppm = -127.5 (s, PH), 14.2 (s, $\text{P}(\text{O})\text{OH}$).

$^{11}\text{B}\{^1\text{H}\}$ NMR (96.29 MHz, 298.0 K, CH_2Cl_2): δ / ppm = 2.1 (br s).

5.5.20 Generation of 1,3,5,7-tetrabutyl-4,8-di(phenylsulfanyl)-1,5-dihydro-4,8-[1,4]diphosphinino[2,3-d:5,6-d']di-2,6-bis(trichloroborato)imidazolium 46



Synthesis

To a solution of 0.015 g (0.02 mmol, 1.0 eq.) of **42** in 94 % purity in a *J Young*[®] NMR tube 0.005 g (0.02 mmol, 1.0 eq.) Ph_2S_2 were added. The resulting yellow solution was analysed via NMR spectroscopy after 0.5 h.

Reaction code: TT-369-3 (10p5a018.21)

Molecular formula: $\text{C}_{34}\text{H}_{46}\text{B}_2\text{Cl}_6\text{N}_4\text{P}_2\text{S}_2$

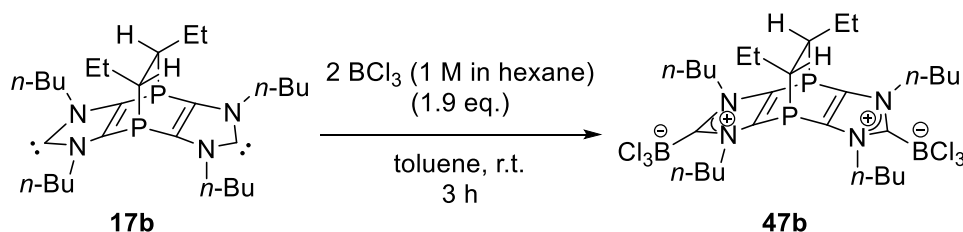
Molecular weight: $871.16 \text{ g mol}^{-1}$

Content in mixture: 85 % ($^{31}\text{P}\{^1\text{H}\}$ NMR integration of reaction mixture)

$^{31}\text{P}\{^1\text{H}\}$ NMR (202.44 MHz, 298.0 K, CD_2Cl_2): δ / ppm = -34.9 (s).

$^{11}\text{B}\{^1\text{H}\}$ NMR (160.43 MHz, 298.0 K, CD_2Cl_2): δ / ppm = 1.9 (br s).

5.5.21 Synthesis of 1,3,5,7-tetrabutyl-9,10-diethyl-1,5-dihydro-4,8-ethano[1,4]diphosphinino[2,3-d:5,6-d']di-2,6-bis(trichloroborato)imidazolium 47b



Synthesis

In a 20 mL Schlenk tube 0.44 mL (0.44 mmol, 1.9 eq.) BCl_3 (1 M in hexane) were added dropwise to a solution of 0.116 g (0.23 mmol, 1.0 eq.) of **17b** in 4 mL toluene. After stirring for 3 h at ambient temperature the solvent was removed *in vacuo* (≤ 0.05 mbar) and the colourless to orange oily residue was extracted with three times 5 mL toluene. After removal of the solvent *in vacuo* (≤ 0.05 mbar) the

colourless residue was washed with two times 3 mL *n*-pentane at $-40\text{ }^{\circ}\text{C}$. After drying for 3 h (≤ 0.02 mbar) a colourless solid was obtained.

Reaction code: TT-763 (TAT230413c5a011)

Molecular formula: $\text{C}_{28}\text{H}_{48}\text{B}_2\text{Cl}_6\text{N}_4\text{P}_2$

Molecular weight: 736.99 g mol^{-1}

Yield: 0.010 g (0.01 mmol, 6 %)

Melting point: $150\text{ }^{\circ}\text{C}$ (dec.)

MS (pos. ESI): m/z (%) = 619.258 (9) $[\text{M}-\text{BCl}_3+\text{H}]^+$, 252.175 (100) $[\text{M}-2\text{BCl}_3+2\text{H}]^{2+}$, 210.128 (87) $[\text{M}-2\text{BCl}_3-\text{C}_6\text{H}_{12}+2\text{H}]^{2+}$.

HRMS (pos. ESI): m/z calculated $[\text{C}_{28}\text{H}_{48}\text{BCl}_3\text{N}_4\text{P}_2\text{H}]^+$: 619.2592; found: 619.2582.

IR (ATR): $\tilde{\nu} / \text{cm}^{-1}$ = 2963 (w, $\nu_{\text{as}}(\text{CH}_3)$, $\nu_{\text{s}}(\text{CH}_2)$), 2932 (w, $\nu_{\text{as}}(\text{CH}_3)$, $\nu_{\text{s}}(\text{CH}_2)$), 2875 (w, $\nu_{\text{s}}(\text{CH}_3)$, $\nu_{\text{as}}(\text{CH}_2)$).

^1H NMR (500.04 MHz, 298.0 K, C_6D_6): δ / ppm = 0.67–0.86 (m, 20H, $\text{CH}_3(n\text{-Bu})$, $\text{CH}_3(\text{Et})$, PCHCH_2), 0.92–0.99 (m, 2H, PCH), 1.00–1.11 (m, 2H, PCHCH_2), 1.19–1.34 (m, 8H, $\text{NCH}_2\text{CH}_2\text{CH}_2$), 1.76–2.02 (m, 8H, NCH_2CH_2), 4.66–4.93 (m, 8H, NCH_2).

$^{13}\text{C}\{^1\text{H}\}$ NMR (125.75 MHz, 298.0 K, C_6D_6): δ / ppm = 13.6–13.8 (m, $\text{CH}_3(n\text{-Bu})$, $\text{CH}_3(\text{Et})$), 20.0 (s, $\text{NCH}_2\text{CH}_2\text{CH}_2$), 20.1 (s, $\text{NCH}_2\text{CH}_2\text{CH}_2$), 27.5 (m, PCHCH_2), 34.7 (m, NCH_2CH_2), 45.8 (dd, $J_{\text{P,C}} = 6.0\text{ Hz}$, PCH), 50.3 (dm, $J_{\text{P,C}} = 10.1\text{ Hz}$, NCH_2), 139.6 (m, PC), 142.7 (m, PC), 158.4 (br s, CBCl_3).

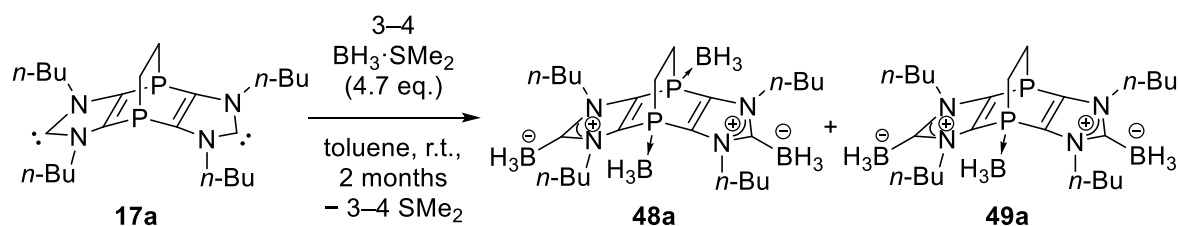
^{31}P NMR (202.44 MHz, 298.0 K, C_6D_6): δ / ppm = -86.8 (m).

$^{31}\text{P}\{^1\text{H}\}$ NMR (202.44 MHz, 298.0 K, C_6D_6): δ / ppm = -86.8 (s).

$^{11}\text{B}\{^1\text{H}\}$ NMR (160.14 MHz, 298.0 K, C_6D_6): δ / ppm = 2.6 (br s).

X-ray diffraction analysis: Gxray7392 (GSTR809), average structure (CD1)

5.5.22 Generation of (1,3,5,7-tetrabutyl-1,3,5,7-tetrahydro-2*H*,6*H*-4,8-ethano[1,4]diphosphinino[2,3-*d*:5,6-*d'*]diimidazole-2,6-ylidene-2κ*C*,6κ*C*,4κ*P*)tris(borane) and (1,3,5,7-tetrabutyl-1,3,5,7-tetrahydro-2*H*,6*H*-4,8-ethano[1,4]diphosphinino[2,3-*d*:5,6-*d'*]diimidazole-2,6-ylidene-2κ*C*,6κ*C*,4κ*P*,8κ*P*)tetrakis(borane) **48a** and **49a**



Synthesis

In a 15 mL Schlenk tube 0.05 mL (0.53 mmol, 4.7 eq.) $\text{BH}_3\cdot\text{SMe}_2$ were added to a solution of 0.050 g (0.11 mmol, 1.0 eq.) of **17a** in 1.5 mL toluene and the reaction solution was stirred at ambient temperature while the reaction course was monitored via $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. After 2 months no change in the composition of the reaction mixture was observed anymore and the solvent was removed *in vacuo* (≤ 0.05 mbar). The resulting colourless residue was washed with three times 3 mL *n*-pentane and after drying for 4 h (≤ 0.02 mbar) the product mixture was obtained as colourless solid and analysed by NMR spectroscopy and SCXRD.

Reaction code: TT-895 (TAT231019p5a042)

Molecular formula: $\text{C}_{24}\text{H}_{52}\text{B}_4\text{N}_4\text{P}_2$ (**48a**), $\text{C}_{24}\text{H}_{49}\text{B}_3\text{N}_4\text{P}_2$ (**49a**)

Molecular weight: 501.90 g mol⁻¹ (**48a**), 488.06 g mol⁻¹ (**49a**)

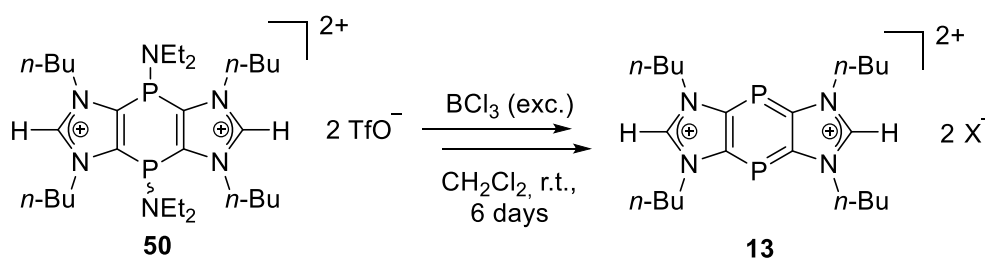
Content in mixture: 62 % (**48a**), 36 % (**49a**) (^{31}P NMR integration of isolated reaction mixture)

^{31}P NMR (202.50 MHz, 298.0 K, CD_2Cl_2): δ / ppm = -99.2 (m, **49a**), -17.7 (br s, **48a**), -15.5 (br s, **49a**).

$^{31}\text{P}\{^1\text{H}\}$ NMR (202.50 MHz, 298.0 K, CD_2Cl_2): δ / ppm = -99.2 (d, $^3J_{\text{P,P}} = 7.3$ Hz, **49a**), -17.7 (s, **48a**), -15.5 (br s, **49a**).

X-ray diffraction analysis: GXray7880_pl (GSTR833)(**48a**), bad structure (E1)

5.5.23 Generation of a salt with the 1,3,5,7-tetrabutyl-1,5-dihydro-[1,4]diphosphino[2,3-d:5,6-d']diimidazolium cation **13**



Synthesis

In a 50 mL *J Young*® flask in the glovebox 1.15 mL (1.15 mmol, 6.0 eq.) BCl_3 (1 M in hexane) were added dropwise to a solution of 0.165 g (0.19 mmol, 1.0 eq.) of **50** in 4 mL dichloromethane leading to a colour change from orange over brown and green to yellow. After stirring for 6 h at ambient temperature the solvent was removed *in vacuo* (≤ 0.05 mbar) yielding a yellow to orange, oily solid which was re-dissolved in 3 mL dichloromethane and another 1.15 mL (1.15 mmol, 6.0 eq.) BCl_3 (1 M in hexane) were added yielding a colour change from red to yellow. After stirring overnight another 1.15 mL (1.15 mmol, 6.0 eq.) BCl_3 (1 M in hexane) were added. After stirring for 19 h the solvent was removed *in vacuo* (≤ 0.05 mbar) yielding a yellow, slightly sticky solid which was washed with five times 2 mL *n*-pentane. After drying for 4 h (≤ 0.02 mbar) a yellow solid was obtained.

Reaction code: TT-888 (TAT230821p5a014)

Molecular formula: $\text{C}_{22}\text{H}_{38}\text{B}_2\text{Cl}_8\text{N}_4\text{P}_2$ ($\text{X} = \text{BCl}_4$), $\text{C}_{22}\text{H}_{38}\text{N}_4\text{P}_2$ (only **13**)

Molecular weight: $725.74 \text{ g mol}^{-1}$ ($\text{X} = \text{BCl}_4$), $420.52 \text{ g mol}^{-1}$ (only **13**)

Yield: not determined due to remaining impurities

Melting point: not determined due to remaining impurities

Content in mixture: 100 % (^{31}P NMR integration of isolated reaction mixture; impurities in $^{11}\text{B}\{^1\text{H}\}$ and ^1H NMR spectra)

MS (pos. ESI): m/z (%) = 603.214 (55) $[\text{M}+\text{OTf}+\text{O}_2+\text{H}]^+$, 569.208 (7) $[\text{M}+\text{OTf}]^+$, 219.133 (27) $[\text{M}+2\text{H}_2\text{O}]^+$, 453.254 (100) $[\text{M}+\text{O}_2+\text{H}]^+$, 437.259 (80) $[\text{M}+\text{OH}]^+$, 210.128 (4) $[\text{M}]^{2+}$. ($\text{M} = \text{13}$)

MS (neg. ESI): m/z (%) = 148.949 (100) $[\text{OTf}]^-$.

HRMS (pos ESI): m/z calculated $[\text{C}_{22}\text{H}_{38}\text{N}_4\text{P}_2\text{OH}]^+$: 437.2594; found: 437.2591.

m/z calculated $[\text{C}_{22}\text{H}_{38}\text{N}_4\text{P}_2\text{F}_3\text{S}_1\text{O}_3]^+$: 569.2086; found: 569.2083.

IR (ATR): $\tilde{\nu}$ / cm^{-1} = 3140 (w, $\nu(\text{CH})$), 3069 (w, $\nu(\text{CH})$), 2963 (w, $\nu_{\text{as}}(\text{CH}_3)$, $\nu_{\text{s}}(\text{CH}_2)$), 2936 (w, $\nu_{\text{as}}(\text{CH}_3)$, $\nu_{\text{s}}(\text{CH}_2)$), 2875 (w, $\nu_{\text{s}}(\text{CH}_3)$, $\nu_{\text{as}}(\text{CH}_2)$).

^1H NMR (499.96 MHz, 298.0 K, CD_2Cl_2): δ / ppm = 1.06 (t, $^3J_{\text{H,H}} = 7.5$ Hz, 12H, CH_3), 1.48–1.60 (m, 8H, $\text{NCH}_2\text{CH}_2\text{CH}_2$), 2.17–2.26 (m, 8H, NCH_2CH_2), 4.81 (t, $^3J_{\text{H,H}} = 7.8$ Hz, 8H, NCH_2), 9.58 (s, 2H, CH).

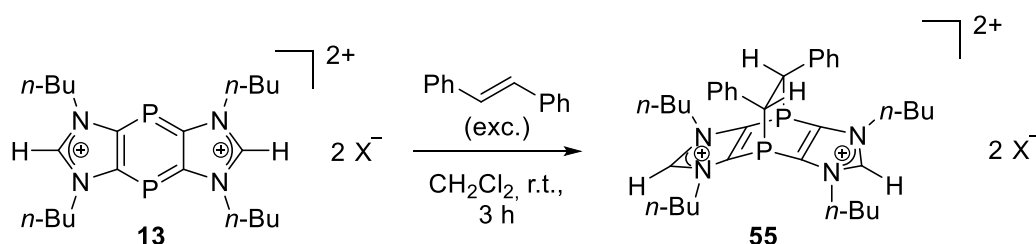
$^{13}\text{C}\{^1\text{H}\}$ NMR (125.73 MHz, 298.0 K, CD_2Cl_2): δ / ppm = 13.6 (s, CH_3), 20.4 (s, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 30.9 (m, NCH_2CH_2), 50.8 (dd, $J_{\text{P,C}} = 4.3$ Hz, NCH_2), 144.4 (t, $^3J_{\text{P,C}} = 3.0$ Hz, CH), 154.5 (t, $J_{\text{P,C}} = 26.7$ Hz, PC).

^{31}P NMR (202.41 MHz, 298.0 K, CD_2Cl_2): δ / ppm = 121.3 (s).

$^{31}\text{P}\{^1\text{H}\}$ NMR (202.41 MHz, 298.0 K, CD_2Cl_2): δ / ppm = 121.3 (s).

$^{11}\text{B}\{^1\text{H}\}$ NMR (160.41 MHz, 298.0 K, CD_2Cl_2): δ / ppm = 6.5 (s, BCl_4).

5.5.24 Generation of a salt with the 1,3,5,7-tetrabutyl-9,10-diphenyl-1,5-dihydro-4,8-ethano[1,4]diphosphinino[2,3-d:5,6-d']diimidazolium cation **55**



Synthesis

A solution of circa 0.050 g of a mixture containing approximately 50 % of **13** (according to ^{31}P NMR spectroscopy) in 3 mL dichloromethane were added to an excess (0.080 g (0.44 mmol)) of *trans*-diphenylethene in a 15 mL Schlenk tube. After stirring for 3 h the solvent was removed *in vacuo* (≤ 0.05 mbar) and the yellow residue was extracted with three times 2–4 mL THF. After solvent removal *in vacuo* (≤ 0.05 mbar) the yellow solid was washed with 5 mL diethyl ether, 5 mL toluene and three times 5 mL *n*-pentane at -40 °C. After drying for 2 h the light-yellow solid was analysed via $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy.

Reaction code: TT-906 (TAT230828m3a004)

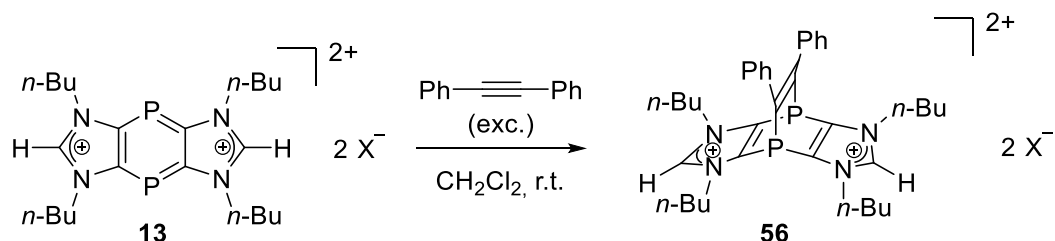
Molecular formula: $\text{C}_{36}\text{H}_{50}\text{N}_4\text{P}_2\text{X}_2$ (**55** with unknown counter ions X)

Molecular weight: $600.77 \text{ g mol}^{-1}$ (only **55**)

Content in mixture: 100 % ($^{31}\text{P}\{^1\text{H}\}$ NMR integration of isolated reaction mixture)

$^{31}\text{P}\{^1\text{H}\}$ NMR (121.51 MHz, 298.0 K, CD_2Cl_2): δ / ppm = -80.6 (s).

5.5.25 Generation of a salt with the 1,3,5,7-tetrabutyl-9,10-diphenyl-1,5-dihydro-4,8-etheno[1,4]diphosphinino[2,3-d:5,6-d']diimidazolium cation **56**



Synthesis

0.010 g of a mixture containing 100 % of **13** (according to ^{31}P NMR spectroscopy) (≈ 0.01 mmol, 1.0 eq.) and 0.046 g (0.26 mmol, ≈ 26 eq.) diphenylethyne were dissolved in 0.5 mL dichloromethane in a *J Young*[®] NMR tube yielding a clear, yellow solution that was analysed via $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy.

Reaction code: TT-900 (TAT230823m3a042)

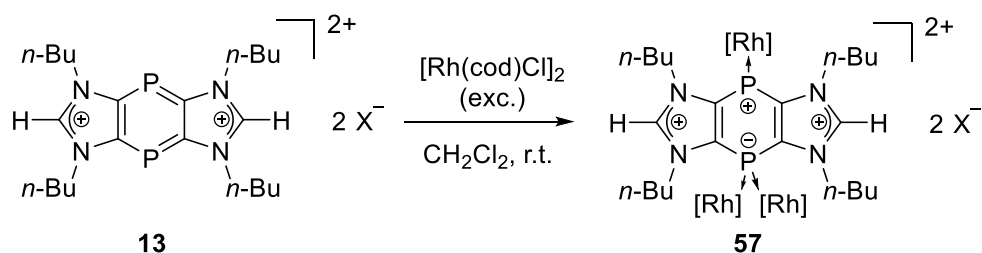
Molecular formula: $\text{C}_{36}\text{H}_{48}\text{N}_4\text{P}_2\text{X}_2$ (**56** with unknown counter ions X)

Molecular weight: $598.33 \text{ g mol}^{-1}$ (only **56**)

Content in mixture: 43 % ($^{31}\text{P}\{^1\text{H}\}$ NMR integration of reaction mixture)

$^{31}\text{P}\{^1\text{H}\}$ NMR (121.51 MHz, 298.0 K, CH_2Cl_2): $\delta / \text{ppm} = -81.2$ (s).

5.5.26 Generation of a salt with the [trichlorido(μ -1,3,5,7-tetrabutyl-1,5-dihydro-[1,4]diphosphinino[2,3-d:5,6-d']diimidazolium-4 κP ,4 κP ,8 κP)tris(η^2,η^2 -cycloocta-1,5-diene)trirhodium(I)] cation **57**



Synthesis

In a 20 mL *J Young*[®] flask a solution of 0.013 g of a mixture containing 100 % of **13** (according to ^{31}P NMR spectroscopy) (≈ 0.02 mmol, 1.0 eq.) in 2 mL dichloromethane was added to 0.037 g (0.08 mmol, ≈ 4.2 eq.) $[\text{Rh}(\text{cod})\text{Cl}]_2$ and stirred for 11 days yielding a brown-yellow solution which was analysed via $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy.

Reaction code: TT-960 (TAT231116m3a022)

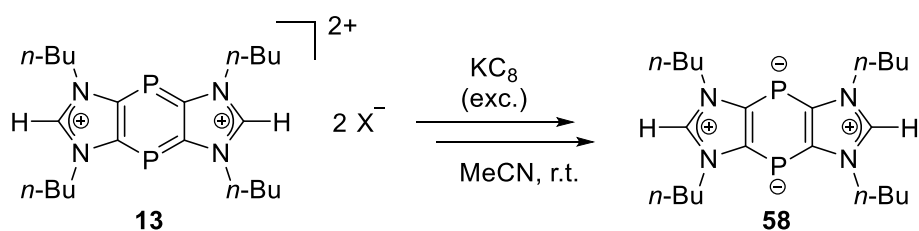
Molecular formula: C₄₆H₇₄Cl₃N₄P₂Rh₃X₂ (**57** with unknown counter ions X)

Molecular weight: 1160.14 g mol⁻¹ (only **57**)

Content in mixture: 100 % (³¹P{¹H} NMR integration of reaction mixture)

³¹P{¹H} NMR (121.51 MHz, 298.0 K, CH₂Cl₂): δ / ppm = -114.6 (t, ¹J_{Rh,P} = 125 Hz, P([Rh])₂), 34.2 (d, ¹J_{Rh,P} = 204 Hz, P[Rh]).

5.5.27 Generation of the double zwitterion 1,3,5,7-tetrabutyl-1,5-dihydro-[1,4]diphosphinino[2,3-d:5,6-d']diimidazolium-4,8-diide **58**



Synthesis

In a *J Young*® NMR tube 0.012 g of a mixture containing 100 % of **13** (according to ³¹P NMR spectroscopy) (≈ 0.02 mmol, 1.0 eq.) and 0.016 g (0.12 mmol, ≈ 7.2 eq.) KC₈ were dissolved in 0.4 mL acetonitrile, immediately yielding a red-brown suspension which was analysed via ³¹P{¹H} NMR spectroscopy over the course of 4 days.

Reaction code: TT-958 (TAT231116m3a022)

Molecular formula: C₂₂H₃₈N₄P₂

Molecular weight: 420.52 g mol⁻¹

Content in mixture: 90 % (³¹P{¹H} NMR integration of reaction mixture)

³¹P{¹H} NMR (121.51 MHz, 298.0 K, CH₂Cl₂): δ / ppm = -79.9 (br s).

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7 APPENDIX

7.1 Abbreviations

7.1.1 Chemical abbreviations

12-crown-4	1,4,7,10-tetraoxacyclododecane
Ad	adamantyl
Ar	aryl
BHT	3,5-di- <i>tert</i> -butyl-4-hydroxytoluene
BINAP	2,2'-bis(diphenylphosphanyl)-1,1'-binaphthalene
Bn	benzyl
cod/COD	cyclooctadiene
cryptand	1,10-diaza-4,7,13,16,21,24-hexaoxabicyclo[8.8.8]hexacosane
DBN	1,5-diazabicyclo[4.3.0]non-5-ene
DIPAMP	bis[(2-methoxyphenyl)phenylphophanyl]ethane
Dipp	2,6-di- <i>iso</i> -propylphenyl
DMAD	dimethyl acetylenedicarboxylate
E	heteroatom
Et	ethyl
HMDS	hexamethyldisilazane = bis(trimethylsilyl)amine
<i>i</i> -Bu	<i>iso</i> -butyl
IMes	1,3-bis(2,4,6-trimethylphenyl)-1,3-dihydro-2 <i>H</i> -imidazol-2-ylidene
<i>i</i> -Pr	<i>iso</i> -propyl
KHMDS	potassium hexamethyldisilazide
M	metal
Me	methyl
Mes	2,4,6-trimethylphenyl
<i>n</i> -Bu	<i>n</i> -butyl
NHC	N-heterocyclic carbene
<i>n</i> -Hex	<i>n</i> -hexyl
<i>n</i> -Pent	<i>n</i> -pentyl
<i>n</i> -Pr	<i>n</i> -propyl
OTf/TfO	trifluoromethane sulfonate

Ph	phenyl
Piv	pivaloyl = 2,2-dimethylpropanoyl
PTA	1,3,5-triaza-7-phosphaadamantane
PTFE	polytetrafluoroethylene
R	organic substituent
<i>t</i> -Amyl	<i>tert</i> -amyl
<i>t</i> -Bu	<i>tert</i> -butyl
thf/THF	tetrahydrofuran
TTF	tetrathiafulvalene
X	halogen

7.1.2 Other abbreviations

$\Delta_r G$	Gibbs reaction energy
$\emptyset$	diameter
1D	one-dimensional
2D	two-dimensional
Å	Ångström (10^{-10} m)
a, b, c, α , β , γ	unit cell parameters
a.u.	arbitrary unit
APCI	atmospheric-pressure chemical ionisation
atm	atmospheric pressure
ATP	adenosine triphosphate
ATR	attenuated total reflection
br	broad
ca.	circa
calc	calculated
COSY	correlated spectroscopy
CPCM	conductor-like polarisable continuum model
CV	cyclic voltammetry
d	doublet
d	day(s)
d	bond distance
dd	doublet of doublets
dm	doublet of multiplets

dec.	decomposition
DFT	density functional theory
DNA	deoxyribonuclei acid
E	orbital energy
E_p^a	anodic peak potential
E_p^c	cathodic peak potential
<i>e.g.</i>	<i>exempli gratia</i> , “for example”
EA	elemental analysis
EI	electron impact ionisation
eq.	equivalent(s)
ESI	electron spray ionisation
exc.	excess
$F(000)$	structure factor evaluated in the 0 th order case ($h = k = l = 0$)
$Fc^{+/0}$	ferrocenium/ferrocene redox couple
FMO	frontier molecular orbital
FTIR	Fourier-transform infrared
FWHM	full width at half maximum
GIAO	Gauge including atomic orbital
h	hour(s)
HMBC	heteronuclear multiple bond correlation
HOMO	highest occupied molecular orbital
HSQC	heteronuclear single quantum coherence
I_p^a	anodic peak current
I_p^c	cathodic peak current
<i>i.e.</i>	<i>id est</i> , “it is”
IR	infrared
irr	irreversible
IUPAC	International Union of Pure and Applied Chemistry
LUMO	lowest unoccupied molecular orbital
<i>m</i>	<i>meta</i>
m	medium
m	multiplet
$[M]^{+•}/[M]^+$	molecular ion
max.	maximum

MBO	Mayer bond order
min	minute(s)
MO	molecular orbital
MS	mass spectrometry
NEB	nudge elastic band
neg.	negative
NICS	nucleus-independent chemical shift
$^nJ_{X,Y}$	coupling constant
NMR	nuclear magnetic resonance
pos.	positive
ppm	parts per million
q	quartet
R^2	coefficient of determination
r.t.	room temperature
RNA	ribonuclei acid
s	strong
s	singlet
sat	satellites
SCXRD	single crystal X-ray diffraction
SPS	solvent purification system
t	triplet
T	temperature
TD-DFT	time-dependent density functional theory
tm	triplet of multiplets
tt	triplet of triplets
UV	ultraviolet
vis	visible
vs	very strong
vs.	versus
w	weak
wt.	weight
Z	number of formula units in a unit cell
ZPE	zero-point energy
δ	chemical shift

ε	dielectric constant
η^n	hapticity
θ	Bragg angle
λ	wavelength
λ^m	number m of all bonds
μ	attenuation coefficient
$\tilde{\nu}$	wave number
ν_{as}	asymmetric stretching vibration
ν_{s}	symmetric stretching vibration
ρ	density
σ^n	number n of σ -bonds
ϕ	volume fraction

7.2 UV/vis spectra

7.2.1 1,3,5,7-Tetrabutyl-9,10-diethyl-1,5-dihydro-4,8-ethano[1,4]diphosphinino[2,3-d:5,6-d']di-2,6-bis(dithiocarboxy)imidazolium **36a**

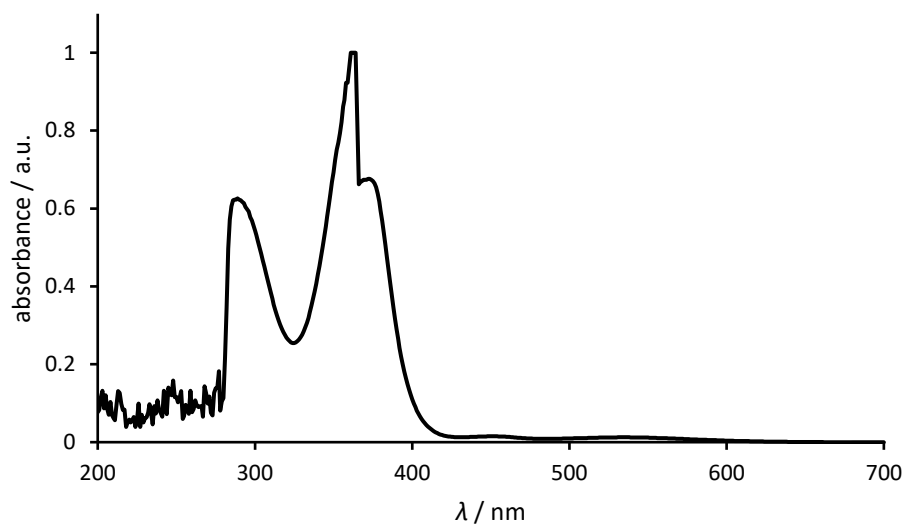


Figure 82. UV/vis spectrum of **36a** in toluene ($c \approx 10^{-6} \text{ mol L}^{-1}$).

7.2.2 1,3,5,7-Tetrabutyl-9,10-diethyl-1,5-dihydro-4,8-ethano[1,4]diphosphinino[2,3-d:5,6-d']di-2,6-bis(dithiocarboxy)imidazolium **36b**

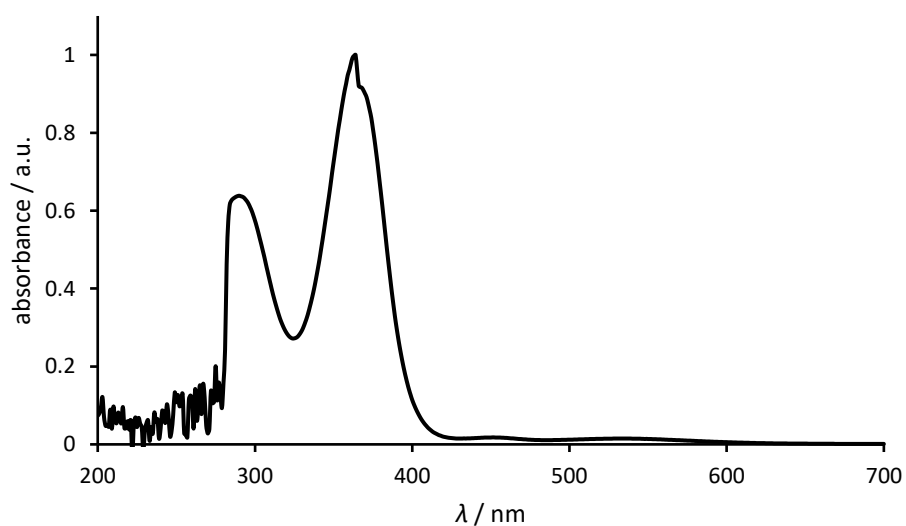


Figure 83. UV/vis spectrum of **36b** in toluene ($c \approx 10^{-6} \text{ mol L}^{-1}$).

7.2.3 1,3,5,7-Tetrabutyl-9-butyl-1,5-dihydro-4,8-ethano[1,4]diphosphinino[2,3-d:5,6-d']di-2,6-bis(dithiocarboxy)imidazolium 36c

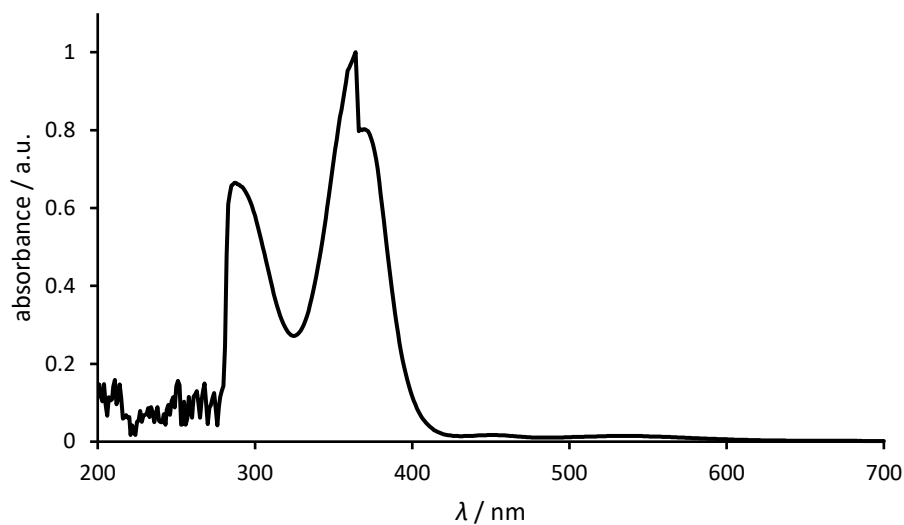


Figure 84. UV/vis spectrum of **36c** in toluene ($c \approx 10^{-6} \text{ mol L}^{-1}$).

7.3 Cyclic voltammograms

7.3.1 [([μ-1,3,5,7-Tetrabutyl-9-butyl-1,3,5,7-tetrahydro-2*H*,6*H*-4,8-ethano[1,4]diphosphinino[2,3-d:5,6-d']diimidazole-2,6-ylidene-2κC,6κC)bis(trifluoromethanesulfonato)disilver(I)] 21c

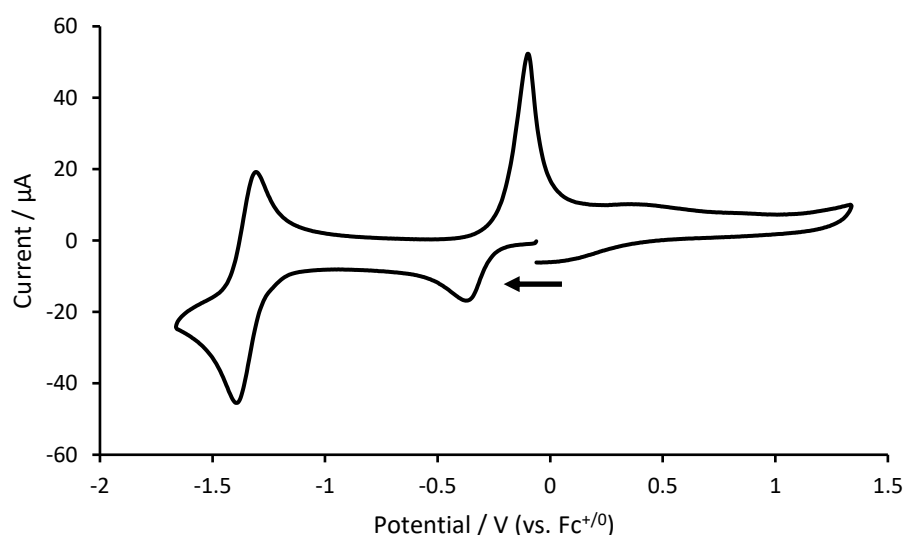


Figure 85. Cyclic voltammogram of **21c** (2.6 mM) with cobaltocenium hexafluorophosphate as internal reference at a Pt electrode in a 0.1 M $n\text{-Bu}_4\text{PF}_6/\text{MeCN}$ solution at a scan rate of 200 mV s^{-1} ; measurement with cathodic initial scan direction (indicated by an arrow); potentials are referenced against $\text{Fc}^{+/0}$.

7.3.2 Salt with the 1,3,5,7-tetrabutyl-1,5-dihydro-[1,4]diphosphinino[2,3-d:5,6-d']diimidazolium cation **13**

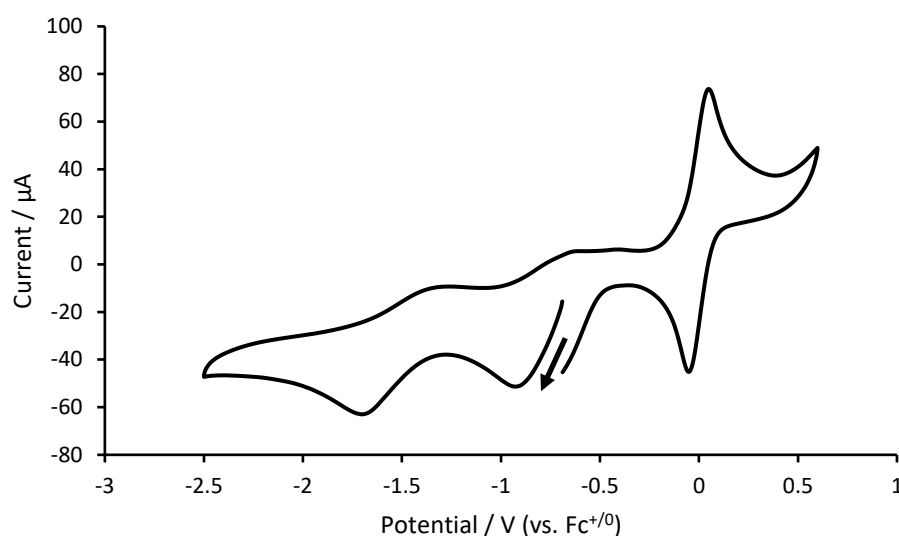


Figure 86. Cyclic voltammogram of **13** (circa 1 mM) with ferrocene as internal reference at a Pt electrode in a 0.1 M *n*-Bu₄PF₆/MeCN solution at a scan rate of 200 mV s⁻¹; measurement with cathodic initial scan direction (indicated by an arrow); potentials are referenced against Fc^{+/0}.

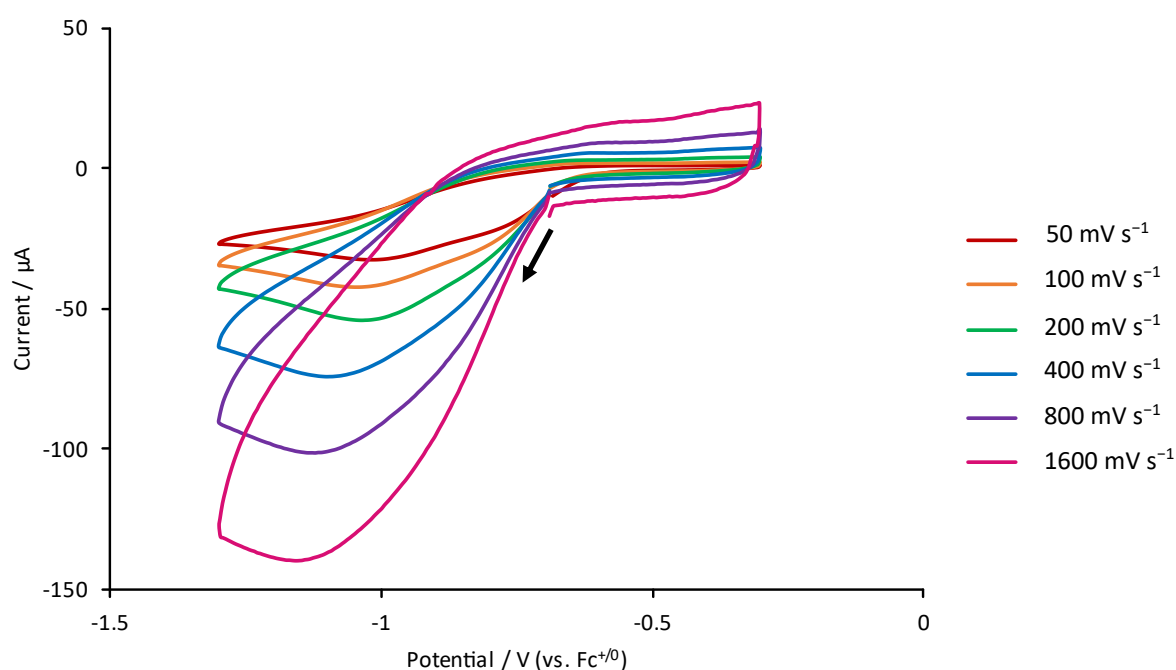


Figure 87. Cyclic voltammogram of the first reduction process of **13** (circa 1 mM) with ferrocene as internal reference at a Pt electrode in a 0.1 M *n*-Bu₄PF₆/MeCN solution at various scan rates; measurement with cathodic initial scan direction (indicated by an arrow); potentials are referenced against Fc^{+/0}.

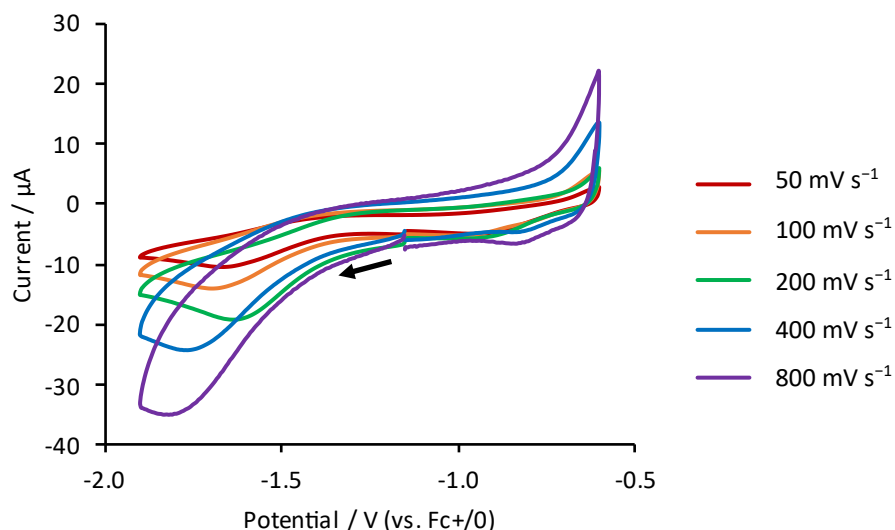


Figure 88. Cyclic voltammogram of the second reduction process of **13** (circa 1 mM) with ferrocene as internal reference at a Pt electrode in a 0.1 M $n\text{-Bu}_4\text{PF}_6/\text{MeCN}$ solution at various scan rates; measurement with cathodic initial scan direction (indicated by an arrow); potentials are referenced against $\text{Fc}^{+/0}$.

7.4 Crystal data and structure refinements

7.4.1 1,3,5,7-Tetrabutyl-9,10-diethyl-1,3,5,7-tetrahydro-2*H*,6*H*-4,8-ethano[1,4]diphosphinino[2,3-*d*:5,6-*d'*]diimidazole-2,6-diselone **2b**

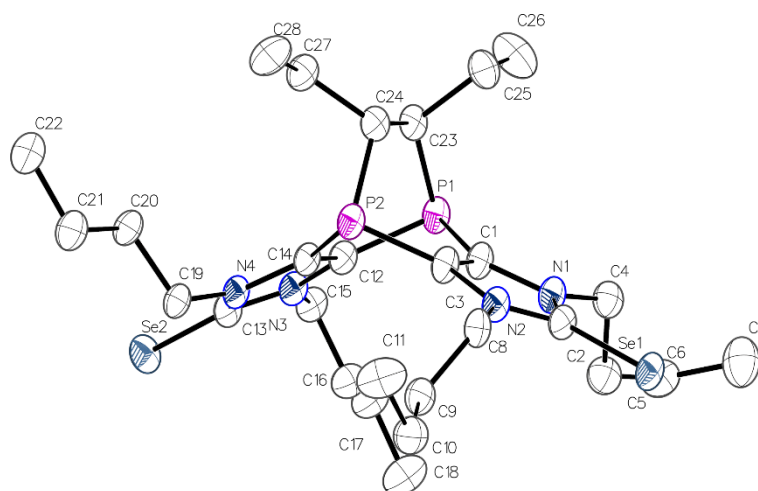


Figure 89. Molecular structure of **2b** in the single crystal. Thermal ellipsoids are set at 50 % probability level. Hydrogen atoms were omitted for clarity.

Table 15. Crystal data and structure refinements for **2b**.

Identification code	GSTR750, TT-500 // GXraycu_6823f
Crystal habitus	clear colourless plank
Device type	Bruker D8 Venture
Empirical formula	$\text{C}_{28}\text{H}_{48}\text{N}_4\text{P}_2\text{Se}_2$

Moiety formula	C ₂₈ H ₄₈ N ₄ P ₂ Se ₂
Formula weight / g mol ⁻¹	660.56
T / K	100
Crystal system	triclinic
Space group	<i>P</i> -1
<i>a</i> / Å	10.1836(4)
<i>b</i> / Å	11.7770(5)
<i>c</i> / Å	14.4181(6)
α / °	108.515(2)
β / °	95.741(3)
γ / °	97.957(3)
<i>V</i> / Å ³	1604.70(12)
<i>Z</i>	2
ρ_{calc} / g cm ⁻³	1.367
μ / mm ⁻¹	3.988
<i>F</i> (000)	684.0
Crystal size / mm ³	0.241 × 0.039 × 0.037
Absorption correction	empirical
<i>T</i> _{min} ; <i>T</i> _{max}	0.4152; 0.7535
Radiation	Cu-K α (λ = 1.54178 Å)
2 θ range for data collection / °	6.542 to 135.462
Completeness to θ	0.970
Index ranges	-12 ≤ <i>h</i> ≤ 12, -14 ≤ <i>k</i> ≤ 14, -17 ≤ <i>l</i> ≤ 17
Reflections collected	19425
Independent reflections	5640 (<i>R</i> _{int} = 0.0612, <i>R</i> _{σ} = 0.0598)
Data / restraints / parameters	5640 / 285 / 331
Goodness-of-fit on <i>F</i> ²	1.141
Final <i>R</i> indexes (<i>I</i> ≥ 2 σ (<i>I</i>))	<i>R</i> ₁ = 0.0700, ωR ₂ = 0.2027
Final <i>R</i> indexes (all data)	<i>R</i> ₁ = 0.0829, ωR ₂ = 0.2108
Largest diff. peak / hole / e Å ⁻³	1.22 / -0.65

Table 16. Bond lengths for 2b.

Atom	Atom	Length / Å	Atom	Atom	Length / Å
Se1	C2	1.837(7)	C1	C3	1.350(11)
Se2	C13	1.837(7)	C4	C5	1.523(11)
P1	C1	1.830(7)	C5	C6	1.528(12)
P1	C12	1.824(8)	C6	C7	1.519(13)
P1	C23	1.875(8)	C8	C9	1.517(11)
P2	C3	1.816(8)	C9	C10	1.535(11)
P2	C14	1.835(7)	C10	C11	1.509(13)
P2	C24	1.890(8)	C12	C14	1.353(10)
N1	C1	1.397(9)	C15	C16	1.529(11)
N1	C2	1.361(10)	C16	C17	1.521(11)
N1	C4	1.459(10)	C17	C18	1.517(12)
N2	C2	1.363(10)	C19	C20	1.531(10)
N2	C3	1.391(9)	C20	C21	1.520(11)
N2	C8	1.478(9)	C21	C22	1.527(12)
N3	C12	1.391(9)	C23	C24	1.560(10)
N3	C13	1.367(10)	C23	C25	1.546(10)
N3	C15	1.457(9)	C24	C27	1.537(10)
N4	C13	1.362(9)	C25	C26	1.510(13)
N4	C14	1.375(9)	C27	C28	1.536(12)
N4	C19	1.463(10)			

Table 17. Bond angles for **2b**.

Atom	Atom	Atom	Angle / °	Atom	Atom	Atom	Angle / °
C1	P1	C23	95.5(3)	C4	C5	C6	111.6(7)
C12	P1	C1	94.2(3)	C7	C6	C5	114.5(7)
C12	P1	C23	95.2(3)	N2	C8	C9	111.0(6)
C3	P2	C14	94.5(3)	C8	C9	C10	112.9(6)
C3	P2	C24	95.8(3)	C11	C10	C9	113.5(7)
C14	P2	C24	95.2(3)	N3	C12	P1	129.6(6)
C1	N1	C4	125.6(6)	C14	C12	P1	123.4(5)
C2	N1	C1	109.4(6)	C14	C12	N3	106.8(6)
C2	N1	C4	125.1(6)	N3	C13	Se2	127.4(5)
C2	N2	C3	110.2(6)	N4	C13	Se2	126.3(6)
C2	N2	C8	125.4(6)	N4	C13	N3	106.3(6)
C3	N2	C8	124.3(6)	N4	C14	P2	129.1(5)
C12	N3	C15	125.3(6)	C12	C14	P2	122.7(5)
C13	N3	C12	109.3(6)	C12	C14	N4	108.1(6)
C13	N3	C15	125.0(6)	N3	C15	C16	111.3(6)
C13	N4	C14	109.4(6)	C17	C16	C15	114.0(6)
C13	N4	C19	125.6(6)	C18	C17	C16	111.9(7)
C14	N4	C19	124.8(6)	N4	C19	C20	112.2(6)
N1	C1	P1	129.1(6)	C21	C20	C19	113.6(6)
C3	C1	P1	123.2(6)	C20	C21	C22	111.7(7)
C3	C1	N1	107.6(6)	C24	C23	P1	119.0(5)
N1	C2	Se1	126.2(6)	C25	C23	P1	110.6(5)
N1	C2	N2	106.0(6)	C25	C23	C24	110.3(6)
N2	C2	Se1	127.8(5)	C23	C24	P2	117.7(5)
N2	C3	P2	129.9(6)	C27	C24	P2	109.0(5)
C1	C3	P2	123.3(5)	C27	C24	C23	111.1(6)
C1	C3	N2	106.8(6)	C26	C25	C23	113.4(7)
N1	C4	C5	112.0(7)	C28	C27	C24	113.9(6)

7.4.2 (1,3,5,7-Tetrabutyl-1,3,5,7-tetrahydro-2*H*,6*H*-4,8-ethano[1,4]diphosphino[2,3-*d*:5,6-*d'*]diimidazole-2,6-diselone- $\kappa P^1, \kappa P^2$)bis(borane) **6a**

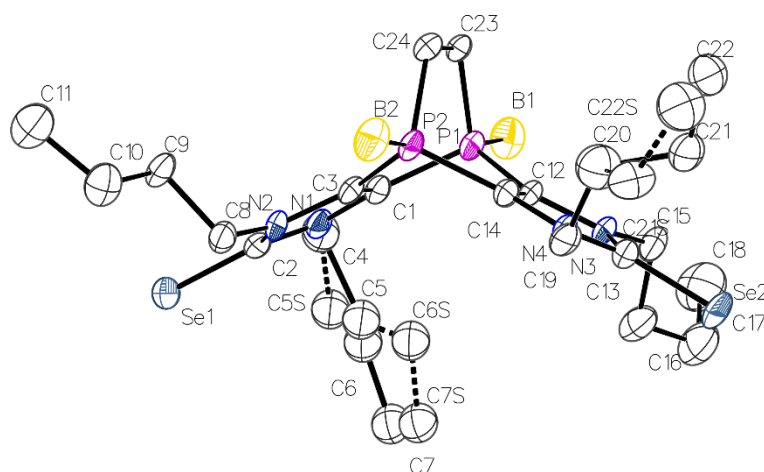


Figure 90. Molecular structure of **6a** in the single crystal. Thermal ellipsoids are set at 50 % probability level. Hydrogen atoms and solvent molecules were omitted for clarity.

Table 18. Crystal data and structure refinements for **6a**.

Identification code	GSTR830, TT-893 // GXraycu_7878f
Crystal habitus	clear colourless plate
Device type	Bruker D8 Venture
Empirical formula	C ₂₅ H ₄₈ B ₂ Cl ₂ N ₄ P ₂ Se ₂
Moiety formula	C ₂₅ H ₄₈ B ₂ Cl ₂ N ₄ P ₂ Se ₂ , CH ₂ Cl ₂
Formula weight / g mol ⁻¹	717.05
T / K	100.0
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> / Å	9.5526(7)
<i>b</i> / Å	15.9233(12)
<i>c</i> / Å	23.092(2)
α / °	90
β / °	101.475(6)
γ / °	90
<i>V</i> / Å ³	3442.3(5)
<i>Z</i>	4
ρ_{calc} / g cm ⁻³	1.384
μ / mm ⁻¹	5.147
<i>F</i> (000)	1472.0
Crystal size / mm ³	0.12 × 0.08 × 0.01
Absorption correction	multi-scan
<i>T</i> _{min} ; <i>T</i> _{max}	0.4963; 0.7538
Radiation	Cu-K α (λ = 1.54178 Å)
2 θ range for data collection / °	6.788 to 135.488
Completeness to θ	0.999
Index ranges	−11 ≤ <i>h</i> ≤ 11, −19 ≤ <i>k</i> ≤ 19, −27 ≤ <i>l</i> ≤ 27
Reflections collected	51353
Independent reflections	6234 (<i>R</i> _{int} = 0.1538, <i>R</i> _{σ} = 0.0841)
Data / restraints / parameters	6234 / 121 / 405
Goodness-of-fit on <i>F</i> ²	1.021
Final <i>R</i> indexes (<i>I</i> ≥ 2 σ (<i>I</i>))	<i>R</i> ₁ = 0.0527, ωR ₂ = 0.1219
Final <i>R</i> indexes (all data)	<i>R</i> ₁ = 0.0856, ωR ₂ = 0.1382
Largest diff. peak / hole / e Å ⁻³	1.10 / −0.86

Table 19. Bond lengths for **6a**.

Atom	Atom	Length / Å	Atom	Atom	Length / Å
Se1	C2	1.837(4)	C1	C3	1.361(7)
Se2	C13	1.847(4)	C4	C5	1.662(13)
P1	C1	1.806(5)	C4	C5S	1.484(8)
P1	C12	1.802(4)	C5	C6	1.503(9)
P1	C23	1.835(5)	C5S	C6S	1.505(9)
P1	B1	1.906(7)	C6	C7	1.508(9)
P2	C3	1.801(5)	C6S	C7S	1.504(9)
P2	C14	1.814(5)	C8	C9	1.517(6)
P2	C24	1.827(5)	C9	C10	1.512(8)
P2	B2	1.909(7)	C10	C11	1.509(8)
N1	C1	1.394(6)	C12	C14	1.357(7)
N1	C2	1.358(6)	C15	C16	1.512(8)
N1	C4	1.463(7)	C16	C17	1.528(8)
N2	C2	1.359(6)	C17	C18	1.503(11)
N2	C3	1.381(6)	C19	C20	1.487(8)
N2	C8	1.474(6)	C20	C21	1.455(7)
N3	C12	1.387(5)	C20	C21S	1.448(8)

N3	C13	1.354(6)	C21	C22	1.513(12)
N3	C15	1.467(7)	C21S	C22S	1.502(17)
N4	C13	1.371(6)	C23	C24	1.538(7)
N4	C14	1.371(6)	Cl1	C27	1.759(6)
N4	C19	1.460(7)	Cl2	C27	1.764(6)

Table 20. Bond angles for 6a.

Atom	Atom	Atom	Angle / °	Atom	Atom	Atom	Angle / °
C1	P1	C23	99.3(2)	C1	C3	P2	120.1(3)
C1	P1	B1	122.2(3)	C1	C3	N2	107.5(4)
C12	P1	C1	97.3(2)	N1	C4	C5	101.6(5)
C12	P1	C23	99.0(2)	N1	C4	C5S	121.5(7)
C12	P1	B1	121.6(2)	C6	C5	C4	111.1(8)
C23	P1	B1	112.8(3)	C4	C5S	C6S	111.0(8)
C3	P2	C14	97.8(2)	C5	C6	C7	110.2(9)
C3	P2	C24	99.0(2)	C5S	C6S	C7S	112.1(8)
C3	P2	B2	120.8(3)	N2	C8	C9	112.4(4)
C14	P2	C24	99.2(2)	C10	C9	C8	111.2(4)
C14	P2	B2	122.3(2)	C11	C10	C9	114.1(5)
C24	P2	B2	113.4(3)	N3	C12	P1	132.6(4)
C1	N1	C4	126.5(4)	C14	C12	P1	120.3(3)
C2	N1	C1	109.0(4)	C14	C12	N3	106.9(4)
C2	N1	C4	124.5(4)	N3	C13	Se2	126.5(3)
C2	N2	C3	109.3(4)	N3	C13	N4	107.2(3)
C2	N2	C8	124.1(4)	N4	C13	Se2	126.3(3)
C3	N2	C8	126.6(4)	N4	C14	P2	131.7(4)
C12	N3	C15	127.1(4)	C12	C14	P2	119.9(3)
C13	N3	C12	109.0(4)	C12	C14	N4	108.3(4)
C13	N3	C15	123.9(4)	N3	C15	C16	112.6(4)
C13	N4	C14	108.4(4)	C15	C16	C17	112.7(5)
C13	N4	C19	125.0(4)	C18	C17	C16	114.2(5)
C14	N4	C19	126.6(4)	N4	C19	C20	113.6(5)
N1	C1	P1	132.7(4)	C21	C20	C19	123.3(6)
C3	C1	P1	120.1(3)	C21S	C20	C19	117.4(7)
C3	C1	N1	107.1(4)	C20	C21	C22	114.6(7)
N1	C2	Se1	126.4(4)	C20	C21S	C22S	112.7(12)
N1	C2	N2	107.1(4)	C24	C23	P1	116.5(3)
N2	C2	Se1	126.5(4)	C23	C24	P2	116.5(3)
N2	C3	P2	132.3(4)	Cl1	C27	Cl2	110.3(3)

7.4.3 [Tetrachlorido(μ -1,3,5,7-tetrabutyl-1,3,5,7-tetrahydro-2*H*,6*H*-4,8-ethano[1,4]diphosphinino[2,3-*d*:5,6-*d'*]diimidazole-2,6-diselone- $\kappa P^1, \kappa P^2, \kappa Se^1, \kappa Se^2$)tetrakis(η^2, η^2 -cycloocta-1,5-diene)tetrarhodium(I)] 9a

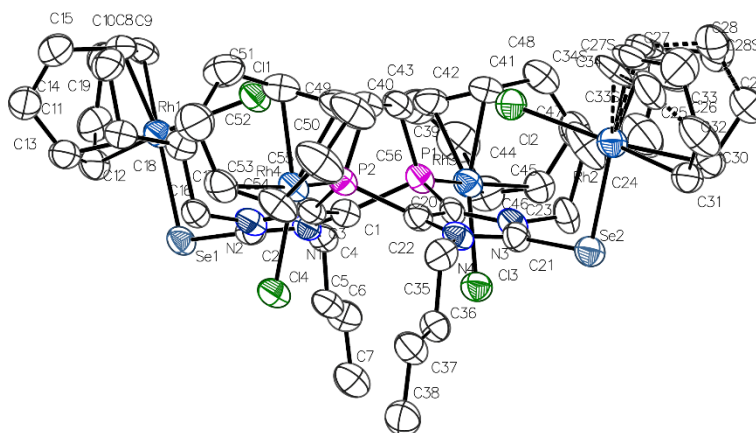


Figure 91. Molecular structure of **9a** in the single crystal. Thermal ellipsoids are set at 50 % probability level. Hydrogen atoms and solvent molecules were omitted for clarity.

Table 21. Crystal data and structure refinements for **9a**.

Identification code	GSTR816, TT-808 // GXray7481
Crystal habitus	clear yellow plate
Device type	STOE STADIVARI
Empirical formula	C ₇₀ H ₁₀₄ Cl ₄ N ₄ P ₂ Rh ₄ Se ₂
Moiety formula	C ₅₆ H ₈₈ Cl ₄ N ₄ P ₂ Rh ₄ Se ₂ , 2 C ₇ H ₈
Formula weight / g mol ⁻¹	1774.87
T / K	100
Crystal system	triclinic
Space group	<i>P</i> -1
<i>a</i> / Å	13.2801(4)
<i>b</i> / Å	15.1405(5)
<i>c</i> / Å	20.6047(7)
α / °	109.728(2)
β / °	92.124(3)
γ / °	106.193(2)
<i>V</i> / Å ³	3705.4(2)
<i>Z</i>	2
ρ_{calc} / g cm ⁻³	1.591
μ / mm ⁻¹	10.254
<i>F</i> (000)	1796.0
Crystal size / mm ³	0.12 × 0.1 × 0.05
Absorption correction	multi-scan
<i>T</i> _{min} ; <i>T</i> _{max}	0.0800; 0.2369
Radiation	Cu-K α (λ = 1.54178 Å)
2 θ range for data collection / °	7.806 to 141.052
Completeness to θ	0.988
Index ranges	-16 ≤ <i>h</i> ≤ 15, -15 ≤ <i>k</i> ≤ 18, -24 ≤ <i>l</i> ≤ 11
Reflections collected	51381
Independent reflections	13818 (<i>R</i> _{int} = 0.0771, <i>R</i> _{σ} = 0.0600)
Data / restraints / parameters	13818 / 229 / 855

Goodness-of-fit on F^2	1.060
Final R indexes ($I \geq 2\sigma(I)$)	$R_1 = 0.0812$, $\omega R_2 = 0.2109$
Final R indexes (all data)	$R_1 = 0.1129$, $\omega R_2 = 0.2397$
Largest diff. peak / hole / $e \text{ \AA}^{-3}$	1.56 / -1.73

Table 22. Bond lengths for 9a.

Atom	Atom	Length / $\text{\AA}$	Atom	Atom	Length / $\text{\AA}$
Rh1	Se1	2.5030(9)	C18	C19	1.545(11)
Rh1	Cl1	2.3964(16)	C20	C22	1.352(8)
Rh1	C8	2.123(7)	C23	C24	1.589(12)
Rh1	C9	2.137(7)	C24	C25	1.432(14)
Rh1	C12	2.119(7)	C25	C26	1.516(16)
Rh1	C13	2.151(7)	C27	C28	1.56(2)
Rh2	Se2	2.4975(10)	C27	C34	1.467(18)
Rh2	Cl2	2.3804(18)	C28	C29	1.397(18)
Rh2	C27	2.195(12)	C27S	C28S	1.56(2)
Rh2	C27S	2.188(15)	C27S	C34S	1.313(19)
Rh2	C30	2.116(8)	C28S	C29	1.65(2)
Rh2	C31	2.121(7)	C29	C30	1.531(11)
Rh2	C34	2.126(15)	C30	C31	1.389(10)
Rh2	C34S	2.152(16)	C31	C32	1.526(12)
Rh3	Cl3	2.3553(18)	C32	C33	1.54(2)
Rh3	P1	2.2568(16)	C32	C33S	1.48(3)
Rh3	C41	2.139(7)	C33	C34	1.497(19)
Rh3	C42	2.113(7)	C33S	C34S	1.56(2)
Rh3	C45	2.231(7)	C35	C36	1.536(11)
Rh3	C46	2.232(7)	C36	C37	1.534(9)
Rh4	Cl4	2.3621(18)	C37	C38	1.486(12)
Rh4	P2	2.2644(16)	C39	C40	1.524(9)
Rh4	C49	2.155(7)	C41	C42	1.378(10)
Rh4	C50	2.143(7)	C41	C48	1.547(10)
Rh4	C53	2.220(7)	C42	C43	1.522(9)
Rh4	C54	2.223(6)	C43	C44	1.479(14)
Se1	C2	1.877(6)	C44	C45	1.545(12)
Se2	C21	1.873(6)	C45	C46	1.374(10)
P1	C1	1.813(6)	C46	C47	1.522(12)
P1	C20	1.824(5)	C47	C48	1.485(13)
P1	C39	1.850(8)	C49	C50	1.432(11)
P2	C3	1.834(6)	C49	C56	1.499(8)
P2	C22	1.821(7)	C50	C51	1.486(9)
P2	C40	1.867(6)	C51	C52	1.467(8)
N1	C1	1.400(7)	C52	C53	1.465(10)
N1	C2	1.332(8)	C53	C54	1.378(11)
N1	C4	1.476(7)	C54	C55	1.475(9)
N2	C2	1.357(7)	C55	C56	1.446(8)
N2	C3	1.388(8)	C57	C58	1.372(17)
N2	C16	1.480(9)	C57	C62	1.423(17)
N3	C20	1.371(8)	C57	C63	1.487(8)
N3	C21	1.350(7)	C58	C59	1.315(19)
N3	C23	1.477(9)	C59	C60	1.30(2)
N4	C21	1.354(9)	C60	C61	1.43(2)
N4	C22	1.378(7)	C61	C62	1.300(18)
N4	C35	1.462(8)	C64	C65	1.3900
C1	C3	1.327(8)	C64	C69	1.3900
C4	C5	1.511(10)	C64	C70	1.501(8)

C5	C6	1.520(9)	C65	C66	1.3900
C6	C7	1.506(12)	C66	C67	1.3900
C8	C9	1.392(9)	C67	C68	1.3900
C8	C15	1.510(10)	C68	C69	1.3900
C9	C10	1.532(9)	C64S	C65S	1.3900
C10	C11	1.533(12)	C64S	C69S	1.3900
C11	C12	1.504(10)	C64S	C70S	1.509(14)
C12	C13	1.403(10)	C65S	C66S	1.3900
C13	C14	1.477(11)	C66S	C67S	1.3900
C14	C15	1.525(11)	C67S	C68S	1.3900
C16	C17	1.532(10)	C68S	C69S	1.3900
C17	C18	1.485(10)			

Table 23. Bond angles for 9a.

Atom	Atom	Atom	Angle / °	Atom	Atom	Atom	Angle / °
Cl1	Rh1	Se1	95.09(5)	C9	C10	C11	111.7(6)
C8	Rh1	Se1	156.06(16)	C12	C11	C10	113.3(6)
C8	Rh1	Cl1	89.79(18)	C11	C12	Rh1	108.8(5)
C8	Rh1	C9	38.1(2)	C13	C12	Rh1	72.1(4)
C8	Rh1	C13	79.9(3)	C13	C12	C11	126.3(7)
C9	Rh1	Se1	164.87(19)	C12	C13	Rh1	69.6(4)
C9	Rh1	Cl1	88.71(19)	C12	C13	C14	123.0(6)
C9	Rh1	C13	89.2(3)	C14	C13	Rh1	114.0(5)
C12	Rh1	Se1	88.1(2)	C13	C14	C15	113.4(6)
C12	Rh1	Cl1	154.7(2)	C8	C15	C14	110.6(6)
C12	Rh1	C8	97.4(3)	N2	C16	C17	110.2(5)
C12	Rh1	C9	82.4(3)	C18	C17	C16	111.8(6)
C12	Rh1	C13	38.3(3)	C17	C18	C19	110.7(6)
C13	Rh1	Se1	90.5(2)	N3	C20	P1	129.7(4)
C13	Rh1	Cl1	165.74(19)	C22	C20	P1	121.0(5)
Cl2	Rh2	Se2	94.48(5)	C22	C20	N3	108.4(5)
C27	Rh2	Se2	151.8(4)	N3	C21	Se2	126.3(5)
C27	Rh2	Cl2	88.3(4)	N3	C21	N4	107.9(5)
C27S	Rh2	Se2	173.1(4)	N4	C21	Se2	125.8(4)
C27S	Rh2	Cl2	88.7(4)	N4	C22	P2	128.7(5)
C30	Rh2	Se2	88.8(2)	C20	C22	P2	121.2(4)
C30	Rh2	Cl2	161.77(19)	C20	C22	N4	106.9(6)
C30	Rh2	C27	80.6(5)	N3	C23	C24	109.0(7)
C30	Rh2	C27S	86.3(5)	C25	C24	C23	112.9(9)
C30	Rh2	C31	38.3(3)	C24	C25	C26	113.1(11)
C30	Rh2	C34	90.8(5)	C28	C27	Rh2	110.5(10)
C30	Rh2	C34S	98.9(6)	C34	C27	Rh2	67.7(7)
C31	Rh2	Se2	89.0(2)	C34	C27	C28	124.6(12)
C31	Rh2	Cl2	159.4(2)	C29	C28	C27	110.6(11)
C31	Rh2	C27	98.2(4)	C28S	C27S	Rh2	106.9(11)
C31	Rh2	C27S	90.2(4)	C34S	C27S	Rh2	70.9(10)
C31	Rh2	C34	83.2(4)	C34S	C27S	C28S	125.5(14)
C31	Rh2	C34S	80.5(6)	C27S	C28S	C29	117.8(13)
C34	Rh2	Se2	167.7(3)	C28	C29	C30	119.4(9)
C34	Rh2	Cl2	89.7(4)	C30	C29	C28S	109.7(8)
C34	Rh2	C27	39.7(5)	C29	C30	Rh2	111.4(6)
C34S	Rh2	Se2	151.0(4)	C31	C30	Rh2	71.0(4)
C34S	Rh2	Cl2	86.8(5)	C31	C30	C29	123.6(7)
C34S	Rh2	C27S	35.2(5)	C30	C31	Rh2	70.7(4)
P1	Rh3	Cl3	86.34(6)	C30	C31	C32	124.1(7)

C41	Rh3	Cl3	163.33(19)	C32	C31	Rh2	111.6(6)
C41	Rh3	P1	95.59(19)	C31	C32	C33	109.9(7)
C41	Rh3	C45	90.7(3)	C33S	C32	C31	119.1(10)
C41	Rh3	C46	81.9(3)	C34	C33	C32	117.3(12)
C42	Rh3	Cl3	158.8(2)	C27	C34	Rh2	72.7(8)
C42	Rh3	P1	92.9(2)	C27	C34	C33	121.3(14)
C42	Rh3	C41	37.8(3)	C33	C34	Rh2	110.8(11)
C42	Rh3	C45	81.8(3)	C32	C33S	C34S	106.2(15)
C42	Rh3	C46	95.8(3)	C27S	C34S	Rh2	73.9(10)
C45	Rh3	Cl3	92.5(2)	C27S	C34S	C33S	125.9(16)
C45	Rh3	P1	162.0(2)	C33S	C34S	Rh2	114.3(14)
C45	Rh3	C46	35.9(3)	N4	C35	C36	110.9(5)
C46	Rh3	Cl3	91.1(2)	C37	C36	C35	112.2(6)
C46	Rh3	P1	161.99(18)	C38	C37	C36	110.8(7)
P2	Rh4	Cl4	87.72(6)	C40	C39	P1	118.0(5)
C49	Rh4	Cl4	158.9(2)	C39	C40	P2	116.8(5)
C49	Rh4	P2	94.11(19)	C42	C41	Rh3	70.1(4)
C49	Rh4	C53	92.1(3)	C42	C41	C48	122.6(6)
C49	Rh4	C54	80.9(2)	C48	C41	Rh3	112.1(5)
C50	Rh4	Cl4	161.71(18)	C41	C42	Rh3	72.1(4)
C50	Rh4	P2	95.66(17)	C41	C42	C43	125.2(7)
C50	Rh4	C49	38.9(3)	C43	C42	Rh3	109.8(6)
C50	Rh4	C53	80.1(3)	C44	C43	C42	116.4(7)
C50	Rh4	C54	92.7(3)	C43	C44	C45	112.3(6)
C53	Rh4	Cl4	91.7(2)	C44	C45	Rh3	110.3(6)
C53	Rh4	P2	164.06(18)	C46	C45	Rh3	72.1(4)
C53	Rh4	C54	36.1(3)	C46	C45	C44	120.3(8)
C54	Rh4	Cl4	90.1(2)	C45	C46	Rh3	72.1(4)
C54	Rh4	P2	159.7(2)	C45	C46	C47	125.6(7)
C2	Se1	Rh1	100.4(2)	C47	C46	Rh3	107.8(5)
C21	Se2	Rh2	99.4(2)	C48	C47	C46	115.4(7)
C1	P1	Rh3	117.92(18)	C47	C48	C41	115.3(6)
C1	P1	C20	97.8(3)	C50	C49	Rh4	70.1(4)
C1	P1	C39	96.1(3)	C50	C49	C56	124.6(8)
C20	P1	Rh3	122.0(2)	C56	C49	Rh4	111.6(5)
C20	P1	C39	96.2(3)	C49	C50	Rh4	71.0(4)
C39	P1	Rh3	121.1(2)	C49	C50	C51	123.9(5)
C3	P2	Rh4	124.6(2)	C51	C50	Rh4	113.1(5)
C3	P2	C40	96.7(3)	C52	C51	C50	115.8(7)
C22	P2	Rh4	116.70(18)	C53	C52	C51	118.2(7)
C22	P2	C3	97.2(3)	C52	C53	Rh4	110.6(4)
C22	P2	C40	96.3(3)	C54	C53	Rh4	72.1(4)
C40	P2	Rh4	119.5(2)	C54	C53	C52	123.5(7)
C1	N1	C4	127.8(5)	C53	C54	Rh4	71.8(4)
C2	N1	C1	108.6(5)	C53	C54	C55	122.9(8)
C2	N1	C4	123.5(5)	C55	C54	Rh4	108.8(4)
C2	N2	C3	107.3(5)	C56	C55	C54	119.7(6)
C2	N2	C16	124.7(5)	C55	C56	C49	116.3(6)
C3	N2	C16	127.1(5)	C58	C57	C62	122.6(10)
C20	N3	C23	127.8(5)	C58	C57	C63	120.6(11)
C21	N3	C20	108.1(5)	C62	C57	C63	116.2(10)
C21	N3	C23	123.6(5)	C59	C58	C57	118.0(14)
C21	N4	C22	108.5(5)	C60	C59	C58	123.1(14)
C21	N4	C35	124.4(5)	C59	C60	C61	118.8(14)
C22	N4	C35	127.0(6)	C62	C61	C60	122.1(15)
N1	C1	P1	127.6(4)	C61	C62	C57	114.7(12)
C3	C1	P1	122.4(4)	C65	C64	C69	120.0

C3	C1	N1	106.9(5)	C65	C64	C70	118.6(6)
N1	C2	Se1	126.1(4)	C69	C64	C70	121.3(6)
N1	C2	N2	108.4(5)	C64	C65	C66	120.0
N2	C2	Se1	125.1(5)	C67	C66	C65	120.0
N2	C3	P2	129.2(5)	C68	C67	C66	120.0
C1	C3	P2	120.8(5)	C69	C68	C67	120.0
C1	C3	N2	108.7(5)	C68	C69	C64	120.0
N1	C4	C5	109.6(5)	C65S	C64S	C69S	120.0
C4	C5	C6	111.5(5)	C65S	C64S	C70S	109.6(13)
C7	C6	C5	113.7(5)	C69S	C64S	C70S	128.5(13)
C9	C8	Rh1	71.5(4)	C64S	C65S	C66S	120.0
C9	C8	C15	125.3(6)	C67S	C66S	C65S	120.0
C15	C8	Rh1	112.7(5)	C66S	C67S	C68S	120.0
C8	C9	Rh1	70.4(4)	C67S	C68S	C69S	120.0
C8	C9	C10	124.6(6)	C68S	C69S	C64S	120.0
C10	C9	Rh1	112.1(5)				

7.4.4 1,3,5,7-Tetrabutyl-1,5-dihydro-4,8-ethano[1,4]diphosphinino[2,3-d:5,6-d']di-2,6-bis(methylseleno)imidazolium bis(trifluoromethanesulfonate) 10a

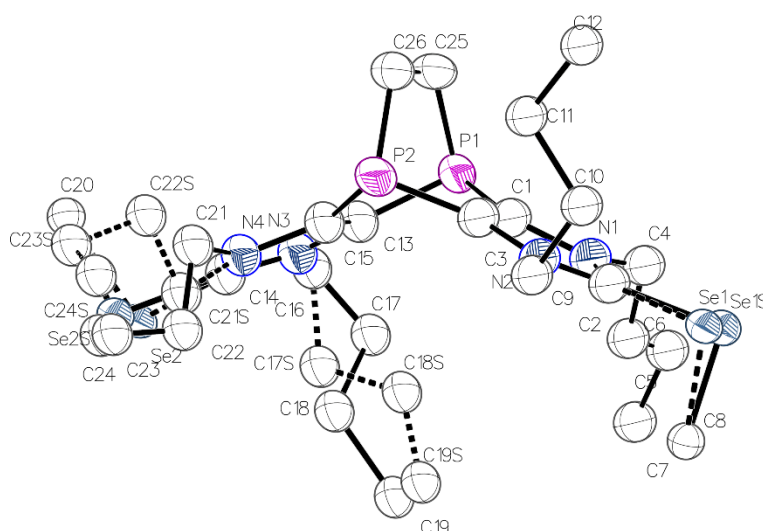


Figure 92. Molecular structure of **10a** in the single crystal. Thermal ellipsoids are set at 50 % probability level. Hydrogen atoms were omitted for clarity. Two OTf anions were squeezed.

Table 24. Crystal data and structure refinements for **10a**.

Identification code	GSTR829, TT-782 // GXray7475
Crystal habitus	clear colourless plate
Device type	STOE STADIVARI
Empirical formula	C ₂₆ H ₄₆ N ₄ P ₂ Se ₂
Moiety formula	C ₂₆ H ₄₆ N ₄ P ₂ Se ₂
Formula weight / g mol ⁻¹	634.53
T / K	100
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> / Å	9.2350(8)
<i>b</i> / Å	32.005(3)

$c / \text{\AA}$	13.6451(11)
$\alpha / ^\circ$	90
$\beta / ^\circ$	103.222(6)
$\gamma / ^\circ$	90.00
$V / \text{\AA}^3$	3926.1(6)
Z	4
$\rho_{\text{calc}} / \text{g cm}^{-3}$	1.073
μ / mm^{-1}	3.242
$F(000)$	1312.0
Crystal size / mm^3	$0.26 \times 0.24 \times 0.04$
Absorption correction	multi-scan
$T_{\text{min}}; T_{\text{max}}$	0.1198; 0.3348
Radiation	Cu-K α ($\lambda = 1.54178 \text{\AA}$)
2θ range for data collection / $^\circ$	5.522 to 140.98
Completeness to θ	0.998
Index ranges	$-10 \leq h \leq 11, -38 \leq k \leq 35, -11 \leq l \leq 16$
Reflections collected	41074
Independent reflections	7447 ($R_{\text{int}} = 0.8292, R_\sigma = 0.4247$)
Data / restraints / parameters	7447 / 687 / 373
Goodness-of-fit on F^2	1.175
Final R indexes ($I \geq 2\sigma(I)$)	$R_1 = 0.2185, \omega R_2 = 0.4613$
Final R indexes (all data)	$R_1 = 0.4281, \omega R_2 = 0.5762$
Largest diff. peak / hole / $\text{e \AA}^{-3}$	3.59 / -1.56

Table 25. Bond lengths for 10a.

Atom	Atom	Length / $\text{\AA}$	Atom	Atom	Length / $\text{\AA}$
Se1	C2	1.851(11)	C9	C10	1.496(10)
Se1	C8	1.94(2)	C10	C11	1.60(4)
Se1S	C2	1.906(8)	C11	C12	1.496(10)
Se1S	C8	1.86(2)	C13	C15	1.4200
Se2	C14	1.876(11)	C13	N3	1.4200
Se2	C20	2.06(2)	C15	N4	1.4200
Se2S	C14	1.903(8)	N4	C14	1.4200
Se2S	C20	1.90(2)	N4	C21	1.472(10)
P1	C1	1.835(15)	N4	C21S	1.468(10)
P1	C13	1.798(11)	C14	N3	1.4200
P1	C25	2.06(3)	N3	C16	1.461(10)
P2	C3	1.765(13)	C16	C17	1.501(10)
P2	C15	1.824(13)	C16	C17S	1.62(4)
P2	C26	1.78(3)	C17	C18	1.75(11)
C1	N1	1.4200	C17S	C18S	1.48(6)
C1	C3	1.4200	C18	C19	1.75(11)
N1	C2	1.4200	C18S	C19S	1.502(10)
N1	C4	1.471(10)	C21	C22	1.503(10)
C2	N2	1.4200	C21S	C22S	1.5000(10)
N2	C3	1.4200	C22	C23	1.496(10)
N2	C9	1.460(10)	C22S	C23S	1.497(10)
C4	C5	1.501(10)	C23	C24	1.493(10)
C5	C6	1.506(10)	C23S	C24S	1.497(10)
C6	C7	1.501(10)	C25	C26	1.499(10)

Table 26. Bond angles for 10a.

Atom	Atom	Atom	Angle / $^\circ$	Atom	Atom	Atom	Angle / $^\circ$
C2	Se1	C8	92.9(10)	C15	C13	P1	121.6(11)
C8	Se1S	C2	93.8(10)	N3	C13	P1	129.8(11)
C14	Se2	C20	93.6(9)	N3	C13	C15	108.0

C20	Se2S	C14	98.1(10)	C13	C15	P2	124.9(11)
C1	P1	C25	85.2(11)	C13	C15	N4	108.0
C13	P1	C1	93.9(10)	N4	C15	P2	126.7(11)
C13	P1	C25	93.1(11)	C15	N4	C14	108.0
C3	P2	C15	95.9(10)	C15	N4	C21	112(2)
C3	P2	C26	97.8(13)	C15	N4	C21S	134.2(17)
C26	P2	C15	99.7(13)	C14	N4	C21	139(2)
N1	C1	P1	126.9(12)	C14	N4	C21S	115.2(16)
N1	C1	C3	108.0	N4	C14	Se2	135.8(10)
C3	C1	P1	125.1(12)	N4	C14	Se2S	110.1(10)
C1	N1	C2	108.0	N3	C14	Se2	116.1(10)
C1	N1	C4	124.2(17)	N3	C14	Se2S	141.9(10)
C2	N1	C4	127.7(16)	N3	C14	N4	108.0
N1	C2	Se1	136.5(11)	C13	N3	C14	108.0
N1	C2	Se1S	112.1(11)	C13	N3	C16	124.2(15)
N2	C2	Se1	114.9(11)	C14	N3	C16	127.6(15)
N2	C2	Se1S	139.4(11)	N3	C16	C17	117(4)
N2	C2	N1	108.0	N3	C16	C17S	102.2(19)
C2	N2	C3	108.0	C16	C17	C18	98(5)
C2	N2	C9	125.5(16)	C18S	C17S	C16	110(3)
C3	N2	C9	126.5(16)	C17	C18	C19	105(5)
C1	C3	P2	121.9(12)	C17S	C18S	C19S	119(3)
C1	C3	N2	108.0	N4	C21	C22	112(2)
N2	C3	P2	130.1(12)	N4	C21S	C22S	101.4(8)
N1	C4	C5	116(2)	C23	C22	C21	113.1(11)
C4	C5	C6	125(2)	C23S	C22S	C21S	106.4(5)
C7	C6	C5	114(2)	C24	C23	C22	113.8(11)
N2	C9	C10	108(2)	C24S	C23S	C22S	113.4(11)
C9	C10	C11	109(2)	C26	C25	P1	127.0(19)
C12	C11	C10	108.0(19)	C25	C26	P2	112(2)

7.4.5 1,3,5,7-Tetrabutyl-9-butyl-1,5-dihydro-4,8-ethano[1,4]diphosphinino[2,3-d:5,6-d']di-2,6-bis(methylseleno)imidazolium bis(trifluoromethanesulfonate) 10c

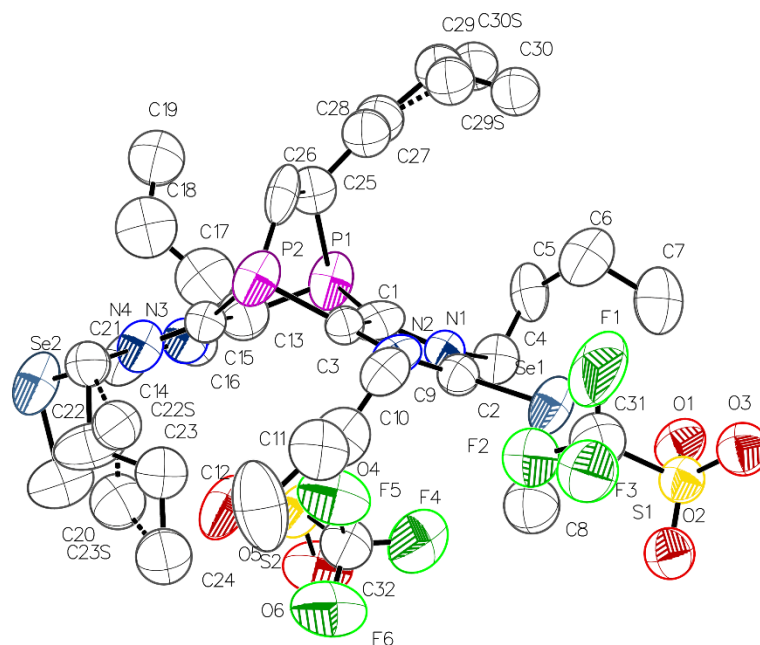


Figure 93. Molecular structure of **10c** in the single crystal. Thermal ellipsoids are set at 50 % probability level. Hydrogen atoms were omitted for clarity.

Table 27. Crystal data and structure refinements for **10c**.

Identification code	GSTR742, TT-430 // GXray6752
Crystal habitus	clear colourless plate
Device type	STOE IPDS-2T
Empirical formula	C ₃₂ H ₅₄ F ₆ N ₄ O ₆ P ₂ S ₂ Se ₂
Moiety formula	C ₃₀ H ₅₄ N ₄ P ₂ Se ₂ , 2 CF ₃ O ₃ S
Formula weight / g mol ⁻¹	988.77
T / K	123
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> / Å	14.3848(13)
<i>b</i> / Å	19.600(3)
<i>c</i> / Å	16.7783(14)
α / °	90
β / °	115.125(6)
γ / °	90
<i>V</i> / Å ³	4283.0(8)
<i>Z</i>	4
ρ_{calc} / g cm ⁻³	1.533
μ / mm ⁻¹	1.969
<i>F</i> (000)	2024.0
Crystal size / mm ³	0.5 × 0.25 × 0.06
Absorption correction	integration
<i>T</i> _{min} ; <i>T</i> _{max}	0.4460; 0.7055
Radiation	Mo-K α (λ = 0.71073 Å)

2 θ range for data collection / °	5.202 to 54
Completeness to θ	0.998
Index ranges	$-15 \leq h \leq 18$, $-25 \leq k \leq 19$, $-21 \leq l \leq 17$
Reflections collected	27091
Independent reflections	9337 ($R_{int} = 0.3277$, $R_{\sigma} = 0.3961$)
Data / restraints / parameters	9337 / 240 / 525
Goodness-of-fit on F^2	0.901
Final R indexes ($I \geq 2\sigma(I)$)	$R_1 = 0.1571$, $\omega R_2 = 0.3469$
Final R indexes (all data)	$R_1 = 0.3667$, $\omega R_2 = 0.4384$
Largest diff. peak / hole / e Å ⁻³	1.38 / -0.87

Table 28. Bond lengths for 10c.

Atom	Atom	Length / Å	Atom	Atom	Length / Å
Se1	C2	1.902(17)	C16	C17	1.40(3)
Se1	C8	1.82(2)	C17	C18	1.45(4)
Se2	C14	1.89(2)	C18	C19	1.46(3)
Se2	C20	1.98(2)	C21	C22	1.507(10)
P1	C1	1.813(19)	C21	C22S	1.500(10)
P1	C13	1.76(2)	C22	C23	1.5000(11)
P1	C25	1.88(2)	C23	C24	1.501(10)
P2	C3	1.824(17)	C22S	C23S	1.496(10)
P2	C15	1.870(19)	C23S	C24	1.501(10)
P2	C26	1.77(2)	C25	C26	1.58(3)
N1	C1	1.34(2)	C25	C27	1.478(10)
N1	C2	1.38(2)	C27	C28	1.507(10)
N1	C4	1.46(2)	C28	C29	1.495(10)
N2	C2	1.37(2)	C28	C29S	1.496(10)
N2	C3	1.35(2)	C29	C30	1.500(10)
N2	C9	1.51(2)	C29S	C30S	1.500(10)
N3	C13	1.46(3)	S1	O1	1.434(15)
N3	C14	1.31(2)	S1	O2	1.304(14)
N3	C16	1.49(2)	S1	O3	1.423(15)
N4	C14	1.36(2)	S1	C31	1.78(3)
N4	C15	1.27(2)	F1	C31	1.27(3)
N4	C21	1.46(2)	F2	C31	1.32(3)
C1	C3	1.42(2)	F3	C31	1.40(3)
C4	C5	1.46(3)	S2	O4	1.422(15)
C5	C6	1.51(3)	S2	O5	1.421(16)
C6	C7	1.54(3)	S2	O6	1.455(14)
C9	C10	1.41(3)	S2	C32	1.86(3)
C10	C11	1.51(3)	F4	C32	1.33(3)
C11	C12	1.45(3)	F5	C32	1.32(2)
C13	C15	1.46(3)	F6	C32	1.26(3)

Table 29. Bond angles for 10c.

Atom	Atom	Atom	Angle / °	Atom	Atom	Atom	Angle / °
C8	Se1	C2	96.9(10)	C13	C15	P2	113.7(15)
C14	Se2	C20	98.6(10)	C17	C16	N3	114.6(18)
C1	P1	C25	95.5(8)	C16	C17	C18	119(2)
C13	P1	C1	96.4(10)	C17	C18	C19	119(3)
C13	P1	C25	93.0(9)	N4	C21	C22	110.0(19)
C3	P2	C15	95.3(8)	N4	C21	C22S	111(2)
C26	P2	C3	94.8(8)	C23	C22	C21	114.4(19)
C26	P2	C15	99.1(8)	C22	C23	C24	112.6(19)

C1	N1	C2	110.1(15)	C23S	C22S	C21	116(2)
C1	N1	C4	125.7(15)	C22S	C23S	C24	113(2)
C2	N1	C4	124.1(15)	C26	C25	P1	114.5(13)
C2	N2	C9	125.1(15)	C27	C25	P1	114.0(14)
C3	N2	C2	110.3(14)	C27	C25	C26	118.5(16)
C3	N2	C9	124.2(15)	C25	C26	P2	123.8(13)
C13	N3	C16	121.1(16)	C25	C27	C28	117.6(15)
C14	N3	C13	110.8(16)	C29	C28	C27	116(2)
C14	N3	C16	128.1(16)	C29S	C28	C27	96.1(17)
C14	N4	C21	123.2(17)	C28	C29	C30	118(2)
C15	N4	C14	110.4(17)	C28	C29S	C30S	104(3)
C15	N4	C21	126.3(15)	O1	S1	C31	101.4(11)
N1	C1	P1	130.2(14)	O2	S1	O1	119.0(9)
N1	C1	C3	107.0(15)	O2	S1	O3	117.0(10)
C3	C1	P1	122.8(14)	O2	S1	C31	102.2(12)
N1	C2	Se1	127.5(13)	O3	S1	O1	110.7(9)
N2	C2	Se1	124.6(13)	O3	S1	C31	103.2(12)
N2	C2	N1	106.0(14)	F1	C31	S1	116(2)
N2	C3	P2	131.2(13)	F1	C31	F2	108(2)
N2	C3	C1	106.3(15)	F1	C31	F3	101(2)
C1	C3	P2	121.1(13)	F2	C31	S1	117(2)
C5	C4	N1	115.4(15)	F2	C31	F3	102(2)
C4	C5	C6	116.7(18)	F3	C31	S1	109.8(19)
C5	C6	C7	110.3(17)	O4	S2	O6	114.5(9)
C10	C9	N2	113.5(16)	O4	S2	C32	102.6(12)
C9	C10	C11	113.8(19)	O5	S2	O4	116.8(9)
C12	C11	C10	120(2)	O5	S2	O6	115.0(11)
N3	C13	P1	131.8(17)	O5	S2	C32	103.7(12)
N3	C13	C15	98.6(17)	O6	S2	C32	101.1(11)
C15	C13	P1	129.5(17)	F4	C32	S2	106(2)
N3	C14	Se2	125.3(14)	F5	C32	S2	108.6(19)
N3	C14	N4	108.3(18)	F5	C32	F4	106(2)
N4	C14	Se2	125.9(15)	F6	C32	S2	112.7(17)
N4	C15	P2	133.4(14)	F6	C32	F4	109(2)
N4	C15	C13	111.8(17)	F6	C32	F5	113(3)

7.4.6 1,3,5,7-Tetrabutyl-1,5-dihydro-4,8-ethano[1,4]diphosphinino[2,3-d:5,6-d']diimidazolium bis(trifluoromethanesulfonate) **11a**

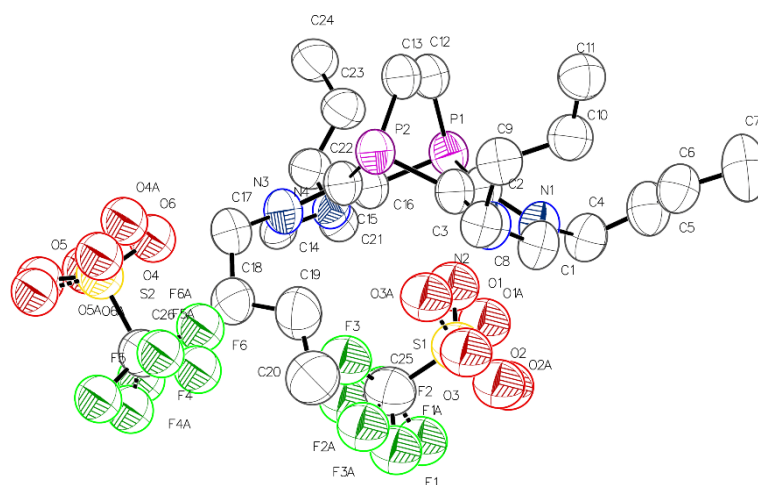


Figure 94. Molecular structure of **11a** in the single crystal. Thermal ellipsoids are set at 50 % probability level. Hydrogen atoms were omitted for clarity.

Table 30. Crystal data and structure refinements for **11a**.

Identification code	GSTR817, TT-809 // GXray7479
Crystal habitus	clear colourless plate
Device type	STOE Stadivari
Empirical formula	C ₂₆ H ₄₂ F ₆ N ₄ O ₆ P ₂ S ₂
Moiety formula	C ₂₄ H ₄₂ N ₄ P ₂ , 2 CF ₃ O ₃ S
Formula weight / g mol ⁻¹	746.69
T / K	100
Crystal system	triclinic
Space group	<i>P</i> -1
<i>a</i> / Å	9.043(3)
<i>b</i> / Å	12.602(3)
<i>c</i> / Å	16.770(5)
α / °	103.29(2)
β / °	90.35(2)
γ / °	109.51(2)
<i>V</i> / Å ³	1746.0(9)
<i>Z</i>	2
ρ_{calc} / g cm ⁻³	1.420
μ / mm ⁻¹	2.929
<i>F</i> (000)	780.0
Crystal size / mm ³	0.18 × 0.09 × 0.03
Absorption correction	multi-scan
<i>T</i> _{min} ; <i>T</i> _{max}	0.0000; 0.6510
Radiation	Cu-K α (λ = 1.54178 Å)
2 θ range for data collection / °	8.246 to 135.45
Completeness to θ	0.989
Index ranges	-10 ≤ <i>h</i> ≤ 10, -10 ≤ <i>k</i> ≤ 15, -20 ≤ <i>l</i> ≤ 18
Reflections collected	24592
Independent reflections	6248 (<i>R</i> _{int} = 0.8540, <i>R</i> _{σ} = 0.5088)
Data / restraints / parameters	6248 / 702 / 529
Goodness-of-fit on <i>F</i> ²	1.193

Final R indexes ($I \geq 2\sigma(I)$)
 Final R indexes (all data)
 Largest diff. peak / hole / $\text{e } \text{\AA}^{-3}$

$R_1 = 0.2408$, $\omega R_2 = 0.4913$
 $R_1 = 0.5351$, $\omega R_2 = 0.6335$
 $0.78 / -0.57$

Table 31. Bond lengths for 11a.

Atom	Atom	Length / $\text{\AA}$	Atom	Atom	Length / $\text{\AA}$
P1	C2	1.81(2)	C21	C22	1.52(3)
P1	C12	1.91(2)	C22	C23	1.49(3)
P1	C16	1.85(2)	C23	C24	1.48(3)
P2	C3	1.86(2)	S1	O1	1.442(14)
P2	C13	1.84(2)	S1	O1A	1.427(7)
P2	C15	1.77(2)	S1	O2	1.449(15)
N1	C1	1.32(3)	S1	O2A	1.421(7)
N1	C2	1.44(3)	S1	O3	1.446(14)
N1	C4	1.47(3)	S1	O3A	1.458(7)
N2	C1	1.30(3)	S1	C25	1.792(10)
N2	C3	1.37(3)	F1	C25	1.340(15)
N2	C8	1.36(3)	F1A	C25	1.346(16)
N3	C14	1.31(2)	F2	C25	1.335(14)
N3	C15	1.40(2)	F2A	C25	1.305(16)
N3	C17	1.48(3)	F3	C25	1.351(15)
N4	C14	1.43(2)	F3A	C25	1.327(17)
N4	C16	1.36(2)	S2	O4	1.442(15)
N4	C21	1.43(2)	S2	O4A	1.393(16)
C2	C3	1.37(3)	S2	O5	1.400(15)
C4	C5	1.47(3)	S2	O5A	1.463(16)
C5	C6	1.38(3)	S2	O6	1.444(15)
C6	C7	1.46(3)	S2	O6A	1.461(16)
C8	C9	1.50(3)	S2	C26	1.792(11)
C9	C10	1.52(3)	F4	C26	1.331(15)
C10	C11	1.39(3)	F4A	C26	1.276(16)
C12	C13	1.40(3)	F5	C26	1.365(15)
C15	C16	1.32(3)	F5A	C26	1.331(15)
C17	C18	1.51(3)	F6	C26	1.292(15)
C18	C19	1.63(3)	F6A	C26	1.376(16)
C19	C20	1.39(4)			

Table 32. Bond angles for 11a.

Atom	Atom	Atom	Angle / $^\circ$	Atom	Atom	Atom	Angle / $^\circ$
C2	P1	C12	91.9(10)	O1	S1	O3	121.5(13)
C2	P1	C16	93.6(10)	O1	S1	C25	107.6(8)
C16	P1	C12	93.0(10)	O1A	S1	O3A	111.9(5)
C13	P2	C3	93.3(10)	O1A	S1	C25	106.5(5)
C15	P2	C3	93.9(10)	O2	S1	C25	101.4(9)
C15	P2	C13	93.6(10)	O2A	S1	O1A	114.2(4)
C1	N1	C2	105.0(18)	O2A	S1	O3A	112.2(4)
C1	N1	C4	129.6(19)	O2A	S1	C25	111.0(6)
C2	N1	C4	125.4(18)	O3	S1	O2	100.9(13)
C1	N2	C3	101.8(18)	O3	S1	C25	109.7(10)
C1	N2	C8	132.0(19)	O3A	S1	C25	99.9(5)
C8	N2	C3	124.7(19)	F1	C25	S1	108.7(9)
C14	N3	C15	108.8(17)	F1	C25	F3	110.1(14)
C14	N3	C17	116.5(16)	F1A	C25	S1	97.2(14)
C15	N3	C17	134.1(17)	F2	C25	S1	111.0(10)

C16	N4	C14	100.7(16)	F2	C25	F1	111.1(14)
C16	N4	C21	135.3(17)	F2	C25	F3	116.5(13)
C21	N4	C14	123.1(15)	F2A	C25	S1	149.1(17)
N2	C1	N1	117(2)	F2A	C25	F1A	91.8(14)
N1	C2	P1	130.3(16)	F2A	C25	F3A	93.2(15)
C3	C2	P1	126.9(17)	F3	C25	S1	98.6(9)
C3	C2	N1	102.5(18)	F3A	C25	S1	116.1(11)
N2	C3	P2	127.5(16)	F3A	C25	F1A	90.8(15)
C2	C3	P2	118.9(16)	O4	S2	O6	107.3(15)
C2	C3	N2	113.6(19)	O4	S2	C26	99.9(11)
C5	C4	N1	115.9(19)	O4A	S2	O5A	107.9(18)
C6	C5	C4	130(2)	O4A	S2	O6A	121.5(19)
C5	C6	C7	127(2)	O4A	S2	C26	118.7(12)
N2	C8	C9	116(2)	O5	S2	O4	119.2(16)
C8	C9	C10	119(2)	O5	S2	O6	117.3(15)
C11	C10	C9	114(2)	O5	S2	C26	112.0(11)
C13	C12	P1	120.4(17)	O5A	S2	C26	101.5(13)
C12	C13	P2	122.4(17)	O6	S2	C26	97.7(11)
N3	C14	N4	110.2(16)	O6A	S2	O5A	101.7(18)
N3	C15	P2	126.8(16)	O6A	S2	C26	102.6(12)
C16	C15	P2	129.0(16)	F4	C26	S2	107.4(12)
C16	C15	N3	104.2(17)	F4	C26	F5	92.9(15)
N4	C16	P1	124.7(16)	F4A	C26	S2	131.7(13)
C15	C16	P1	119.7(15)	F4A	C26	F5A	116.2(16)
C15	C16	N4	115.1(18)	F4A	C26	F6A	111.4(15)
N3	C17	C18	115.3(19)	F5	C26	S2	107.5(12)
C17	C18	C19	107.9(18)	F5A	C26	S2	100.8(15)
C20	C19	C18	115(2)	F5A	C26	F6A	95.7(18)
N4	C21	C22	108.6(17)	F6	C26	S2	130.9(13)
C23	C22	C21	117.9(16)	F6	C26	F4	108.3(16)
C24	C23	C22	115.9(17)	F6	C26	F5	103.3(15)
O1	S1	O2	113.9(13)	F6A	C26	S2	93.6(14)

7.4.7 1,3,5,7-Tetrabutyl-9,10-diethyl-1,5-dihydro-4,8-ethano[1,4]diphosphino[2,3-d:5,6-d']diimidazolium bis(trifluoromethanesulfonate) **11b**

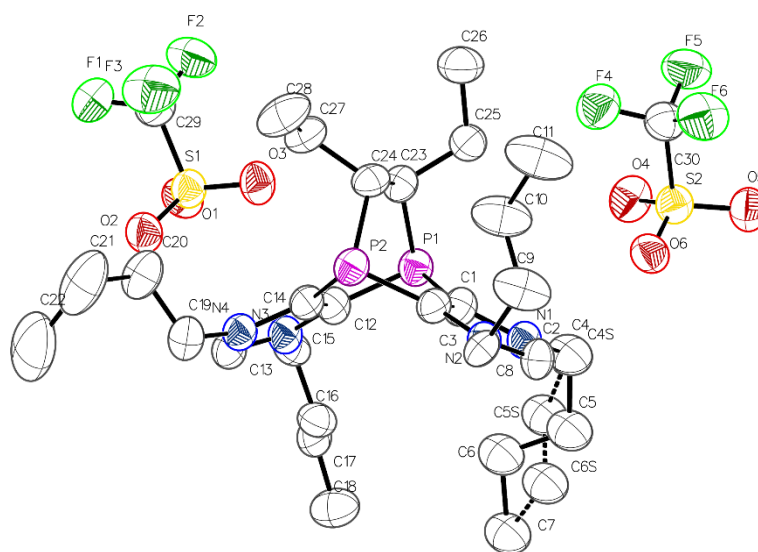


Figure 95. Molecular structure of **11b** in the single crystal. Thermal ellipsoids are set at 50 % probability level. Hydrogen atoms were omitted for clarity.

Table 33. Crystal data and structure refinements for **11b**.

Identification code	GSTR757, TT-537 // GXray6856
Crystal habitus	clear colourless plate
Device type	STOE IPDS-2T
Empirical formula	$C_{30}H_{50}F_6N_4O_6P_2S_2$
Moiety formula	2 CF_3O_3S , $C_{28}H_{50}N_4P_2$
Formula weight / $g\ mol^{-1}$	802.80
T / K	123
Crystal system	triclinic
Space group	$P\bar{1}$
$a / \text{\AA}$	9.6005(16)
$b / \text{\AA}$	12.2140(17)
$c / \text{\AA}$	17.674(3)
$\alpha / ^\circ$	94.597(12)
$\beta / ^\circ$	103.001(13)
$\gamma / ^\circ$	90.396(13)
$V / \text{\AA}^3$	2012.2(6)
Z	2
$\rho_{calc} / g\ cm^{-3}$	1.325
μ / mm^{-1}	0.283
$F(000)$	844.0
Crystal size / mm^3	$0.09 \times 0.09 \times 0.03$
Absorption correction	multi-scan
T_{min} ; T_{max}	0.6338; 0.9435
Radiation	Mo-K α ($\lambda = 0.71073\ \text{\AA}$)
2θ range for data collection / $^\circ$	5.412 to 55.998
Completeness to θ	0.990
Index ranges	$-12 \leq h \leq 12$, $-16 \leq k \leq 16$, $-20 \leq l \leq 23$
Reflections collected	19218
Independent reflections	9576 ($R_{int} = 0.2821$, $R_\sigma = 0.6038$)

Data / restraints / parameters	9576 / 475 / 485
Goodness-of-fit on F^2	0.703
Final R indexes ($I \geq 2\sigma(I)$)	$R_1 = 0.0594$, $\omega R_2 = 0.0768$
Final R indexes (all data)	$R_1 = 0.3686$, $\omega R_2 = 0.1256$
Largest diff. peak / hole / $e \text{ \AA}^{-3}$	0.29 / -0.49

Table 34. Bond lengths for 11b.

Atom	Atom	Length / $\text{\AA}$	Atom	Atom	Length / $\text{\AA}$
S1	O1	1.445(4)	N3	C13	1.356(6)
S1	O2	1.459(4)	N3	C15	1.478(6)
S1	O3	1.441(4)	N4	C13	1.332(6)
S1	C29	1.788(7)	N4	C14	1.413(6)
F1	C29	1.346(7)	N4	C19	1.475(7)
F2	C29	1.357(7)	C1	C3	1.349(7)
F3	C29	1.290(7)	C4	C5	1.509(9)
S2	O4	1.432(4)	C4S	C5S	1.504(10)
S2	O5	1.452(4)	C5	C6	1.501(8)
S2	O6	1.443(4)	C5S	C6S	1.492(10)
S2	C30	1.805(6)	C6	C7	1.580(7)
F4	C30	1.327(7)	C6S	C7	1.528(9)
F5	C30	1.363(8)	C8	C9	1.516(6)
F6	C30	1.310(7)	C9	C10	1.445(8)
P1	C1	1.825(6)	C10	C11	1.518(7)
P1	C12	1.826(6)	C12	C14	1.342(7)
P1	C23	1.862(5)	C15	C16	1.526(6)
P2	C3	1.794(6)	C16	C17	1.504(6)
P2	C14	1.805(5)	C17	C18	1.510(6)
P2	C24	1.892(6)	C19	C20	1.476(7)
N1	C1	1.394(6)	C20	C21	1.525(8)
N1	C2	1.325(7)	C21	C22	1.566(9)
N1	C4	1.484(10)	C23	C24	1.548(7)
N1	C4S	1.479(10)	C23	C25	1.544(7)
N2	C2	1.334(6)	C24	C27	1.530(7)
N2	C3	1.414(7)	C25	C26	1.553(6)
N2	C8	1.478(6)	C27	C28	1.544(7)
N3	C12	1.396(6)			

Table 35. Bond angles for 11b.

Atom	Atom	Atom	Angle / $^\circ$	Atom	Atom	Atom	Angle / $^\circ$
O1	S1	O2	113.7(2)	C13	N4	C14	108.4(5)
O1	S1	C29	105.8(3)	C13	N4	C19	123.0(5)
O2	S1	C29	102.3(3)	C14	N4	C19	128.4(5)
O3	S1	O1	114.8(3)	N1	C1	P1	129.2(5)
O3	S1	O2	115.6(3)	C3	C1	P1	122.4(5)
O3	S1	C29	102.5(3)	C3	C1	N1	108.4(6)
F1	C29	S1	111.0(5)	N1	C2	N2	109.7(6)
F1	C29	F2	104.1(6)	N2	C3	P2	128.8(5)
F2	C29	S1	111.9(5)	C1	C3	P2	125.4(5)
F3	C29	S1	115.4(6)	C1	C3	N2	105.8(5)
F3	C29	F1	107.3(6)	N1	C4	C5	110.3(9)
F3	C29	F2	106.4(6)	N1	C4S	C5S	114.5(17)
O4	S2	O5	116.4(3)	C6	C5	C4	112.2(10)

O4	S2	O6	113.6(3)	C6S	C5S	C4S	115(2)
O4	S2	C30	104.4(3)	C5	C6	C7	106.9(7)
O5	S2	C30	104.3(3)	C5S	C6S	C7	107.9(14)
O6	S2	O5	113.7(3)	N2	C8	C9	111.7(5)
O6	S2	C30	102.4(3)	C10	C9	C8	117.6(6)
F4	C30	S2	113.1(5)	C9	C10	C11	115.8(6)
F4	C30	F5	106.0(6)	N3	C12	P1	128.1(5)
F5	C30	S2	110.2(5)	C14	C12	P1	123.1(5)
F6	C30	S2	112.7(5)	C14	C12	N3	108.4(5)
F6	C30	F4	108.5(6)	N4	C13	N3	109.0(5)
F6	C30	F5	106.0(6)	N4	C14	P2	128.8(5)
C1	P1	C12	92.3(3)	C12	C14	P2	124.5(5)
C1	P1	C23	94.5(3)	C12	C14	N4	106.7(5)
C12	P1	C23	95.4(3)	N3	C15	C16	111.2(5)
C3	P2	C14	93.6(3)	C17	C16	C15	112.3(5)
C3	P2	C24	94.7(3)	C16	C17	C18	113.8(5)
C14	P2	C24	94.4(3)	N4	C19	C20	113.0(5)
C1	N1	C4	127.9(10)	C19	C20	C21	112.4(6)
C1	N1	C4S	127.2(16)	C20	C21	C22	113.9(7)
C2	N1	C1	107.8(5)	C24	C23	P1	120.9(4)
C2	N1	C4	124.3(10)	C25	C23	P1	106.2(4)
C2	N1	C4S	124.9(16)	C25	C23	C24	111.5(4)
C2	N2	C3	108.2(5)	C23	C24	P2	117.1(4)
C2	N2	C8	125.3(5)	C27	C24	P2	108.4(4)
C3	N2	C8	126.3(5)	C27	C24	C23	112.5(5)
C12	N3	C15	127.9(5)	C23	C25	C26	113.8(5)
C13	N3	C12	107.4(5)	C24	C27	C28	113.7(5)
C13	N3	C15	124.7(5)				

7.4.8 (1,3,5,7-Tetrabutyl-1,5-dihydro-4,8-ethano[1,4]diphosphinino[2,3-d:5,6-d']diimidazolium- κP^1)borane bis(trifluoromethanesulfonate) **14a**

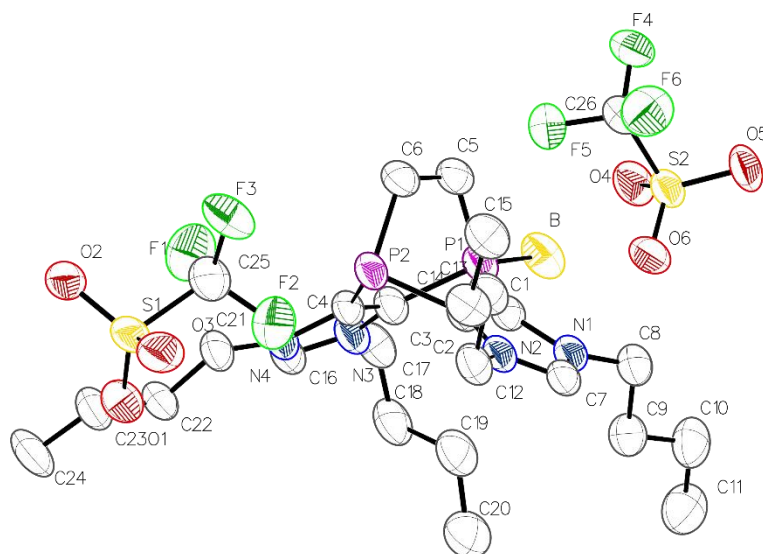


Figure 96. Molecular structure of **14a** in the single crystal. Thermal ellipsoids are set at 50 % probability level. Hydrogen atoms were omitted for clarity.

Table 36. Crystal data and structure refinements for **14a**.

Identification code	GSTR832, TT-894 // GXray7904
Crystal habitus	clear colourless plate
Device type	STOE STADIVARI
Empirical formula	$C_{26}H_{45}BF_6N_4O_6P_2S_2$
Moiety formula	$C_{24}H_{45}BN_4P_2$, 2 CF_3O_3S
Formula weight / $g\ mol^{-1}$	760.53
T / K	100
Crystal system	monoclinic
Space group	$P2_1/n$
$a / \text{\AA}$	12.4696(11)
$b / \text{\AA}$	24.3876(14)
$c / \text{\AA}$	12.4417(10)
$\alpha / ^\circ$	90.00
$\beta / ^\circ$	99.427(7)
$\gamma / ^\circ$	90.00
$V / \text{\AA}^3$	3732.4(5)
Z	4
$\rho_{calc} / g\ cm^{-3}$	1.353
μ / mm^{-1}	2.75
$F(000)$	1592.0
Crystal size / mm^3	$0.38 \times 0.28 \times 0.02$
Absorption correction	multi-scan
$T_{min}; T_{max}$	0.2443; 0.4943
Radiation	Cu-K α ($\lambda = 1.54178\ \text{\AA}$)
2θ range for data collection / $^\circ$	7.25 to 135.49
Completeness to θ	0.998
Index ranges	$-14 \leq h \leq 14, -28 \leq k \leq 10, -14 \leq l \leq 14$
Reflections collected	46229
Independent reflections	6741 ($R_{int} = 0.1497, R_\sigma = 0.0857$)

Data / restraints / parameters	6741 / 369 / 440
Goodness-of-fit on F^2	1.208
Final R indexes ($I \geq 2\sigma(I)$)	$R_1 = 0.1093$, $\omega R_2 = 0.2789$
Final R indexes (all data)	$R_1 = 0.1438$, $\omega R_2 = 0.3220$
Largest diff. peak / hole / $e \text{ \AA}^{-3}$	1.16 / -0.57

Table 37. Bond lengths for 14a.

Atom	Atom	Length / $\text{\AA}$	Atom	Atom	Length / $\text{\AA}$
P1	C1	1.812(5)	C10	C11	1.505(11)
P1	C3	1.807(5)	C12	C13	1.526(9)
P1	C5	1.822(6)	C13	C14	1.500(9)
P1	B	1.912(8)	C14	C15	1.516(9)
P2	C2	1.826(6)	C17	C18	1.486(10)
P2	C4	1.834(6)	C18	C19	1.547(10)
P2	C6	1.872(6)	C19	C20	1.533(11)
N1	C1	1.378(7)	C21	C22	1.522(8)
N1	C7	1.330(7)	C22	C23	1.511(9)
N1	C8	1.463(8)	C23	C24	1.541(9)
N2	C2	1.389(7)	S1	O1	1.447(5)
N2	C7	1.325(8)	S1	O2	1.439(5)
N2	C12	1.475(8)	S1	O3	1.436(5)
N3	C3	1.391(7)	S1	C25	1.832(8)
N3	C16	1.319(7)	F1	C25	1.306(8)
N3	C17	1.472(9)	F2	C25	1.345(9)
N4	C4	1.398(6)	F3	C25	1.341(8)
N4	C16	1.321(8)	S2	O4	1.431(4)
N4	C21	1.468(8)	S2	O5	1.448(4)
C1	C2	1.335(8)	S2	O6	1.440(4)
C3	C4	1.336(8)	S2	C26	1.812(7)
C5	C6	1.530(9)	F4	C26	1.321(7)
C8	C9	1.529(9)	F5	C26	1.346(7)
C9	C10	1.519(10)	F6	C26	1.330(8)

Table 38. Bond angles for 14a.

Atom	Atom	Atom	Angle / $^\circ$	Atom	Atom	Atom	Angle / $^\circ$
C1	P1	C5	99.0(3)	C10	C9	C8	111.3(5)
C1	P1	B	121.6(3)	C11	C10	C9	112.4(6)
C3	P1	C1	95.8(2)	N2	C12	C13	112.1(5)
C3	P1	C5	100.0(3)	C14	C13	C12	113.0(5)
C3	P1	B	121.5(3)	C13	C14	C15	113.7(5)
C5	P1	B	114.4(3)	N3	C16	N4	110.4(5)
C2	P2	C4	92.7(3)	N3	C17	C18	111.2(6)
C2	P2	C6	96.1(3)	C17	C18	C19	114.9(5)
C4	P2	C6	94.1(3)	C20	C19	C18	114.4(6)
C1	N1	C8	127.5(5)	N4	C21	C22	112.3(5)
C7	N1	C1	106.9(5)	C23	C22	C21	109.4(5)
C7	N1	C8	125.5(5)	C22	C23	C24	111.4(6)
C2	N2	C12	126.1(5)	O1	S1	C25	103.5(4)
C7	N2	C2	107.8(5)	O2	S1	O1	114.7(3)
C7	N2	C12	126.0(5)	O2	S1	C25	103.2(3)
C3	N3	C17	128.7(5)	O3	S1	O1	114.4(3)
C16	N3	C3	107.4(5)	O3	S1	O2	115.3(3)
C16	N3	C17	123.7(5)	O3	S1	C25	103.4(3)
C4	N4	C21	124.7(5)	F1	C25	S1	112.7(5)
C16	N4	C4	107.5(5)	F1	C25	F2	108.7(7)

C16	N4	C21	127.5(4)	F1	C25	F3	106.8(6)
N1	C1	P1	132.0(5)	F2	C25	S1	110.5(5)
C2	C1	P1	119.3(4)	F3	C25	S1	110.4(6)
C2	C1	N1	108.7(5)	F3	C25	F2	107.5(5)
N2	C2	P2	128.6(4)	O4	S2	O5	115.9(3)
C1	C2	P2	124.6(4)	O4	S2	O6	115.1(3)
C1	C2	N2	106.6(5)	O4	S2	C26	103.4(3)
N3	C3	P1	133.7(4)	O5	S2	C26	103.4(3)
C4	C3	P1	118.4(4)	O6	S2	O5	113.6(3)
C4	C3	N3	107.7(5)	O6	S2	C26	103.0(3)
N4	C4	P2	127.6(4)	F4	C26	S2	112.3(5)
C3	C4	P2	125.5(4)	F4	C26	F5	106.7(5)
C3	C4	N4	106.9(5)	F4	C26	F6	106.9(5)
C6	C5	P1	116.7(4)	F5	C26	S2	110.8(4)
C5	C6	P2	119.0(4)	F6	C26	S2	111.7(5)
N2	C7	N1	110.0(5)	F6	C26	F5	108.3(6)
N1	C8	C9	112.1(5)				

7.4.9 [Dichlorido(μ -1,3,5,7-tetrabutyl-1,5-dihydro-4,8-ethano[1,4]diphosphino[2,3-d:5,6-d']diimidazolium- $\kappa P^1, \kappa P^2$)bis(η^2, η^2 -cycloocta-1,5-diene)dirhodium(I)] bis(trifluoromethanesulfonate) **16a**

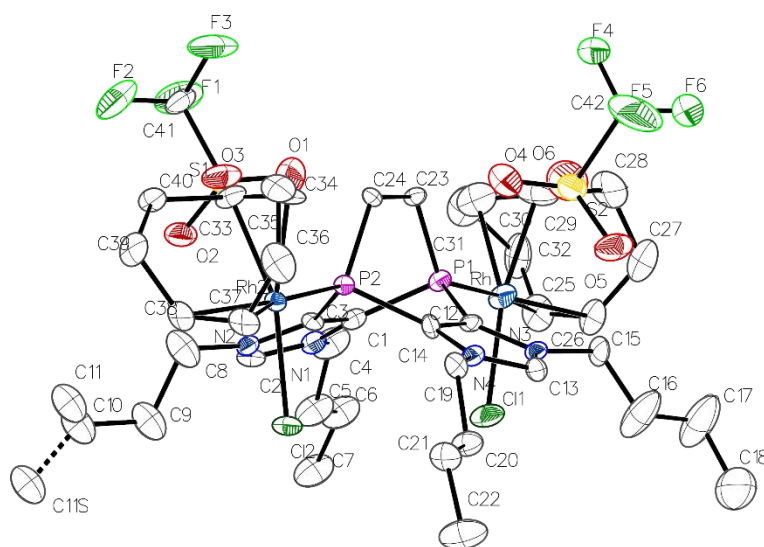


Figure 97. Molecular structure of **16a** in the single crystal. Thermal ellipsoids are set at 50 % probability level. Hydrogen atoms and solvent molecules were omitted for clarity.

Table 39. Crystal data and structure refinements for **16a**.

Identification code	GSTR827, TT-876 // GXraymo_7738_0m_4g
Crystal habitus	clear yellow plank
Device type	Bruker D8 Venture
Empirical formula	C ₄₄ H ₇₀ Cl ₆ F ₆ N ₄ O ₆ P ₂ Rh ₂ S ₂
Moiety formula	C ₄₀ H ₆₆ Cl ₂ N ₄ P ₂ Rh ₂ , 2 CH ₂ Cl ₂ , 2 CF ₃ O ₃ S
Formula weight / g mol ⁻¹	1409.62
T / K	100.0
Crystal system	orthorhombic
Space group	<i>Pna</i> 2 ₁

$a / \text{\AA}$	13.0905(15)
$b / \text{\AA}$	21.056(2)
$c / \text{\AA}$	21.789(3)
$\alpha / ^\circ$	90
$\beta / ^\circ$	90
$\gamma / ^\circ$	90
$V / \text{\AA}^3$	6005.7(12)
Z	4
$\rho_{\text{calc}} / \text{g cm}^{-3}$	1.559
μ / mm^{-1}	1.003
$F(000)$	2872.0
Crystal size / mm^3	$0.28 \times 0.12 \times 0.1$
Absorption correction	empirical
$T_{\text{min}}; T_{\text{max}}$	0.084647; 0.746156
Radiation	Mo-K α ($\lambda = 0.71073 \text{\AA}$)
2θ range for data collection / $^\circ$	3.664 to 55.996
Completeness to θ	1.000
Index ranges	$-17 \leq h \leq 17, -27 \leq k \leq 27, 0 \leq l \leq 28$
Reflections collected	27965
Independent reflections	7433 ($R_{\text{int}} = 0.1200, R_{\sigma} = 0.0870$)
Data / restraints / parameters	7433 / 68 / 664
Goodness-of-fit on F^2	1.146
Final R indexes ($I \geq 2\sigma(I)$)	$R_1 = 0.0748, \omega R_2 = 0.1635$
Final R indexes (all data)	$R_1 = 0.0876, \omega R_2 = 0.1729$
Largest diff. peak / hole / $\text{e \AA}^{-3}$	3.37 / -0.92

Table 40. Bond lengths for 16a.

Atom	Atom	Length / $\text{\AA}$	Atom	Atom	Length / $\text{\AA}$
Rh1	Se1	2.5030(9)	C18	C19	1.545(11)
Rh1	Cl1	2.3964(16)	C20	C22	1.352(8)
Rh1	C8	2.123(7)	C23	C24	1.589(12)
Rh1	C9	2.137(7)	C24	C25	1.432(14)
Rh1	C12	2.119(7)	C25	C26	1.516(16)
Rh1	C13	2.151(7)	C27	C28	1.56(2)
Rh2	Se2	2.4975(10)	C27	C34	1.467(18)
Rh2	Cl2	2.3804(18)	C28	C29	1.397(18)
Rh2	C27	2.195(12)	C27S	C28S	1.56(2)
Rh2	C27S	2.188(15)	C27S	C34S	1.313(19)
Rh2	C30	2.116(8)	C28S	C29	1.65(2)
Rh2	C31	2.121(7)	C29	C30	1.531(11)
Rh2	C34	2.126(15)	C30	C31	1.389(10)
Rh2	C34S	2.152(16)	C31	C32	1.526(12)
Rh3	Cl3	2.3553(18)	C32	C33	1.54(2)
Rh3	P1	2.2568(16)	C32	C33S	1.48(3)
Rh3	C41	2.139(7)	C33	C34	1.497(19)
Rh3	C42	2.113(7)	C33S	C34S	1.56(2)
Rh3	C45	2.231(7)	C35	C36	1.536(11)
Rh3	C46	2.232(7)	C36	C37	1.534(9)
Rh4	Cl4	2.3621(18)	C37	C38	1.486(12)
Rh4	P2	2.2644(16)	C39	C40	1.524(9)
Rh4	C49	2.155(7)	C41	C42	1.378(10)
Rh4	C50	2.143(7)	C41	C48	1.547(10)
Rh4	C53	2.220(7)	C42	C43	1.522(9)
Rh4	C54	2.223(6)	C43	C44	1.479(14)
Se1	C2	1.877(6)	C44	C45	1.545(12)
Se2	C21	1.873(6)	C45	C46	1.374(10)

P1	C1	1.813(6)	C46	C47	1.522(12)
P1	C20	1.824(5)	C47	C48	1.485(13)
P1	C39	1.850(8)	C49	C50	1.432(11)
P2	C3	1.834(6)	C49	C56	1.499(8)
P2	C22	1.821(7)	C50	C51	1.486(9)
P2	C40	1.867(6)	C51	C52	1.467(8)
N1	C1	1.400(7)	C52	C53	1.465(10)
N1	C2	1.332(8)	C53	C54	1.378(11)
N1	C4	1.476(7)	C54	C55	1.475(9)
N2	C2	1.357(7)	C55	C56	1.446(8)
N2	C3	1.388(8)	C57	C58	1.372(17)
N2	C16	1.480(9)	C57	C62	1.423(17)
N3	C20	1.371(8)	C57	C63	1.487(8)
N3	C21	1.350(7)	C58	C59	1.315(19)
N3	C23	1.477(9)	C59	C60	1.30(2)
N4	C21	1.354(9)	C60	C61	1.43(2)
N4	C22	1.378(7)	C61	C62	1.300(18)
N4	C35	1.462(8)	C64	C65	1.3900
C1	C3	1.327(8)	C64	C69	1.3900
C4	C5	1.511(10)	C64	C70	1.501(8)
C5	C6	1.520(9)	C65	C66	1.3900
C6	C7	1.506(12)	C66	C67	1.3900
C8	C9	1.392(9)	C67	C68	1.3900
C8	C15	1.510(10)	C68	C69	1.3900
C9	C10	1.532(9)	C64S	C65S	1.3900
C10	C11	1.533(12)	C64S	C69S	1.3900
C11	C12	1.504(10)	C64S	C70S	1.509(14)
C12	C13	1.403(10)	C65S	C66S	1.3900
C13	C14	1.477(11)	C66S	C67S	1.3900
C14	C15	1.525(11)	C67S	C68S	1.3900
C16	C17	1.532(10)	C68S	C69S	1.3900
C17	C18	1.485(10)			

Table 41. Bond angles for 16a.

Atom	Atom	Atom	Angle / °	Atom	Atom	Atom	Angle / °
Cl1	Rh1	Se1	95.09(5)	C9	C10	C11	111.7(6)
C8	Rh1	Se1	156.06(16)	C12	C11	C10	113.3(6)
C8	Rh1	Cl1	89.79(18)	C11	C12	Rh1	108.8(5)
C8	Rh1	C9	38.1(2)	C13	C12	Rh1	72.1(4)
C8	Rh1	C13	79.9(3)	C13	C12	C11	126.3(7)
C9	Rh1	Se1	164.87(19)	C12	C13	Rh1	69.6(4)
C9	Rh1	Cl1	88.71(19)	C12	C13	C14	123.0(6)
C9	Rh1	C13	89.2(3)	C14	C13	Rh1	114.0(5)
C12	Rh1	Se1	88.1(2)	C13	C14	C15	113.4(6)
C12	Rh1	Cl1	154.7(2)	C8	C15	C14	110.6(6)
C12	Rh1	C8	97.4(3)	N2	C16	C17	110.2(5)
C12	Rh1	C9	82.4(3)	C18	C17	C16	111.8(6)
C12	Rh1	C13	38.3(3)	C17	C18	C19	110.7(6)
C13	Rh1	Se1	90.5(2)	N3	C20	P1	129.7(4)
C13	Rh1	Cl1	165.74(19)	C22	C20	P1	121.0(5)
Cl2	Rh2	Se2	94.48(5)	C22	C20	N3	108.4(5)
C27	Rh2	Se2	151.8(4)	N3	C21	Se2	126.3(5)
C27	Rh2	Cl2	88.3(4)	N3	C21	N4	107.9(5)
C27S	Rh2	Se2	173.1(4)	N4	C21	Se2	125.8(4)
C27S	Rh2	Cl2	88.7(4)	N4	C22	P2	128.7(5)

C30	Rh2	Se2	88.8(2)	C20	C22	P2	121.2(4)
C30	Rh2	Cl2	161.77(19)	C20	C22	N4	106.9(6)
C30	Rh2	C27	80.6(5)	N3	C23	C24	109.0(7)
C30	Rh2	C27S	86.3(5)	C25	C24	C23	112.9(9)
C30	Rh2	C31	38.3(3)	C24	C25	C26	113.1(11)
C30	Rh2	C34	90.8(5)	C28	C27	Rh2	110.5(10)
C30	Rh2	C34S	98.9(6)	C34	C27	Rh2	67.7(7)
C31	Rh2	Se2	89.0(2)	C34	C27	C28	124.6(12)
C31	Rh2	Cl2	159.4(2)	C29	C28	C27	110.6(11)
C31	Rh2	C27	98.2(4)	C28S	C27S	Rh2	106.9(11)
C31	Rh2	C27S	90.2(4)	C34S	C27S	Rh2	70.9(10)
C31	Rh2	C34	83.2(4)	C34S	C27S	C28S	125.5(14)
C31	Rh2	C34S	80.5(6)	C27S	C28S	C29	117.8(13)
C34	Rh2	Se2	167.7(3)	C28	C29	C30	119.4(9)
C34	Rh2	Cl2	89.7(4)	C30	C29	C28S	109.7(8)
C34	Rh2	C27	39.7(5)	C29	C30	Rh2	111.4(6)
C34S	Rh2	Se2	151.0(4)	C31	C30	Rh2	71.0(4)
C34S	Rh2	Cl2	86.8(5)	C31	C30	C29	123.6(7)
C34S	Rh2	C27S	35.2(5)	C30	C31	Rh2	70.7(4)
P1	Rh3	Cl3	86.34(6)	C30	C31	C32	124.1(7)
C41	Rh3	Cl3	163.33(19)	C32	C31	Rh2	111.6(6)
C41	Rh3	P1	95.59(19)	C31	C32	C33	109.9(7)
C41	Rh3	C45	90.7(3)	C33S	C32	C31	119.1(10)
C41	Rh3	C46	81.9(3)	C34	C33	C32	117.3(12)
C42	Rh3	Cl3	158.8(2)	C27	C34	Rh2	72.7(8)
C42	Rh3	P1	92.9(2)	C27	C34	C33	121.3(14)
C42	Rh3	C41	37.8(3)	C33	C34	Rh2	110.8(11)
C42	Rh3	C45	81.8(3)	C32	C33S	C34S	106.2(15)
C42	Rh3	C46	95.8(3)	C27S	C34S	Rh2	73.9(10)
C45	Rh3	Cl3	92.5(2)	C27S	C34S	C33S	125.9(16)
C45	Rh3	P1	162.0(2)	C33S	C34S	Rh2	114.3(14)
C45	Rh3	C46	35.9(3)	N4	C35	C36	110.9(5)
C46	Rh3	Cl3	91.1(2)	C37	C36	C35	112.2(6)
C46	Rh3	P1	161.99(18)	C38	C37	C36	110.8(7)
P2	Rh4	Cl4	87.72(6)	C40	C39	P1	118.0(5)
C49	Rh4	Cl4	158.9(2)	C39	C40	P2	116.8(5)
C49	Rh4	P2	94.11(19)	C42	C41	Rh3	70.1(4)
C49	Rh4	C53	92.1(3)	C42	C41	C48	122.6(6)
C49	Rh4	C54	80.9(2)	C48	C41	Rh3	112.1(5)
C50	Rh4	Cl4	161.71(18)	C41	C42	Rh3	72.1(4)
C50	Rh4	P2	95.66(17)	C41	C42	C43	125.2(7)
C50	Rh4	C49	38.9(3)	C43	C42	Rh3	109.8(6)
C50	Rh4	C53	80.1(3)	C44	C43	C42	116.4(7)
C50	Rh4	C54	92.7(3)	C43	C44	C45	112.3(6)
C53	Rh4	Cl4	91.7(2)	C44	C45	Rh3	110.3(6)
C53	Rh4	P2	164.06(18)	C46	C45	Rh3	72.1(4)
C53	Rh4	C54	36.1(3)	C46	C45	C44	120.3(8)
C54	Rh4	Cl4	90.1(2)	C45	C46	Rh3	72.1(4)
C54	Rh4	P2	159.7(2)	C45	C46	C47	125.6(7)
C2	Se1	Rh1	100.4(2)	C47	C46	Rh3	107.8(5)
C21	Se2	Rh2	99.4(2)	C48	C47	C46	115.4(7)
C1	P1	Rh3	117.92(18)	C47	C48	C41	115.3(6)
C1	P1	C20	97.8(3)	C50	C49	Rh4	70.1(4)
C1	P1	C39	96.1(3)	C50	C49	C56	124.6(8)
C20	P1	Rh3	122.0(2)	C56	C49	Rh4	111.6(5)
C20	P1	C39	96.2(3)	C49	C50	Rh4	71.0(4)
C39	P1	Rh3	121.1(2)	C49	C50	C51	123.9(5)

C3	P2	Rh4	124.6(2)	C51	C50	Rh4	113.1(5)
C3	P2	C40	96.7(3)	C52	C51	C50	115.8(7)
C22	P2	Rh4	116.70(18)	C53	C52	C51	118.2(7)
C22	P2	C3	97.2(3)	C52	C53	Rh4	110.6(4)
C22	P2	C40	96.3(3)	C54	C53	Rh4	72.1(4)
C40	P2	Rh4	119.5(2)	C54	C53	C52	123.5(7)
C1	N1	C4	127.8(5)	C53	C54	Rh4	71.8(4)
C2	N1	C1	108.6(5)	C53	C54	C55	122.9(8)
C2	N1	C4	123.5(5)	C55	C54	Rh4	108.8(4)
C2	N2	C3	107.3(5)	C56	C55	C54	119.7(6)
C2	N2	C16	124.7(5)	C55	C56	C49	116.3(6)
C3	N2	C16	127.1(5)	C58	C57	C62	122.6(10)
C20	N3	C23	127.8(5)	C58	C57	C63	120.6(11)
C21	N3	C20	108.1(5)	C62	C57	C63	116.2(10)
C21	N3	C23	123.6(5)	C59	C58	C57	118.0(14)
C21	N4	C22	108.5(5)	C60	C59	C58	123.1(14)
C21	N4	C35	124.4(5)	C59	C60	C61	118.8(14)
C22	N4	C35	127.0(6)	C62	C61	C60	122.1(15)
N1	C1	P1	127.6(4)	C61	C62	C57	114.7(12)
C3	C1	P1	122.4(4)	C65	C64	C69	120.0
C3	C1	N1	106.9(5)	C65	C64	C70	118.6(6)
N1	C2	Se1	126.1(4)	C69	C64	C70	121.3(6)
N1	C2	N2	108.4(5)	C64	C65	C66	120.0
N2	C2	Se1	125.1(5)	C67	C66	C65	120.0
N2	C3	P2	129.2(5)	C68	C67	C66	120.0
C1	C3	P2	120.8(5)	C69	C68	C67	120.0
C1	C3	N2	108.7(5)	C68	C69	C64	120.0
N1	C4	C5	109.6(5)	C65S	C64S	C69S	120.0
C4	C5	C6	111.5(5)	C65S	C64S	C70S	109.6(13)
C7	C6	C5	113.7(5)	C69S	C64S	C70S	128.5(13)
C9	C8	Rh1	71.5(4)	C64S	C65S	C66S	120.0
C9	C8	C15	125.3(6)	C67S	C66S	C65S	120.0
C15	C8	Rh1	112.7(5)	C66S	C67S	C68S	120.0
C8	C9	Rh1	70.4(4)	C67S	C68S	C69S	120.0
C8	C9	C10	124.6(6)	C68S	C69S	C64S	120.0
C10	C9	Rh1	112.1(5)				

7.4.10 1,3,5,7-Tetrabutyl-9,10-diethyl-1,3,5,7-tetrahydro-2*H*,6*H*-4,8-ethano[1,4]diphosphinino[2,3-*d*:5,6-*d'*]diimidazole-2,6-ylidene 17b

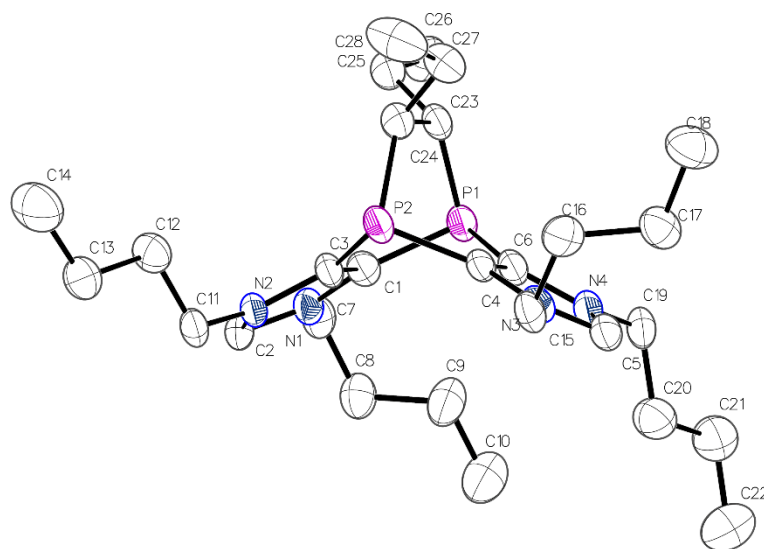


Figure 98. Molecular structure of **17b** in the single crystal (one of two independent molecules). Thermal ellipsoids are set at 50 % probability level. Hydrogen atoms were omitted for clarity.

Table 42. Crystal data and structure refinements for **17b**.

Identification code	GSTR778, TT-592 // GXray6966
Crystal habitus	clear colourless plate
Device type	Stadivari
Empirical formula	C ₂₈ H ₄₈ N ₄ P ₂
Moiety formula	C ₂₈ H ₄₈ N ₄ P ₂
Formula weight / g mol ⁻¹	502.64
T / K	100
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> / Å	17.3905(7)
<i>b</i> / Å	14.4115(4)
<i>c</i> / Å	24.3244(11)
α / °	90
β / °	103.089(3)
γ / °	90
<i>V</i> / Å ³	5937.9(4)
<i>Z</i>	8
ρ_{calc} / g cm ⁻³	1.125
μ / mm ⁻¹	1.482
<i>F</i> (000)	2192.0
Crystal size / mm ³	0.2 × 0.2 × 0.01
Absorption correction	multi-scan
<i>T</i> _{min} ; <i>T</i> _{max}	0.6694; 0.8969
Radiation	Cu-K α (λ = 1.54178 Å)
2 θ range for data collection / °	7.18 to 135.492
Completeness to θ	0.978
Index ranges	-15 ≤ <i>h</i> ≤ 20, -17 ≤ <i>k</i> ≤ 14, -29 ≤ <i>l</i> ≤ 27
Reflections collected	73734
Independent reflections	10503 (<i>R</i> _{int} = 0.1397, <i>R</i> _{σ} = 0.0720)

Data / restraints / parameters	10503 / 541 / 636
Goodness-of-fit on F^2	1.043
Final R indexes ($I \geq 2\sigma(I)$)	$R_1 = 0.0890$, $\omega R_2 = 0.2054$
Final R indexes (all data)	$R_1 = 0.1519$, $\omega R_2 = 0.2474$
Largest diff. peak / hole / $e \text{ \AA}^{-3}$	0.49 / -0.50

Table 43. Bond lengths for 17b.

Atom	Atom	Length / $\text{\AA}$	Atom	Atom	Length / $\text{\AA}$
P1	C1	1.817(5)	P1'	C6'	1.816(5)
P1	C6	1.815(5)	P1'	C23'	1.900(5)
P1	C23	1.891(5)	P2'	C3'	1.806(6)
P2	C3	1.819(5)	P2'	C4'	1.825(5)
P2	C4	1.815(5)	P2'	C24'	1.881(5)
P2	C24	1.901(5)	N1'	C1'	1.392(7)
N1	C1	1.399(7)	N1'	C2'	1.373(7)
N1	C2	1.381(7)	N1'	C7'	1.450(7)
N1	C7	1.451(7)	N2'	C2'	1.359(7)
N2	C2	1.367(7)	N2'	C3'	1.393(7)
N2	C3	1.398(6)	N2'	C11'	1.468(7)
N2	C11	1.474(6)	N3'	C4'	1.387(6)
N3	C4	1.396(6)	N3'	C5'	1.370(7)
N3	C5	1.371(7)	N3'	C15'	1.464(7)
N3	C15	1.462(7)	N4'	C5'	1.373(7)
N4	C5	1.356(7)	N4'	C6'	1.394(6)
N4	C6	1.402(7)	N4'	C19'	1.466(7)
N4	C19	1.464(7)	C1'	C3'	1.343(8)
C1	C3	1.360(7)	C4'	C6'	1.354(7)
C4	C6	1.361(7)	C7'	C8'	1.518(9)
C7	C8	1.520(8)	C8'	C9'	1.510(10)
C8	C9	1.522(8)	C9'	C10'	1.539(11)
C9	C10	1.515(9)	C11'	C12'	1.528(8)
C11	C12	1.506(8)	C12'	C13'	1.526(9)
C12	C13	1.514(8)	C13'	C14'	1.524(9)
C13	C14	1.497(10)	C15'	C16'	1.520(9)
C15	C16	1.506(8)	C16'	C17'	1.501(9)
C16	C17	1.549(9)	C17'	C18'	1.343(14)
C17	C18	1.512(9)	C17'	C18''	1.487(14)
C19	C20	1.512(8)	C19'	C20'	1.528(8)
C20	C21	1.509(9)	C20'	C21'	1.511(9)
C21	C22	1.493(10)	C21'	C22'	1.538(10)
C23	C24	1.541(7)	C23'	C24'	1.553(7)
C23	C25	1.521(7)	C23'	C25'	1.539(7)
C24	C27	1.530(8)	C24'	C27'	1.543(8)
C25	C26	1.520(8)	C25'	C26'	1.519(8)
C27	C28	1.545(9)	C27'	C28'	1.524(8)
P1'	C1'	1.825(5)			

Table 44. Bond angles for 17b.

Atom	Atom	Atom	Angle / $^\circ$	Atom	Atom	Atom	Angle / $^\circ$
C1	P1	C23	94.9(2)	C6'	P1'	C1'	95.0(2)
C6	P1	C1	95.0(2)	C6'	P1'	C23'	94.1(2)
C6	P1	C23	96.2(2)	C3'	P2'	C4'	95.7(2)
C3	P2	C24	94.8(2)	C3'	P2'	C24'	96.1(2)
C4	P2	C3	96.0(2)	C4'	P2'	C24'	95.3(2)
C4	P2	C24	95.4(2)	C1'	N1'	C7'	126.4(5)

C1	N1	C7	125.9(4)	C2'	N1'	C1'	111.7(5)
C2	N1	C1	112.1(4)	C2'	N1'	C7'	121.8(5)
C2	N1	C7	122.0(4)	C2'	N2'	C3'	112.3(5)
C2	N2	C3	112.5(4)	C2'	N2'	C11'	123.3(5)
C2	N2	C11	121.6(4)	C3'	N2'	C11'	124.4(5)
C3	N2	C11	125.8(4)	C4'	N3'	C15'	124.9(4)
C4	N3	C15	124.4(5)	C5'	N3'	C4'	112.6(4)
C5	N3	C4	112.4(4)	C5'	N3'	C15'	122.5(4)
C5	N3	C15	123.2(4)	C5'	N4'	C6'	112.8(4)
C5	N4	C6	113.4(4)	C5'	N4'	C19'	122.2(4)
C5	N4	C19	122.3(4)	C6'	N4'	C19'	125.0(4)
C6	N4	C19	124.3(4)	N1'	C1'	P1'	130.5(4)
N1	C1	P1	130.6(4)	C3'	C1'	P1'	122.8(4)
C3	C1	P1	123.2(4)	C3'	C1'	N1'	106.7(5)
C3	C1	N1	106.3(4)	N2'	C2'	N1'	102.9(4)
N2	C2	N1	102.7(4)	N2'	C3'	P2'	130.0(4)
N2	C3	P2	131.1(4)	C1'	C3'	P2'	123.4(4)
C1	C3	P2	122.5(4)	C1'	C3'	N2'	106.5(5)
C1	C3	N2	106.4(4)	N3'	C4'	P2'	131.5(4)
N3	C4	P2	130.5(4)	C6'	C4'	P2'	121.5(4)
C6	C4	P2	122.9(4)	C6'	C4'	N3'	106.8(4)
C6	C4	N3	106.5(4)	N3'	C5'	N4'	102.0(4)
N4	C5	N3	102.5(4)	N4'	C6'	P1'	130.1(4)
N4	C6	P1	131.9(4)	C4'	C6'	P1'	124.1(4)
C4	C6	P1	122.9(4)	C4'	C6'	N4'	105.7(4)
C4	C6	N4	105.2(4)	N1'	C7'	C8'	112.8(5)
N1	C7	C8	114.2(4)	C9'	C8'	C7'	112.5(6)
C7	C8	C9	114.5(5)	C8'	C9'	C10'	111.4(7)
C10	C9	C8	112.7(6)	N2'	C11'	C12'	113.5(5)
N2	C11	C12	115.1(4)	C13'	C12'	C11'	113.7(5)
C11	C12	C13	110.9(5)	C14'	C13'	C12'	112.1(6)
C14	C13	C12	115.4(5)	N3'	C15'	C16'	113.2(4)
N3	C15	C16	112.9(4)	C17'	C16'	C15'	113.2(5)
C15	C16	C17	113.7(5)	C18'	C17'	C16'	116.3(10)
C18	C17	C16	112.6(6)	C18''	C17'	C16'	114.3(9)
N4	C19	C20	111.8(5)	N4'	C19'	C20'	112.1(4)
C21	C20	C19	112.7(5)	C21'	C20'	C19'	111.9(5)
C22	C21	C20	111.9(6)	C20'	C21'	C22'	113.2(6)
C24	C23	P1	118.5(3)	C24'	C23'	P1'	117.4(3)
C25	C23	P1	109.9(4)	C25'	C23'	P1'	107.7(4)
C25	C23	C24	110.5(4)	C25'	C23'	C24'	111.5(4)
C23	C24	P2	117.9(4)	C23'	C24'	P2'	118.5(4)
C27	C24	P2	109.8(4)	C27'	C24'	P2'	108.0(4)
C27	C24	C23	110.8(4)	C27'	C24'	C23'	112.2(4)
C26	C25	C23	115.6(5)	C26'	C25'	C23'	114.5(5)
C24	C27	C28	114.3(5)	C28'	C27'	C24'	114.2(5)
C1'	P1'	C23'	96.4(2)				

7.4.11 1,3,5,7-Tetrabutyl-9-butyl-1,3,5,7-tetrahydro-2*H*,6*H*-4,8-ethano[1,4]diphosphinino[2,3-*d*:5,6-*d'*]diimidazole-2,6-ylidene 17c

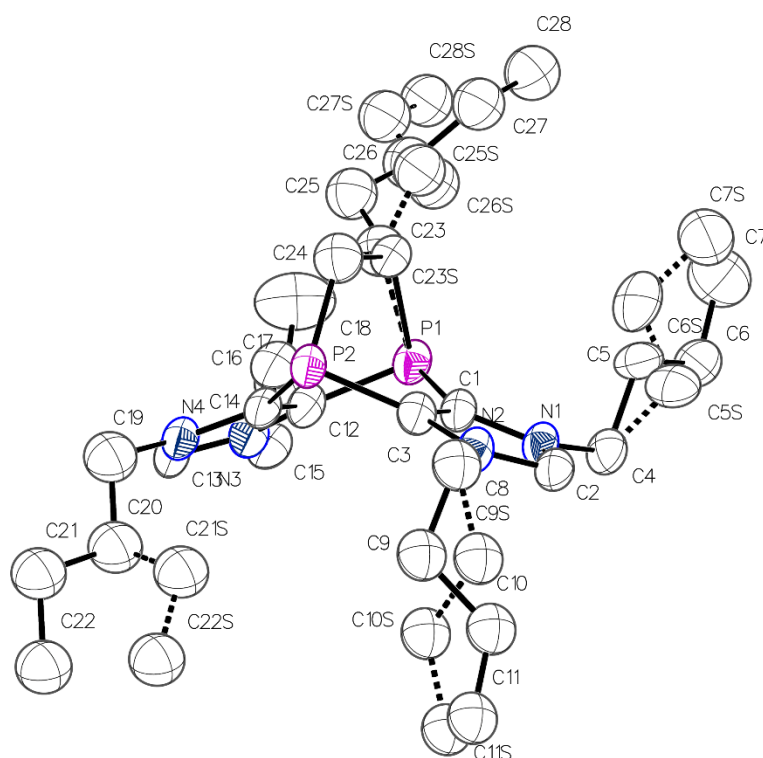


Figure 99. Molecular structure of **17c** in the single crystal. Thermal ellipsoids are set at 50 % probability level. Hydrogen atoms were omitted for clarity.

Table 45. Crystal data and structure refinements for **17c**.

Identification code	GSTR803, TT-730 // GXray7213
Crystal habitus	clear colourless block
Device type	STOE STADIVARI
Empirical formula	C ₂₈ H ₄₈ N ₄ P ₂
Moiety formula	C ₂₈ H ₄₈ N ₄ P ₂
Formula weight / g mol ⁻¹	502.64
T / K	100
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> / Å	14.0275(4)
<i>b</i> / Å	23.4564(6)
<i>c</i> / Å	9.1631(2)
α / °	90
β / °	98.352(2)
γ / °	90
<i>V</i> / Å ³	2983.00(13)
<i>Z</i>	4
ρ_{calc} / g cm ⁻³	1.119
μ / mm ⁻¹	1.475
<i>F</i> (000)	1096.0
Crystal size / mm ³	0.18 × 0.15 × 0.08
Absorption correction	multi-scan

$T_{min}; T_{max}$	0.2621; 0.4135
Radiation	Cu-K α ($\lambda = 1.54178 \text{ \AA}$)
2θ range for data collection / °	7.538 to 135.458
Completeness to θ	0.999
Index ranges	$-14 \leq h \leq 16, -28 \leq k \leq 22, -10 \leq l \leq 9$
Reflections collected	35748
Independent reflections	5387 ($R_{int} = 0.0727, R_{\sigma} = 0.0412$)
Data / restraints / parameters	5387 / 274 / 437
Goodness-of-fit on F^2	1.995
Final R indexes ($I \geq 2\sigma(I)$)	$R_1 = 0.1299, \omega R_2 = 0.3947$
Final R indexes (all data)	$R_1 = 0.1416, \omega R_2 = 0.4185$
Largest diff. peak / hole / e $\text{\AA}^{-3}$	1.67 / -1.77

Table 46. Bond lengths for 17c.

Atom	Atom	Length / $\text{\AA}$	Atom	Atom	Length / $\text{\AA}$
P1	C1	1.805(5)	C8	C9	1.479(11)
P1	C12	1.804(5)	C8	C9S	1.5004(10)
P1	C23	1.908(9)	C9	C10	1.546(15)
P1	C23S	1.92(3)	C9S	C10S	1.504(9)
P2	C3	1.829(5)	C10	C11	1.444(14)
P2	C14	1.829(4)	C10S	C11S	1.501(9)
P2	C24	1.880(6)	C12	C14	1.348(7)
N1	C1	1.388(5)	C15	C16	1.5001(10)
N1	C2	1.367(6)	C16	C17	1.522(7)
N1	C4	1.476(6)	C17	C18	1.499(10)
N2	C2	1.372(6)	C19	C20	1.489(7)
N2	C3	1.384(5)	C20	C21	1.499(8)
N2	C8	1.472(6)	C20	C21S	1.486(10)
N3	C12	1.401(5)	C21	C22	1.504(8)
N3	C13	1.344(6)	C21S	C22S	1.503(10)
N3	C15	1.471(6)	C23	C24	1.526(10)
N4	C13	1.387(6)	C23	C25	1.546(11)
N4	C14	1.392(5)	C23S	C24	1.69(2)
N4	C19	1.464(7)	C23S	C25S	1.502(10)
C1	C3	1.360(6)	C25	C26	1.516(13)
C4	C5	1.557(13)	C25S	C26S	1.479(7)
C4	C5S	1.461(18)	C26	C27	1.5002(10)
C5	C6	1.494(16)	C26S	C27S	1.478(10)
C5S	C6S	1.52(3)	C27	C28	1.5002(10)
C6	C7	1.519(17)	C27S	C28S	1.5001(10)
C6S	C7S	1.49(2)			

Table 47. Bond angles for 17b.

Atom	Atom	Atom	Angle / °	Atom	Atom	Atom	Angle / °
C1	P1	C23	92.5(2)	N2	C8	C9S	111.8(7)
C1	P1	C23S	102.1(9)	C8	C9	C10	113.3(8)
C12	P1	C1	96.4(2)	C8	C9S	C10S	119.2(8)
C12	P1	C23	96.4(3)	C11	C10	C9	119.0(9)
C12	P1	C23S	93.7(10)	C11S	C10S	C9S	123.5(11)
C3	P2	C14	95.46(19)	N3	C12	P1	130.2(4)
C3	P2	C24	94.4(2)	C14	C12	P1	124.1(3)
C14	P2	C24	94.4(2)	C14	C12	N3	105.4(4)
C1	N1	C4	124.3(4)	N3	C13	N4	102.5(4)
C2	N1	C1	113.1(4)	N4	C14	P2	130.3(3)

C2	N1	C4	122.6(4)	C12	C14	P2	122.4(3)
C2	N2	C3	113.2(4)	C12	C14	N4	107.1(4)
C2	N2	C8	122.6(4)	N3	C15	C16	112.8(4)
C3	N2	C8	124.2(4)	C15	C16	C17	111.3(4)
C12	N3	C15	124.7(4)	C18	C17	C16	112.3(5)
C13	N3	C12	113.5(4)	N4	C19	C20	112.0(5)
C13	N3	C15	121.7(4)	C19	C20	C21	114.2(6)
C13	N4	C14	111.5(4)	C21S	C20	C19	120.8(9)
C13	N4	C19	121.3(4)	C20	C21	C22	113.3(7)
C14	N4	C19	127.1(4)	C20	C21S	C22S	109.2(15)
N1	C1	P1	131.1(3)	C24	C23	P1	117.7(5)
C3	C1	P1	122.7(3)	C24	C23	C25	111.3(7)
C3	C1	N1	106.0(4)	C25	C23	P1	108.5(5)
N1	C2	N2	101.7(4)	C24	C23S	P1	109.4(11)
N2	C3	P2	130.4(4)	C25S	C23S	P1	123.1(18)
C1	C3	P2	123.3(3)	C25S	C23S	C24	122.5(18)
C1	C3	N2	106.0(4)	C23	C24	P2	119.3(5)
N1	C4	C5	108.9(6)	C23S	C24	P2	121.7(10)
C5S	C4	N1	118.8(7)	C26	C25	C23	117.3(8)
C6	C5	C4	112.2(9)	C26S	C25S	C23S	107.5(9)
C4	C5S	C6S	112.5(15)	C27	C26	C25	115.2(7)
C5	C6	C7	114.3(10)	C27S	C26S	C25S	106.0(8)
C7S	C6S	C5S	112.6(14)	C26	C27	C28	114.9(8)
N2	C8	C9	113.0(6)	C26S	C27S	C28S	107.2(13)

7.4.12 [Octacarbonyl(μ -1,3,5,7-tetrabutyl-9-butyl-1,3,5,7-tetrahydro-2*H*,6*H*-4,8-ethano[1,4]diphosphinino[2,3-*d*:5,6-*d'*]diimidazole-2,6-ylidene-2*k*C,6*k*C)diiron(0)] 23b

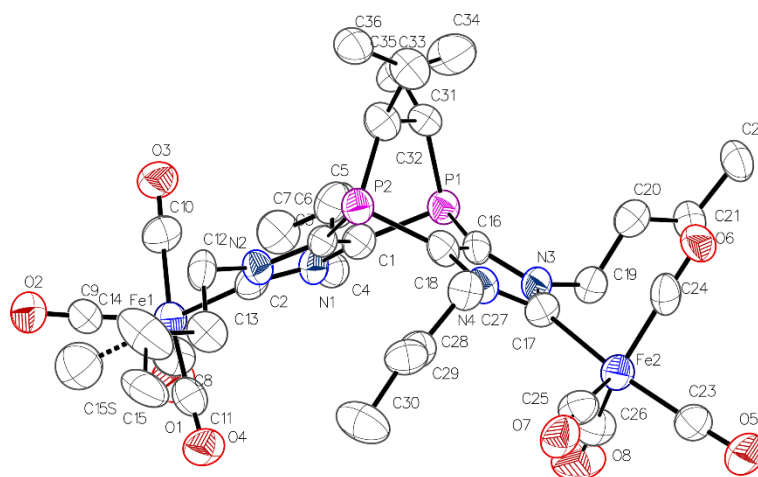


Figure 100. Molecular structure of **23b** in the single crystal. Thermal ellipsoids are set at 50 % probability level. Hydrogen atoms were omitted for clarity.

Table 48. Crystal data and structure refinements for **23b**.

Identification code	GSTR810, TT-710 // GXray7393
Crystal habitus	clear yellow plate
Device type	STOE STADIVARI

Empirical formula	C ₃₆ H ₄₈ Fe ₂ N ₄ O ₈ P ₂
Moiety formula	C ₃₆ H ₄₈ Fe ₂ N ₄ O ₈ P ₂
Formula weight / g mol ⁻¹	838.42
T / K	100
Crystal system	orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁
<i>a</i> / Å	14.2792(9)
<i>b</i> / Å	14.3014(8)
<i>c</i> / Å	19.5382(12)
α / °	90.00
β / °	90.00
γ / °	90.00
<i>V</i> / Å ³	3990.0(4)
<i>Z</i>	4
ρ_{calc} / g cm ⁻³	1.396
μ / mm ⁻¹	7.04
<i>F</i> (000)	1752.0
Crystal size / mm ³	0.18 × 0.16 × 0.06
Absorption correction	multi-scan
<i>T</i> _{min} ; <i>T</i> _{max}	0.0996; 0.3404
Radiation	Cu-K α (λ = 1.54186 Å)
2 θ range for data collection / °	7.66 to 141.344
Completeness to θ	1.000
Index ranges	-12 ≤ <i>h</i> ≤ 17, -17 ≤ <i>k</i> ≤ 15, -23 ≤ <i>l</i> ≤ 19
Reflections collected	38913
Independent reflections	7474 (<i>R</i> _{int} = 0.1659, <i>R</i> _{σ} = 0.1184)
Data / restraints / parameters	7474 / 18 / 486
Goodness-of-fit on <i>F</i> ²	1.061
Final <i>R</i> indexes (<i>I</i> ≥ 2 σ (<i>I</i>))	<i>R</i> ₁ = 0.0961, ωR_2 = 0.2196
Final <i>R</i> indexes (all data)	<i>R</i> ₁ = 0.1575, ωR_2 = 0.2637
Largest diff. peak / hole / e Å ⁻³	0.56 / -0.67
Flack parameter	-0.002(14)

Table 49. Bond lengths for **23b**.

Atom	Atom	Length / Å	Atom	Atom	Length / Å
Fe1	C2	1.995(15)	N2	C3	1.385(16)
Fe1	C8	1.770(17)	N2	C12	1.471(17)
Fe1	C9	1.774(15)	N3	C16	1.369(18)
Fe1	C10	1.797(15)	N3	C17	1.368(17)
Fe1	C11	1.773(18)	N3	C19	1.477(18)
Fe2	C17	1.995(14)	N4	C17	1.383(18)
Fe2	C23	1.753(17)	N4	C18	1.364(17)
Fe2	C24	1.763(17)	N4	C27	1.442(17)
Fe2	C25	1.791(15)	C1	C3	1.353(19)
Fe2	C26	1.800(18)	C4	C5	1.50(2)
P1	C1	1.803(15)	C5	C6	1.50(2)
P1	C16	1.820(15)	C6	C7	1.50(2)
P1	C31	1.921(14)	C12	C13	1.51(2)
P2	C3	1.816(14)	C13	C14	1.495(12)
P2	C18	1.843(15)	C14	C15	1.484(13)
P2	C32	1.872(14)	C14	C15S	1.487(14)
O1	C8	1.162(19)	C16	C18	1.354(19)
O2	C9	1.150(17)	C19	C20	1.53(2)
O3	C10	1.136(16)	C20	C21	1.52(2)
O4	C11	1.161(18)	C21	C22	1.51(2)

O5	C23	1.170(18)	C27	C28	1.49(2)
O6	C24	1.165(18)	C28	C29	1.51(2)
O7	C25	1.161(17)	C29	C30	1.51(2)
O8	C26	1.139(19)	C31	C32	1.54(2)
N1	C1	1.419(18)	C31	C33	1.50(2)
N1	C2	1.366(17)	C32	C35	1.52(2)
N1	C4	1.472(18)	C33	C34	1.54(2)
N2	C2	1.384(18)	C35	C36	1.56(2)

Table 50. Bond angles for 23b.

Atom	Atom	Atom	Angle / °	Atom	Atom	Atom	Angle / °
C8	Fe1	C2	123.6(7)	N2	C2	Fe1	126.7(10)
C8	Fe1	C9	109.4(8)	N2	C3	P2	129.8(10)
C8	Fe1	C10	95.6(7)	C1	C3	P2	122.0(10)
C8	Fe1	C11	93.4(7)	C1	C3	N2	108.1(12)
C9	Fe1	C2	126.9(7)	N1	C4	C5	113.0(12)
C9	Fe1	C10	88.9(7)	C6	C5	C4	115.1(14)
C10	Fe1	C2	83.7(7)	C5	C6	C7	113.8(14)
C11	Fe1	C2	85.4(6)	O1	C8	Fe1	177.0(17)
C11	Fe1	C9	94.9(7)	O2	C9	Fe1	176.3(15)
C11	Fe1	C10	168.5(7)	O3	C10	Fe1	177.5(15)
C23	Fe2	C17	167.7(6)	O4	C11	Fe1	178.4(14)
C23	Fe2	C24	90.9(7)	N2	C12	C13	113.4(11)
C23	Fe2	C25	91.0(7)	C14	C13	C12	110.3(14)
C23	Fe2	C26	89.6(7)	C15	C14	C13	118(2)
C24	Fe2	C17	84.3(7)	C15S	C14	C13	120(2)
C24	Fe2	C25	116.3(8)	N3	C16	P1	130.2(11)
C24	Fe2	C26	134.5(8)	C18	C16	P1	123.8(11)
C25	Fe2	C17	101.3(7)	C18	C16	N3	106.0(12)
C25	Fe2	C26	109.2(8)	N3	C17	Fe2	126.2(10)
C26	Fe2	C17	85.7(7)	N3	C17	N4	103.3(11)
C1	P1	C16	94.1(6)	N4	C17	Fe2	130.4(9)
C1	P1	C31	96.1(7)	N4	C18	P2	129.9(10)
C16	P1	C31	95.3(7)	C16	C18	P2	121.9(11)
C3	P2	C18	94.9(6)	C16	C18	N4	108.2(13)
C3	P2	C32	94.2(6)	N3	C19	C20	112.6(11)
C18	P2	C32	96.6(7)	C21	C20	C19	112.7(12)
C1	N1	C4	123.2(11)	C22	C21	C20	113.6(12)
C2	N1	C1	111.2(11)	O5	C23	Fe2	177.4(14)
C2	N1	C4	125.5(12)	O6	C24	Fe2	177.1(15)
C2	N2	C3	110.8(11)	O7	C25	Fe2	171.3(15)
C2	N2	C12	126.2(12)	O8	C26	Fe2	177.1(17)
C3	N2	C12	122.7(11)	N4	C27	C28	116.1(12)
C16	N3	C19	121.3(11)	C27	C28	C29	113.5(13)
C17	N3	C16	112.0(12)	C28	C29	C30	113.4(15)
C17	N3	C19	126.0(12)	C32	C31	P1	116.0(9)
C17	N4	C27	126.1(12)	C33	C31	P1	109.3(12)
C18	N4	C17	110.4(11)	C33	C31	C32	114.3(13)
C18	N4	C27	123.2(12)	C31	C32	P2	120.6(10)
N1	C1	P1	129.3(10)	C35	C32	P2	112.9(11)
C3	C1	P1	124.6(11)	C35	C32	C31	110.8(12)
C3	C1	N1	105.7(12)	C31	C33	C34	112.8(14)
N1	C2	Fe1	129.1(11)	C32	C35	C36	112.5(13)

7.4.13 [Tetrachlorido(μ -1,3,5,7-tetrabutyl-1,3,5,7-tetrahydro-2*H*,6*H*-4,8-ethano[1,4]diphosphinino[2,3-*d*:5,6-*d'*]diimidazole-2,6-ylidene-2 κ C,6 κ C, κ P¹, κ P²)tetrakis(η^2,η^2 -cycloocta-1,5-diene)tetrarhodium(I)] 29a

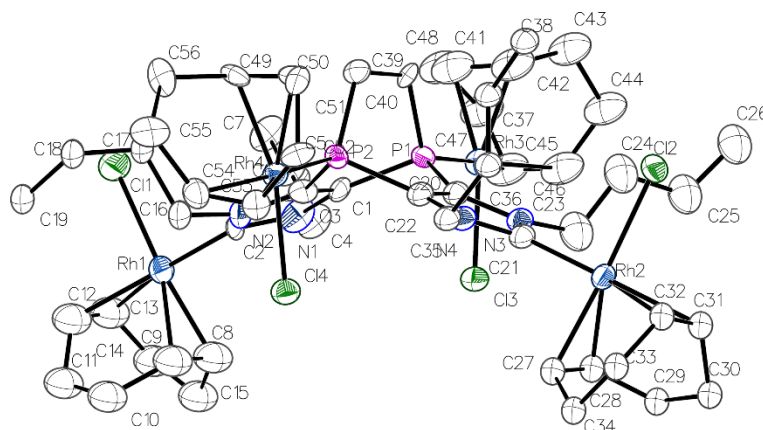


Figure 101. Molecular structure of **29a** in the single crystal. Thermal ellipsoids are set at 50 % probability level. Hydrogen atoms and solvent molecules were omitted for clarity.

Table 51. Crystal data and structure refinements for **29a**.

Identification code	GSTR828, TT-898 // GXraymo_7837f
Crystal habitus	clear yellow needle
Device type	Bruker D8 Venture
Empirical formula	C ₇₀ H ₁₀₄ Cl ₄ N ₄ P ₂ Rh ₄
Moiety formula	C ₅₆ H ₈₈ Cl ₄ N ₄ P ₂ Rh ₄ , 2 C ₇ H ₈
Formula weight / g mol ⁻¹	1616.95
T / K	100.0
Crystal system	orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁
<i>a</i> / Å	16.638(10)
<i>b</i> / Å	17.271(11)
<i>c</i> / Å	24.315(14)
α / °	90
β / °	90
γ / °	90
<i>V</i> / Å ³	6987(7)
<i>Z</i>	4
ρ_{calc} / g cm ⁻³	1.537
μ / mm ⁻¹	1.170
<i>F</i> (000)	3320.0
Crystal size / mm ³	0.18 × 0.04 × 0.02
Absorption correction	multi-scan
<i>T</i> _{min} ; <i>T</i> _{max}	0.3472; 0.7462
Radiation	Mo-K α (λ = 0.71073 Å)
2 θ range for data collection / °	4.096 to 56
Completeness to θ	0.999
Index ranges	-21 ≤ <i>h</i> ≤ 21, -21 ≤ <i>k</i> ≤ 22, -28 ≤ <i>l</i> ≤ 32
Reflections collected	68293
Independent reflections	16845 (<i>R</i> _{int} = 0.4100, <i>R</i> _{σ} = 0.4117)
Data / restraints / parameters	16845 / 288 / 752
Goodness-of-fit on <i>F</i> ²	0.940

Final R indexes ($I \geq 2\sigma(I)$)	$R_1 = 0.1000$, $\omega R_2 = 0.1982$
Final R indexes (all data)	$R_1 = 0.2606$, $\omega R_2 = 0.2798$
Largest diff. peak / hole / $e \text{ \AA}^{-3}$	1.46 / -1.04
Flack parameter	-0.11(12)

Table 52. Bond lengths for 29a.

Atom	Atom	Length / $\text{\AA}$	Atom	Atom	Length / $\text{\AA}$
Rh1	Cl1	2.378(7)	C13	C14	1.49(4)
Rh1	C2	1.99(2)	C14	C15	1.49(4)
Rh1	C8	2.07(3)	C16	C17	1.51(4)
Rh1	C9	2.13(3)	C17	C18	1.53(3)
Rh1	C12	2.16(3)	C18	C19	1.54(3)
Rh1	C13	2.15(3)	C20	C22	1.38(3)
Rh2	Cl2	2.367(7)	C23	C24	1.47(4)
Rh2	C21	2.05(2)	C24	C25	1.57(4)
Rh2	C27	2.11(3)	C25	C26	1.42(4)
Rh2	C28	2.07(3)	C27	C28	1.38(4)
Rh2	C31	2.20(3)	C27	C34	1.54(3)
Rh2	C32	2.18(3)	C28	C29	1.48(3)
Rh3	Cl3	2.386(7)	C29	C30	1.59(3)
Rh3	P1	2.253(7)	C30	C31	1.54(4)
Rh3	C41	2.11(3)	C31	C32	1.37(3)
Rh3	C42	2.10(3)	C32	C33	1.49(3)
Rh3	C45	2.17(3)	C33	C34	1.52(3)
Rh3	C46	2.24(3)	C35	C36	1.54(3)
Rh4	Cl4	2.364(6)	C36	C37	1.50(3)
Rh4	P2	2.271(6)	C37	C38	1.48(3)
Rh4	C49	2.10(2)	C39	C40	1.62(3)
Rh4	C50	2.15(2)	C41	C42	1.44(4)
Rh4	C53	2.20(2)	C41	C48	1.52(4)
Rh4	C54	2.20(3)	C42	C43	1.43(4)
P1	C1	1.80(3)	C43	C44	1.52(4)
P1	C20	1.78(3)	C44	C45	1.51(4)
P1	C39	1.83(2)	C45	C46	1.40(4)
P2	C3	1.84(2)	C46	C47	1.54(4)
P2	C22	1.82(3)	C47	C48	1.45(4)
P2	C40	1.87(2)	C49	C50	1.35(4)
N1	C1	1.39(3)	C49	C56	1.53(3)
N1	C2	1.38(3)	C50	C51	1.53(4)
N1	C4	1.49(3)	C51	C52	1.52(4)
N2	C2	1.36(3)	C52	C53	1.51(3)
N2	C3	1.37(3)	C53	C54	1.32(4)
N2	C16	1.49(3)	C54	C55	1.52(4)
N3	C20	1.42(3)	C55	C56	1.54(4)
N3	C21	1.35(3)	C57	C58	1.35(4)
N3	C23	1.47(3)	C57	C62	1.38(4)
N4	C21	1.33(3)	C57	C63	1.56(4)
N4	C22	1.39(3)	C58	C59	1.37(4)
N4	C35	1.45(3)	C59	C60	1.36(4)
C1	C3	1.36(3)	C60	C61	1.42(4)
C4	C5	1.49(4)	C61	C62	1.42(4)
C5	C6	1.47(3)	C64	C65	1.3900
C6	C7	1.48(4)	C64	C69	1.3900
C8	C9	1.44(4)	C64	C70	1.46(4)
C8	C15	1.53(4)	C65	C66	1.3900

C9	C10	1.51(4)	C66	C67	1.3900
C10	C11	1.43(4)	C67	C68	1.3900
C11	C12	1.46(4)	C68	C69	1.3900
C12	C13	1.34(4)			

Table 53. Bond angles for 29a.

Atom	Atom	Atom	Angle / °	Atom	Atom	Atom	Angle / °
C2	Rh1	Cl1	91.8(7)	C15	C8	Rh1	114(2)
C2	Rh1	C8	90.9(11)	C8	C9	Rh1	67.6(18)
C2	Rh1	C9	91.6(11)	C8	C9	C10	127(3)
C2	Rh1	C12	164.0(11)	C10	C9	Rh1	111(2)
C2	Rh1	C13	159.3(12)	C11	C10	C9	113(3)
C8	Rh1	Cl1	163.2(9)	C10	C11	C12	116(3)
C8	Rh1	C9	40.1(12)	C11	C12	Rh1	113(2)
C8	Rh1	C12	90.7(13)	C13	C12	Rh1	71.5(19)
C8	Rh1	C13	81.4(13)	C13	C12	C11	121(3)
C9	Rh1	Cl1	156.2(9)	C12	C13	Rh1	72.2(19)
C9	Rh1	C12	79.5(12)	C12	C13	C14	130(3)
C9	Rh1	C13	94.6(12)	C14	C13	Rh1	109(2)
C12	Rh1	Cl1	91.2(9)	C13	C14	C15	114(3)
C13	Rh1	Cl1	90.4(9)	C14	C15	C8	112(3)
C13	Rh1	C12	36.3(11)	N2	C16	C17	113(2)
C21	Rh2	Cl2	92.3(7)	C16	C17	C18	112(2)
C21	Rh2	C27	90.7(10)	C17	C18	C19	115(2)
C21	Rh2	C28	91.8(10)	N3	C20	P1	133.3(19)
C21	Rh2	C31	166.3(10)	C22	C20	P1	121.6(19)
C21	Rh2	C32	157.0(10)	C22	C20	N3	105(2)
C27	Rh2	Cl2	167.8(7)	N3	C21	Rh2	126.1(18)
C27	Rh2	C31	90.4(10)	N4	C21	Rh2	126.4(18)
C27	Rh2	C32	82.5(10)	N4	C21	N3	107(2)
C28	Rh2	Cl2	153.0(7)	N4	C22	P2	131.4(18)
C28	Rh2	C27	38.6(10)	C20	C22	P2	120.3(19)
C28	Rh2	C31	80.6(10)	C20	C22	N4	108(2)
C28	Rh2	C32	96.3(10)	N3	C23	C24	114(2)
C31	Rh2	Cl2	89.5(7)	C23	C24	C25	110(3)
C32	Rh2	Cl2	90.2(7)	C26	C25	C24	115(3)
C32	Rh2	C31	36.5(9)	C28	C27	Rh2	68.9(15)
P1	Rh3	Cl3	87.8(2)	C28	C27	C34	123(2)
C41	Rh3	Cl3	158.1(10)	C34	C27	Rh2	111.8(17)
C41	Rh3	P1	95.6(8)	C27	C28	Rh2	72.5(16)
C41	Rh3	C45	93.7(12)	C27	C28	C29	131(2)
C41	Rh3	C46	80.2(12)	C29	C28	Rh2	113.5(16)
C42	Rh3	Cl3	161.5(9)	C28	C29	C30	111(2)
C42	Rh3	P1	94.5(8)	C31	C30	C29	109(2)
C42	Rh3	C41	40.0(12)	C30	C31	Rh2	112.3(17)
C42	Rh3	C45	80.0(12)	C32	C31	Rh2	70.9(15)
C42	Rh3	C46	91.4(12)	C32	C31	C30	123(2)
C45	Rh3	Cl3	91.0(9)	C31	C32	Rh2	72.7(15)
C45	Rh3	P1	157.8(9)	C31	C32	C33	129(3)
C45	Rh3	C46	36.9(11)	C33	C32	Rh2	106.5(16)
C46	Rh3	Cl3	91.0(9)	C32	C33	C34	114(2)
C46	Rh3	P1	165.3(9)	C33	C34	C27	112(2)
P2	Rh4	Cl4	85.6(2)	N4	C35	C36	114(2)
C49	Rh4	Cl4	161.7(7)	C37	C36	C35	114(2)
C49	Rh4	P2	97.1(7)	C38	C37	C36	115(2)

C49	Rh4	C50	37.1(9)	C40	C39	P1	118.0(17)
C49	Rh4	C53	95.8(10)	C39	C40	P2	112.8(16)
C49	Rh4	C54	80.4(10)	C42	C41	Rh3	69.8(18)
C50	Rh4	Cl4	160.8(7)	C42	C41	C48	131(3)
C50	Rh4	P2	96.6(7)	C48	C41	Rh3	111(2)
C50	Rh4	C53	82.4(10)	C41	C42	Rh3	70.2(18)
C50	Rh4	C54	88.6(10)	C43	C42	Rh3	117(2)
C53	Rh4	Cl4	88.1(8)	C43	C42	C41	115(3)
C53	Rh4	P2	156.9(7)	C42	C43	C44	114(3)
C54	Rh4	Cl4	93.1(8)	C45	C44	C43	113(3)
C54	Rh4	P2	167.8(8)	C44	C45	Rh3	111(2)
C54	Rh4	C53	34.8(9)	C46	C45	Rh3	74.0(19)
C1	P1	Rh3	117.1(8)	C46	C45	C44	122(3)
C1	P1	C39	99.6(11)	C45	C46	Rh3	69.1(18)
C20	P1	Rh3	121.0(9)	C45	C46	C47	124(3)
C20	P1	C1	100.7(11)	C47	C46	Rh3	110.0(19)
C20	P1	C39	94.3(11)	C48	C47	C46	114(3)
C39	P1	Rh3	119.5(8)	C47	C48	C41	115(3)
C3	P2	Rh4	117.5(9)	C50	C49	Rh4	73.4(15)
C3	P2	C40	96.1(12)	C50	C49	C56	127(3)
C22	P2	Rh4	116.4(8)	C56	C49	Rh4	110.5(17)
C22	P2	C3	98.7(11)	C49	C50	Rh4	69.6(14)
C22	P2	C40	99.1(11)	C49	C50	C51	124(2)
C40	P2	Rh4	124.2(8)	C51	C50	Rh4	111.4(16)
C1	N1	C4	125(2)	C52	C51	C50	113.0(19)
C2	N1	C1	113(2)	C53	C52	C51	115(2)
C2	N1	C4	122(2)	C52	C53	Rh4	105.3(16)
C2	N2	C3	112(2)	C54	C53	Rh4	72.5(15)
C2	N2	C16	120(2)	C54	C53	C52	127(3)
C3	N2	C16	128(2)	C53	C54	Rh4	72.7(15)
C20	N3	C23	127(2)	C53	C54	C55	125(3)
C21	N3	C20	110(2)	C55	C54	Rh4	114.1(19)
C21	N3	C23	123(2)	C54	C55	C56	110(2)
C21	N4	C22	110(2)	C49	C56	C55	114(2)
C21	N4	C35	125(2)	C58	C57	C62	122(3)
C22	N4	C35	125(2)	C58	C57	C63	120(3)
N1	C1	P1	135.3(19)	C62	C57	C63	117(2)
C3	C1	P1	120.7(18)	C57	C58	C59	120(3)
C3	C1	N1	104(2)	C60	C59	C58	120(3)
N1	C2	Rh1	126.9(19)	C59	C60	C61	121(3)
N2	C2	Rh1	130.0(18)	C62	C61	C60	118(3)
N2	C2	N1	103(2)	C57	C62	C61	118(3)
N2	C3	P2	130.2(19)	C65	C64	C69	120.0
C1	C3	P2	120.8(19)	C65	C64	C70	120(2)
C1	C3	N2	109(2)	C69	C64	C70	120(2)
C5	C4	N1	116(2)	C66	C65	C64	120.0
C6	C5	C4	114(2)	C65	C66	C67	120.0
C5	C6	C7	116(2)	C66	C67	C68	120.0
C9	C8	Rh1	72.4(19)	C69	C68	C67	120.0
C9	C8	C15	123(3)	C68	C69	C64	120.0

7.4.14 1,3,5,7-Tetrabutyl-9,10-diethyl-1,5-dihydro-4,8-ethano[1,4]diphosphino[2,3-d:5,6-d']di-2,6-bis(diphenylphosphino)imidazolium bis(trifluoromethanesulfonate) 35a

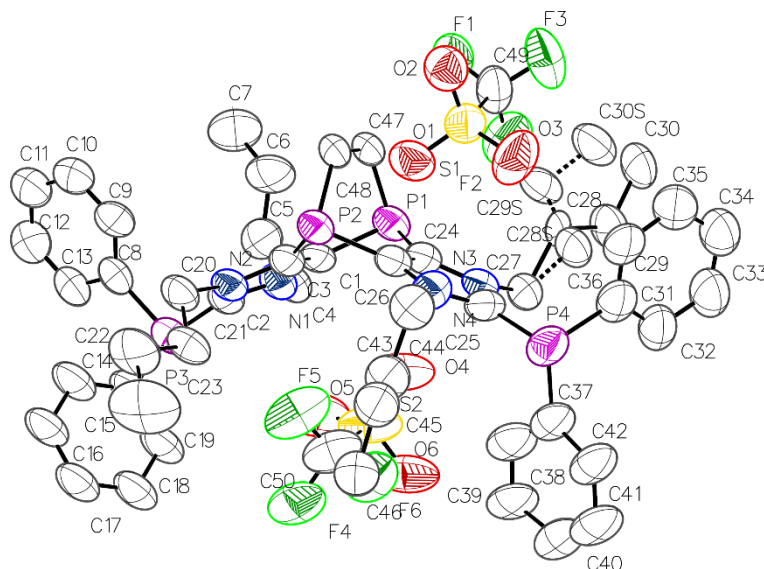


Figure 102. Molecular structure of **35a** in the single crystal. Thermal ellipsoids are set at 50 % probability level. Hydrogen atoms and solvent molecules were omitted for clarity.

Table 54. Crystal data and structure refinements for **35a**.

Identification code	GSTR821, TT-869 // GXraycu_7656f_pl
Crystal habitus	clear colourless plate
Device type	Bruker D8 Venture
Empirical formula	C ₅₄ H ₇₀ F ₆ N ₄ O ₇ P ₄ S ₂
Moiety formula	C ₄₈ H ₆₀ N ₄ P ₄ , 2(CF ₃ O ₃ S), C ₄ H ₁₀ O
Formula weight / g mol ⁻¹	1189.14
T / K	100
Crystal system	triclinic
Space group	P-1
a / Å	12.787(2)
b / Å	16.863(3)
c / Å	16.898(3)
α / °	62.276(12)
β / °	89.329(13)
γ / °	84.679(13)
V / Å ³	3209.4(10)
Z	2
ρ _{calc} / g cm ⁻³	1.231
μ / mm ⁻¹	2.254
F(000)	1248.0
Crystal size / mm ³	0.28 × 0.08 × 0.04
Absorption correction	multi-scan
T _{min} ; T _{max}	0.4897; 0.7533
Radiation	Cu-Kα (λ = 1.54178 Å)
2θ range for data collection / °	5.912 to 135.486
Completeness to θ	0.956

Index ranges	$-15 \leq h \leq 13, -19 \leq k \leq 19, -19 \leq l \leq 20$
Reflections collected	64180
Independent reflections	11118 ($R_{int} = 0.3523, R_{\sigma} = 0.2971$)
Data / restraints / parameters	11118 / 684 / 710
Goodness-of-fit on F^2	1.275
Final R indexes ($I \geq 2\sigma(I)$)	$R_1 = 0.1881, \omega R_2 = 0.4426$
Final R indexes (all data)	$R_1 = 0.3632, \omega R_2 = 0.5185$
Largest diff. peak / hole / $e \text{ \AA}^{-3}$	0.56 / -0.91

Table 55. Bond lengths for 35a.

Atom	Atom	Length / $\text{\AA}$	Atom	Atom	Length / $\text{\AA}$
P1	C1	1.805(15)	C22	C23	1.49(3)
P1	C24	1.825(16)	C24	C26	1.354(19)
P1	C47	1.893(15)	C27	C28	1.58(4)
P2	C3	1.828(16)	C27	C28S	1.45(4)
P2	C26	1.841(15)	C28	C29	1.503(10)
P2	C48	1.854(14)	C29	C30	1.52(5)
P3	C2	1.812(16)	C28S	C29S	1.70(5)
P3	C8	1.821(16)	C29S	C30S	1.54(5)
P3	C14	1.822(8)	C31	C32	1.40(2)
P4	C25	1.866(17)	C31	C36	1.33(2)
P4	C31	1.842(19)	C32	C33	1.41(2)
P4	C37	1.86(2)	C33	C34	1.46(3)
N1	C1	1.437(18)	C34	C35	1.40(3)
N1	C2	1.324(16)	C35	C36	1.40(2)
N1	C4	1.421(17)	C37	C38	1.38(3)
N2	C2	1.383(17)	C37	C42	1.38(2)
N2	C3	1.397(17)	C38	C39	1.39(3)
N2	C20	1.506(17)	C39	C40	1.42(3)
N3	C24	1.380(17)	C40	C41	1.31(3)
N3	C25	1.329(19)	C41	C42	1.41(3)
N3	C27	1.456(18)	C43	C44	1.58(2)
N4	C25	1.375(18)	C44	C45	1.495(9)
N4	C26	1.394(18)	C45	C46	1.513(9)
N4	C43	1.45(2)	C47	C48	1.557(19)
C1	C3	1.373(18)	S1	O1	1.453(12)
C4	C5	1.469(19)	S1	O2	1.421(12)
C5	C6	1.51(2)	S1	O3	1.404(12)
C6	C7	1.46(2)	S1	C49	1.759(19)
C8	C9	1.41(2)	F1	C49	1.344(18)
C8	C13	1.36(2)	F2	C49	1.43(2)
C9	C10	1.37(2)	F3	C49	1.280(19)
C10	C11	1.36(2)	S2	O4	1.431(15)
C11	C12	1.39(2)	S2	O5	1.468(16)
C12	C13	1.42(2)	S2	O6	1.445(13)
C14	C15	1.3900	S2	C50	1.75(2)
C14	C19	1.3900	F4	C50	1.40(3)
C15	C16	1.3900	F5	C50	1.30(2)
C16	C17	1.3900	F6	C50	1.36(2)
C17	C18	1.3900	O7	C52	1.370(9)
C18	C19	1.3900	O7	C53	1.30(2)
C20	C21	1.46(2)	C51	C52	1.490(10)
C21	C22	1.53(2)	C53	C54	1.482(10)

Table 56. Bond angles for 35a.

Atom	Atom	Atom	Angle / °	Atom	Atom	Atom	Angle / °
C1	P1	C24	94.1(7)	N3	C25	N4	109.0(13)
C1	P1	C47	94.0(6)	N4	C25	P4	116.9(12)
C24	P1	C47	95.5(7)	N4	C26	P2	127.8(11)
C3	P2	C26	92.6(7)	C24	C26	P2	123.3(12)
C3	P2	C48	95.3(7)	C24	C26	N4	108.9(13)
C26	P2	C48	95.4(6)	N3	C27	C28	108.0(15)
C2	P3	C8	100.5(7)	C28S	C27	N3	119(2)
C2	P3	C14	106.7(6)	C29	C28	C27	118(3)
C8	P3	C14	103.4(6)	C28	C29	C30	117(3)
C31	P4	C25	101.6(7)	C27	C28S	C29S	106(3)
C31	P4	C37	106.2(9)	C30S	C29S	C28S	105(3)
C37	P4	C25	102.5(9)	C32	C31	P4	119.0(16)
C2	N1	C1	110.0(12)	C36	C31	P4	117.3(15)
C2	N1	C4	126.6(14)	C36	C31	C32	123.6(19)
C4	N1	C1	123.4(12)	C31	C32	C33	117(2)
C2	N2	C3	111.1(11)	C32	C33	C34	119(2)
C2	N2	C20	127.4(13)	C35	C34	C33	119.4(19)
C3	N2	C20	121.5(12)	C36	C35	C34	119(2)
C24	N3	C27	123.9(13)	C31	C36	C35	121.3(19)
C25	N3	C24	109.4(13)	C38	C37	P4	125.2(14)
C25	N3	C27	126.4(13)	C38	C37	C42	119.0(19)
C25	N4	C26	106.0(13)	C42	C37	P4	114.2(18)
C25	N4	C43	129.5(14)	C37	C38	C39	122.7(19)
C26	N4	C43	124.2(13)	C38	C39	C40	113(2)
N1	C1	P1	129.4(10)	C41	C40	C39	128(2)
C3	C1	P1	123.3(12)	C40	C41	C42	116(2)
C3	C1	N1	107.1(12)	C37	C42	C41	121(2)
N1	C2	P3	120.4(12)	N4	C43	C44	106.8(13)
N1	C2	N2	106.4(13)	C45	C44	C43	111.1(13)
N2	C2	P3	133.0(11)	C44	C45	C46	109.5(14)
N2	C3	P2	130.3(10)	C48	C47	P1	118.5(9)
C1	C3	P2	123.7(12)	C47	C48	P2	119.6(10)
C1	C3	N2	105.5(13)	O1	S1	C49	103.5(8)
N1	C4	C5	111.9(12)	O2	S1	O1	112.4(7)
C4	C5	C6	117.9(15)	O2	S1	C49	101.4(9)
C7	C6	C5	117.9(17)	O3	S1	O1	116.0(8)
C9	C8	P3	127.2(13)	O3	S1	O2	114.7(9)
C13	C8	P3	115.8(13)	O3	S1	C49	107.0(8)
C13	C8	C9	117.0(15)	F1	C49	S1	115.6(12)
C10	C9	C8	122.1(17)	F1	C49	F2	100.5(14)
C11	C10	C9	120.3(18)	F2	C49	S1	107.8(13)
C10	C11	C12	119.9(18)	F3	C49	S1	116.1(14)
C11	C12	C13	118.9(18)	F3	C49	F1	109.5(16)
C8	C13	C12	121.6(17)	F3	C49	F2	105.6(14)
C15	C14	P3	124.8(6)	O4	S2	O5	117.3(9)
C15	C14	C19	120.0	O4	S2	O6	117.3(10)
C19	C14	P3	115.2(6)	O4	S2	C50	102.5(11)
C16	C15	C14	120.0	O5	S2	C50	97.7(11)
C15	C16	C17	120.0	O6	S2	O5	112.4(9)
C18	C17	C16	120.0	O6	S2	C50	106.1(9)
C17	C18	C19	120.0	F4	C50	S2	112.7(15)
C18	C19	C14	120.0	F5	C50	S2	116.7(16)
C21	C20	N2	115.1(12)	F5	C50	F4	107(2)
C20	C21	C22	111.3(14)	F5	C50	F6	107.2(17)

C23	C22	C21	110.1(17)	F6	C50	S2	113.5(17)
N3	C24	P1	129.6(11)	F6	C50	F4	98.3(15)
C26	C24	P1	123.7(12)	C53	O7	C52	118.6(16)
C26	C24	N3	106.6(13)	O7	C52	C51	123.9(19)
N3	C25	P4	134.1(12)	O7	C53	C54	118.0(19)

7.4.15 1,3,5,7-Tetrabutyl-9-butyl-1,5-dihydro-4,8-ethano[1,4]diphosphinino[2,3-d:5,6-d']di-2,6-bis(diphenylphosphino)imidazolium bis(trifluoromethanesulfonate) 35c

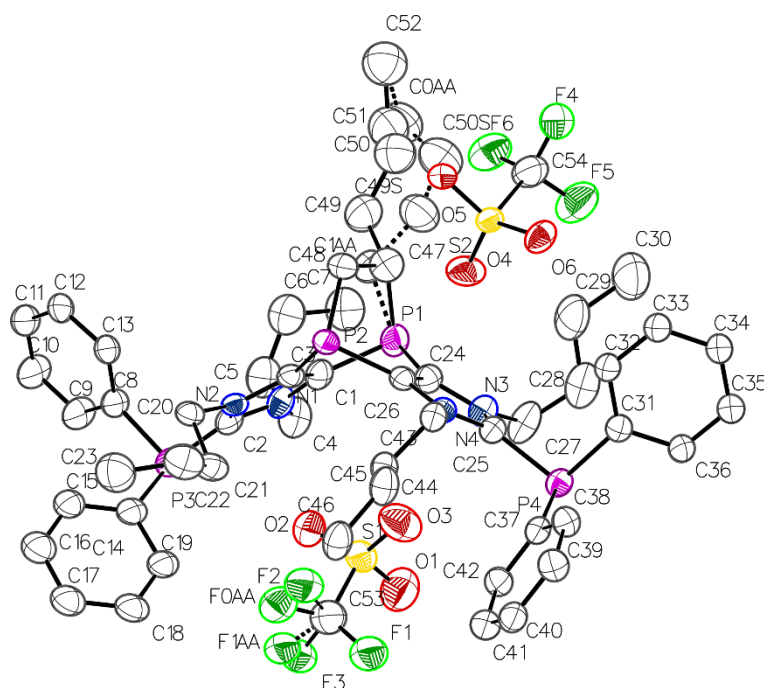


Figure 103. Molecular structure of **35c** in the single crystal. Thermal ellipsoids are set at 50 % probability level. Hydrogen atoms were omitted for clarity.

Table 57. Crystal data and structure refinements for **35c**.

Identification code	GSTR764, TT-556 // GXraymo_6889f
Crystal habitus	clear colourless plate
Device type	Bruker D8 Venture
Empirical formula	C ₅₄ H ₆₈ F ₆ N ₄ O ₆ P ₄ S ₂
Moiety formula	2(CF ₃ O ₃ S), C ₅₂ H ₆₈ N ₄ P ₄
Formula weight / g mol ⁻¹	1171.12
T / K	100.0
Crystal system	triclinic
Space group	P-1
<i>a</i> / Å	13.5458(9)
<i>b</i> / Å	13.9350(8)
<i>c</i> / Å	16.4729(11)
α / °	71.799(2)
β / °	88.467(3)
γ / °	76.810(2)
<i>V</i> / Å ³	2872.6(3)

Z	2
$\rho_{\text{calc}} / \text{g cm}^{-3}$	1.354
μ / mm^{-1}	0.275
$F(000)$	1228.0
Crystal size / mm^3	$0.21 \times 0.2 \times 0.08$
Absorption correction	empirical
$T_{\text{min}}; T_{\text{max}}$	0.6337; 0.7460
Radiation	Mo-K α ($\lambda = 0.71073 \text{ \AA}$)
2θ range for data collection / $^\circ$	4.138 to 55.998
Completeness to θ	0.999
Index ranges	$-17 \leq h \leq 17, -18 \leq k \leq 18, -21 \leq l \leq 21$
Reflections collected	118213
Independent reflections	13873 ($R_{\text{int}} = 0.0787, R_{\sigma} = 0.0449$)
Data / restraints / parameters	13873 / 726 / 742
Goodness-of-fit on F^2	1.916
Final R indexes ($I \geq 2\sigma(I)$)	$R_1 = 0.1279, \omega R_2 = 0.3841$
Final R indexes (all data)	$R_1 = 0.1642, \omega R_2 = 0.4473$
Largest diff. peak / hole / $\text{e \AA}^{-3}$	2.98 / -1.26

Table 58. Bond lengths for 35c.

Atom	Atom	Length / $\text{\AA}$	Atom	Atom	Length / $\text{\AA}$
S1	O1	1.407(6)	C1AA	C49S	1.59(3)
S1	O2	1.427(4)	C4	C5	1.509(9)
S1	O3	1.399(6)	C5	C6	1.488(11)
S1	C53	1.777(8)	C6	C7	1.500(11)
F0AA	C53	1.319(12)	C8	C9	1.391(7)
F1	C53	1.333(8)	C8	C13	1.399(7)
F1AA	C53	1.212(13)	C9	C10	1.409(8)
F2	C53	1.493(12)	C10	C11	1.367(9)
F3	C53	1.432(10)	C11	C12	1.398(8)
S2	O4	1.425(5)	C12	C13	1.408(7)
S2	O5	1.457(4)	C14	C15	1.413(9)
S2	O6	1.430(4)	C14	C19	1.409(7)
S2	C54	1.821(7)	C15	C16	1.355(9)
F4	C54	1.320(9)	C16	C17	1.390(9)
F5	C54	1.339(8)	C17	C18	1.422(10)
F6	C54	1.327(8)	C18	C19	1.396(9)
P1	C1	1.828(6)	C20	C21	1.535(7)
P1	C1AA	1.78(2)	C21	C22	1.509(9)
P1	C24	1.822(5)	C22	C23	1.457(11)
P1	C47	1.944(11)	C24	C26	1.348(7)
P2	C3	1.836(5)	C27	C28	1.494(11)
P2	C26	1.836(5)	C28	C29	1.501(12)
P2	C48	1.861(6)	C29	C30	1.563(13)
P3	C2	1.847(5)	C31	C32	1.387(7)
P3	C8	1.822(5)	C31	C36	1.410(7)
P3	C14	1.818(6)	C32	C33	1.388(7)
P4	C25	1.844(5)	C33	C34	1.383(8)
P4	C31	1.820(5)	C34	C35	1.378(9)
P4	C37	1.833(5)	C35	C36	1.384(8)
N1	C1	1.367(7)	C37	C38	1.404(7)
N1	C2	1.352(7)	C37	C42	1.378(7)
N1	C4	1.486(8)	C38	C39	1.384(7)
N2	C2	1.346(6)	C39	C40	1.381(8)
N2	C3	1.369(6)	C40	C41	1.391(9)

N2	C20	1.477(6)	C41	C42	1.392(8)
N3	C24	1.368(7)	C43	C44	1.517(7)
N3	C25	1.346(6)	C44	C45	1.525(7)
N3	C27	1.487(7)	C45	C46	1.508(9)
N4	C25	1.352(6)	C47	C48	1.477(12)
N4	C26	1.394(6)	C47	C49	1.463(8)
N4	C43	1.461(6)	C49	C50	1.473(9)
C0AA	C50S	1.513(10)	C49S	C50S	1.499(7)
C0AA	C52	1.524(10)	C50	C51	1.513(7)
C1	C3	1.372(8)	C51	C52	1.474(7)
C1AA	C48	1.75(2)			

Table 59. Bond angles for 35c.

Atom	Atom	Atom	Angle / °	Atom	Atom	Atom	Angle / °
O1	S1	O2	114.4(3)	N2	C3	C1	106.8(5)
O1	S1	C53	101.5(4)	C1	C3	P2	122.6(4)
O2	S1	C53	103.8(3)	N1	C4	C5	113.4(6)
O3	S1	O1	106.8(4)	C6	C5	C4	111.4(6)
O3	S1	O2	121.9(3)	C5	C6	C7	111.2(7)
O3	S1	C53	106.2(4)	C9	C8	P3	115.5(4)
F0AA	C53	S1	118.0(6)	C9	C8	C13	119.2(5)
F0AA	C53	F1	111.8(7)	C13	C8	P3	125.3(4)
F0AA	C53	F3	97.3(8)	C8	C9	C10	120.3(6)
F1	C53	S1	116.0(5)	C11	C10	C9	120.2(5)
F1	C53	F2	94.8(6)	C10	C11	C12	120.8(5)
F1	C53	F3	106.7(6)	C11	C12	C13	119.2(5)
F1AA	C53	S1	129.5(9)	C8	C13	C12	120.3(5)
F1AA	C53	F1	107.4(7)	C15	C14	P3	123.3(4)
F1AA	C53	F2	96.6(10)	C19	C14	P3	118.0(5)
F2	C53	S1	104.1(5)	C19	C14	C15	118.2(6)
F3	C53	S1	104.3(5)	C16	C15	C14	121.1(6)
O4	S2	O5	116.2(3)	C15	C16	C17	122.2(7)
O4	S2	O6	114.8(3)	C16	C17	C18	117.6(6)
O4	S2	C54	102.7(3)	C19	C18	C17	120.9(6)
O5	S2	C54	103.2(3)	C18	C19	C14	119.9(6)
O6	S2	O5	114.6(3)	N2	C20	C21	110.6(4)
O6	S2	C54	102.7(3)	C22	C21	C20	112.6(5)
F4	C54	S2	111.6(5)	C23	C22	C21	109.5(7)
F4	C54	F5	105.0(6)	N3	C24	P1	129.0(4)
F4	C54	F6	107.9(5)	C26	C24	P1	123.4(4)
F5	C54	S2	112.5(4)	C26	C24	N3	107.6(4)
F6	C54	S2	110.6(5)	N3	C25	P4	118.7(4)
F6	C54	F5	109.0(6)	N3	C25	N4	107.6(4)
C1	P1	C47	100.1(4)	N4	C25	P4	133.1(4)
C1AA	P1	C1	92.6(7)	N4	C26	P2	129.6(4)
C1AA	P1	C24	107.1(8)	C24	C26	P2	123.1(4)
C24	P1	C1	92.8(2)	C24	C26	N4	107.3(4)
C24	P1	C47	89.4(3)	N3	C27	C28	115.2(6)
C3	P2	C26	93.2(2)	C27	C28	C29	113.9(6)
C3	P2	C48	93.7(3)	C28	C29	C30	116.0(7)
C26	P2	C48	96.8(2)	C32	C31	P4	125.5(4)
C8	P3	C2	102.1(2)	C32	C31	C36	119.0(5)
C14	P3	C2	105.5(2)	C36	C31	P4	115.3(4)
C14	P3	C8	103.3(3)	C31	C32	C33	120.7(5)
C31	P4	C25	101.8(2)	C34	C33	C32	119.8(5)

C31	P4	C37	104.3(2)	C35	C34	C33	120.2(6)
C37	P4	C25	106.5(2)	C34	C35	C36	120.7(5)
C1	N1	C4	126.6(5)	C35	C36	C31	119.6(5)
C2	N1	C1	109.3(5)	C38	C37	P4	122.6(4)
C2	N1	C4	123.7(5)	C42	C37	P4	117.0(4)
C2	N2	C3	109.6(4)	C42	C37	C38	119.9(5)
C2	N2	C20	128.8(4)	C39	C38	C37	119.6(5)
C3	N2	C20	121.6(4)	C40	C39	C38	120.5(6)
C24	N3	C27	124.7(4)	C39	C40	C41	119.7(5)
C25	N3	C24	109.4(4)	C40	C41	C42	120.2(6)
C25	N3	C27	125.9(4)	C37	C42	C41	120.0(5)
C25	N4	C26	108.1(4)	N4	C43	C44	113.3(4)
C25	N4	C43	127.8(4)	C43	C44	C45	112.9(5)
C26	N4	C43	124.1(4)	C46	C45	C44	112.3(5)
C50S	C0AA	C52	105.7(9)	C48	C47	P1	116.6(6)
N1	C1	P1	129.9(4)	C49	C47	P1	113.6(8)
N1	C1	C3	107.2(5)	C49	C47	C48	102.1(8)
C3	C1	P1	122.9(4)	C1AA	C48	P2	119.5(8)
C48	C1AA	P1	112.1(11)	C47	C48	P2	119.3(5)
C49S	C1AA	P1	114.9(16)	C47	C49	C50	118.7(9)
C49S	C1AA	C48	108.5(18)	C50S	C49S	C1AA	148.3(17)
N1	C2	P3	119.6(4)	C49	C50	C51	103.4(7)
N2	C2	P3	133.2(4)	C49S	C50S	C0AA	124.8(15)
N2	C2	N1	107.2(5)	C52	C51	C50	95.7(8)
N2	C3	P2	130.6(4)				

7.4.16 1,3,5,7-Tetrabutyl-9,10-diethyl-1,5-dihydro-4,8-ethano[1,4]diphosphinino[2,3-d:5,6-d']di-2,6-bis(dithiocarboxy)imidazolium 36a

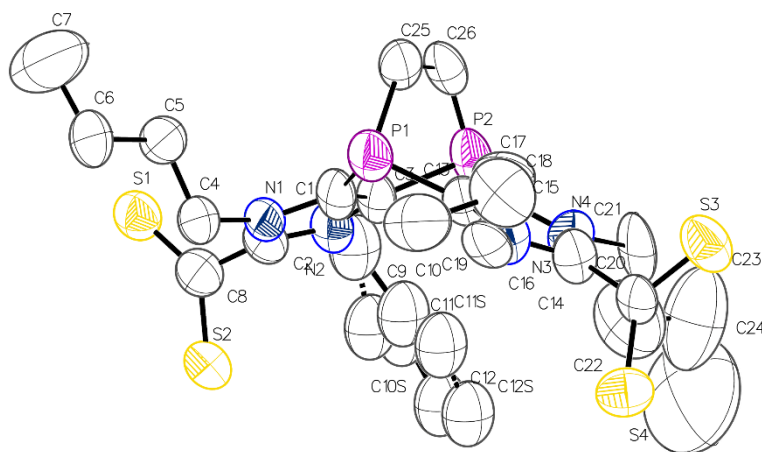


Figure 104. Molecular structure of **36a** in the single crystal. Thermal ellipsoids are set at 50 % probability level. Hydrogen atoms and solvent molecules were omitted for clarity.

Table 60. Crystal data and structure refinements for **36a**.

Identification code	GSTR825, TT-851 // GXray7591
Crystal habitus	clear orangish red plate
Device type	STOE STADIVARI
Empirical formula	C ₅₉ H ₈₈ N ₈ P ₄ S ₈
Moiety formula	2(C ₂₆ H ₄₀ N ₄ P ₂ S ₄), C ₇ H ₈

Formula weight / g mol ⁻¹	1289.73
T / K	100
Crystal system	triclinic
Space group	P-1
<i>a</i> / Å	13.6024(12)
<i>b</i> / Å	17.4770(14)
<i>c</i> / Å	19.5244(18)
α / °	92.302(7)
β / °	103.677(7)
γ / °	109.793(7)
<i>V</i> / Å ³	4206.6(7)
<i>Z</i>	2
ρ_{calc} / g cm ⁻³	1.018
μ / mm ⁻¹	2.92
<i>F</i> (000)	1372.0
Crystal size / mm ³	0.3 × 0.25 × 0.08
Absorption correction	multi-scan
<i>T</i> _{min} ; <i>T</i> _{max}	0.2423; 0.4286
Radiation	Cu-K α (λ = 1.54186 Å)
2 θ range for data collection / °	6.692 to 141.408
Completeness to θ	0.991
Index ranges	-12 ≤ <i>h</i> ≤ 16, -20 ≤ <i>k</i> ≤ 21, -23 ≤ <i>l</i> ≤ 23
Reflections collected	55410
Independent reflections	15693 (<i>R</i> _{int} = 0.3582, <i>R</i> _{σ} = 0.2643)
Data / restraints / parameters	15693 / 300 / 736
Goodness-of-fit on <i>F</i> ²	1.024
Final <i>R</i> indexes (<i>I</i> ≥ 2 σ (<i>I</i>))	<i>R</i> ₁ = 0.1477, ωR ₂ = 0.3455
Final <i>R</i> indexes (all data)	<i>R</i> ₁ = 0.2903, ωR ₂ = 0.4362
Largest diff. peak / hole / e Å ⁻³	0.74 / -0.55

Table 61. Bond lengths for 36a.

Atom	Atom	Length / Å	Atom	Atom	Length / Å
S1	C8	1.612(14)	C1	C3	1.333(16)
S1A	C8A	1.678(14)	C1A	C3A	1.341(14)
S2	C8	1.685(14)	C2	C8	1.522(19)
S2A	C8A	1.629(13)	C2A	C8A	1.518(14)
S3	C20	1.666(13)	C4	C5	1.554(16)
S3A	C20A	1.669(13)	C4A	C5A	1.522(15)
S4	C20	1.640(12)	C5	C6	1.487(17)
S4A	C20A	1.730(12)	C5A	C6A	1.480(17)
P1	C1	1.848(15)	C6	C7	1.58(2)
P1	C13	1.846(13)	C6A	C7A	1.520(17)
P1	C25	1.864(12)	C9	C10	1.502(10)
P1A	C1A	1.800(10)	C9	C10S	1.494(10)
P1A	C13A	1.818(11)	C9A	C10A	1.513(16)
P1A	C25A	1.895(11)	C10	C11	1.487(10)
P2	C3	1.863(12)	C10S	C11S	1.53(6)
P2	C15	1.846(13)	C10A	C11A	1.495(17)
P2	C26	1.826(15)	C11	C12	1.521(10)
P2A	C3A	1.838(10)	C11A	C12A	1.50(2)
P2A	C15A	1.830(11)	C11S	C12S	1.509(10)
P2A	C26A	1.856(11)	C13	C15	1.342(16)
N1	C1	1.376(15)	C13A	C15A	1.312(14)
N1	C2	1.363(16)	C14	C20	1.467(17)
N1	C4	1.475(14)	C14A	C20A	1.424(17)

N1A	C1A	1.418(11)	C16	C17	1.458(17)
N1A	C2A	1.327(13)	C16A	C17A	1.535(15)
N1A	C4A	1.441(13)	C17	C18	1.51(2)
N2	C2	1.336(15)	C17A	C18A	1.469(16)
N2	C3	1.370(16)	C18	C19	1.58(2)
N2	C9	1.532(16)	C18A	C19A	1.562(17)
N2A	C2A	1.323(13)	C21	C22	1.45(2)
N2A	C3A	1.395(13)	C21A	C22A	1.494(16)
N2A	C9A	1.516(14)	C22	C23	1.493(10)
N3	C13	1.379(14)	C22A	C23A	1.517(18)
N3	C14	1.322(15)	C23	C24	1.492(10)
N3	C16	1.507(14)	C23A	C24A	1.62(3)
N3A	C13A	1.408(14)	C25	C26	1.541(18)
N3A	C14A	1.378(14)	C25A	C26A	1.526(16)
N3A	C16A	1.462(14)	C27	C28	1.3900
N4	C14	1.406(15)	C27	C32	1.3900
N4	C15	1.332(15)	C27	C33	1.486(10)
N4	C21	1.539(16)	C28	C29	1.3900
N4A	C14A	1.350(14)	C29	C30	1.3900
N4A	C15A	1.386(13)	C30	C31	1.3900
N4A	C21A	1.460(14)	C31	C32	1.3900

Table 62. Bond angles for 36a.

Atom	Atom	Atom	Angle / °	Atom	Atom	Atom	Angle / °
C1	P1	C25	93.3(6)	C2	C8	S2	109.3(10)
C13	P1	C1	94.2(6)	S2A	C8A	S1A	131.5(7)
C13	P1	C25	94.8(6)	C2A	C8A	S1A	113.8(9)
C1A	P1A	C13A	92.6(4)	C2A	C8A	S2A	114.4(9)
C1A	P1A	C25A	95.5(5)	C10	C9	N2	111.8(11)
C13A	P1A	C25A	93.8(5)	C10S	C9	N2	113(2)
C15	P2	C3	95.0(5)	C10A	C9A	N2A	112.5(10)
C26	P2	C3	94.6(6)	C11	C10	C9	102.8(8)
C26	P2	C15	94.8(6)	C9	C10S	C11S	107(3)
C3A	P2A	C26A	95.1(5)	C11A	C10A	C9A	114.3(12)
C15A	P2A	C3A	93.3(5)	C10	C11	C12	115.8(16)
C15A	P2A	C26A	94.7(5)	C10A	C11A	C12A	110.3(15)
C1	N1	C4	128.2(11)	C12S	C11S	C10S	104(3)
C2	N1	C1	105.8(10)	N3	C13	P1	129.4(9)
C2	N1	C4	125.9(11)	C15	C13	P1	123.9(9)
C1A	N1A	C4A	124.9(9)	C15	C13	N3	106.6(10)
C2A	N1A	C1A	108.3(8)	N3A	C13A	P1A	126.3(8)
C2A	N1A	C4A	126.8(8)	C15A	C13A	P1A	125.2(9)
C2	N2	C3	107.5(11)	C15A	C13A	N3A	108.5(9)
C2	N2	C9	125.0(12)	N3	C14	N4	105.5(11)
C3	N2	C9	127.2(10)	N3	C14	C20	127.8(11)
C2A	N2A	C3A	109.3(9)	N4	C14	C20	126.3(11)
C2A	N2A	C9A	127.0(9)	N3A	C14A	C20A	124.5(11)
C3A	N2A	C9A	123.4(8)	N4A	C14A	N3A	106.9(10)
C13	N3	C16	124.8(10)	N4A	C14A	C20A	128.2(12)
C14	N3	C13	110.3(10)	N4	C15	P2	128.4(9)
C14	N3	C16	124.3(10)	N4	C15	C13	109.0(11)
C13A	N3A	C16A	127.1(9)	C13	C15	P2	122.6(9)
C14A	N3A	C13A	107.1(9)	N4A	C15A	P2A	129.1(9)
C14A	N3A	C16A	125.8(10)	C13A	C15A	P2A	122.7(8)
C14	N4	C21	121.7(10)	C13A	C15A	N4A	108.2(10)

C15	N4	C14	108.4(10)	C17	C16	N3	114.3(10)
C15	N4	C21	129.7(10)	N3A	C16A	C17A	111.5(9)
C14A	N4A	C15A	109.2(10)	C16	C17	C18	111.4(12)
C14A	N4A	C21A	123.7(10)	C18A	C17A	C16A	113.2(10)
C15A	N4A	C21A	127.1(10)	C17	C18	C19	108.7(16)
N1	C1	P1	125.8(9)	C17A	C18A	C19A	113.1(11)
C3	C1	P1	125.1(10)	S4	C20	S3	131.3(8)
C3	C1	N1	109.0(12)	C14	C20	S3	113.7(9)
N1A	C1A	P1A	129.2(8)	C14	C20	S4	115.0(9)
C3A	C1A	P1A	124.1(7)	S3A	C20A	S4A	127.4(8)
C3A	C1A	N1A	106.6(8)	C14A	C20A	S3A	118.9(9)
N1	C2	C8	124.6(11)	C14A	C20A	S4A	113.8(9)
N2	C2	N1	109.6(12)	C22	C21	N4	110.6(11)
N2	C2	C8	125.9(13)	N4A	C21A	C22A	113.9(9)
N1A	C2A	C8A	122.9(9)	C21	C22	C23	102.0(18)
N2A	C2A	N1A	108.8(9)	C21A	C22A	C23A	114.3(11)
N2A	C2A	C8A	128.2(10)	C24	C23	C22	100.7(9)
N2	C3	P2	130.4(9)	C22A	C23A	C24A	108.1(16)
C1	C3	P2	121.3(11)	C26	C25	P1	118.3(10)
C1	C3	N2	108.0(10)	C26A	C25A	P1A	118.7(8)
N2A	C3A	P2A	129.8(8)	C25	C26	P2	120.9(9)
C1A	C3A	P2A	123.0(7)	C25A	C26A	P2A	119.5(8)
C1A	C3A	N2A	107.1(9)	C28	C27	C32	120.0
N1	C4	C5	110.0(9)	C28	C27	C33	124.0(18)
N1A	C4A	C5A	114.5(9)	C32	C27	C33	115.9(18)
C6	C5	C4	111.9(11)	C27	C28	C29	120.0
C6A	C5A	C4A	113.6(10)	C30	C29	C28	120.0
C5	C6	C7	109.2(14)	C29	C30	C31	120.0
C5A	C6A	C7A	113.0(11)	C32	C31	C30	120.0
S1	C8	S2	133.1(9)	C31	C32	C27	120.0
C2	C8	S1	117.5(10)				

7.4.17 1,3,5,7-Tetrabutyl-9,10-diethyl-1,5-dihydro-4,8-ethano[1,4]diphosphinino[2,3-d:5,6-d']di-2,6-bis(dithiocarboxy)imidazolium 36b

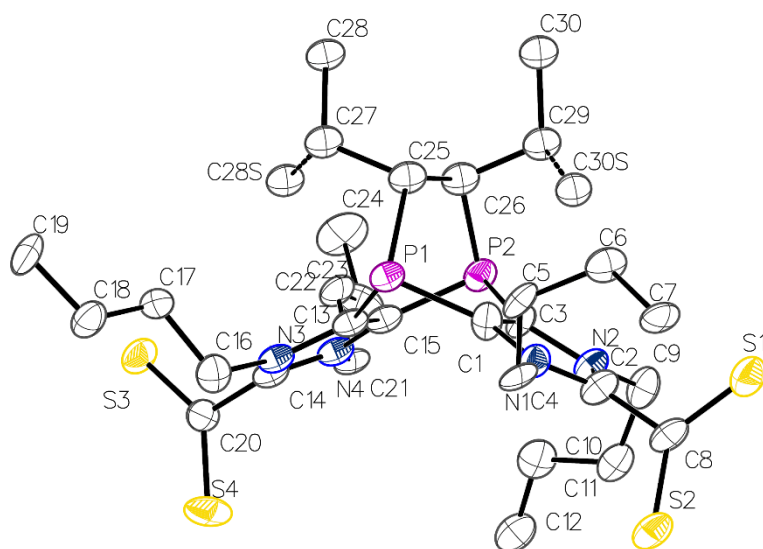


Figure 105. Molecular structure of **36b** in the single crystal. Thermal ellipsoids are set at 50 % probability level. Hydrogen atoms were omitted for clarity.

Table 63. Crystal data and structure refinements for **36b**.

Identification code	GSTR838, TT-790 // GXray7570
Crystal habitus	clear reddish yellow plate
Device type	STOE Stadivari
Empirical formula	C ₃₀ H ₄₈ N ₄ P ₂ S ₄
Moiety formula	C ₃₀ H ₄₈ N ₄ P ₂ S ₄
Formula weight / g mol ⁻¹	654.90
T / K	100
Crystal system	monoclinic
Space group	P2 ₁
<i>a</i> / Å	10.7891(4)
<i>b</i> / Å	10.9092(3)
<i>c</i> / Å	15.4285(7)
α / °	90.00
β / °	106.330(3)
γ / °	90.00
<i>V</i> / Å ³	1742.68(12)
<i>Z</i>	2
ρ_{calc} / g cm ⁻³	1.248
μ / mm ⁻¹	3.565
<i>F</i> (000)	700.0
Crystal size / mm ³	0.13 × 0.12 × 0.09
Absorption correction	multi-scan
<i>T</i> _{min} ; <i>T</i> _{max}	0.3677; 0.5511
Radiation	Cu-K α (λ = 1.54186 Å)
2 θ range for data collection / °	8.54 to 135.484
Completeness to θ	0.989
Index ranges	-12 ≤ <i>h</i> ≤ 12, -13 ≤ <i>k</i> ≤ 13, -13 ≤ <i>l</i> ≤ 18
Reflections collected	23477
Independent reflections	6195 (<i>R</i> _{int} = 0.0721, <i>R</i> _{σ} = 0.0518)
Data / restraints / parameters	6195 / 82 / 382
Goodness-of-fit on <i>F</i> ²	1.959
Final <i>R</i> indexes (<i>I</i> ≥ 2 σ (<i>I</i>))	<i>R</i> ₁ = 0.1472, ωR ₂ = 0.3987
Final <i>R</i> indexes (all data)	<i>R</i> ₁ = 0.1598, ωR ₂ = 0.4159
Largest diff. peak / hole / e Å ⁻³	2.26 / -1.28
Flack parameter	0.09(8)

Table 64. Bond lengths for **36b**.

Atom	Atom	Length / Å	Atom	Atom	Length / Å
S1	C8	1.676(19)	C2	C8	1.52(2)
S2	C8	1.636(17)	C4	C5	1.54(2)
S3	C20	1.665(16)	C5	C6	1.54(2)
S4	C20	1.659(16)	C6	C7	1.55(2)
P1	C1	1.856(18)	C9	C10	1.53(3)
P1	C13	1.822(15)	C10	C11	1.52(3)
P1	C25	1.915(16)	C11	C12	1.50(3)
P2	C3	1.820(15)	C13	C15	1.33(2)
P2	C15	1.830(16)	C14	C20	1.52(2)
P2	C26	1.888(17)	C16	C17	1.53(2)
N1	C1	1.36(2)	C17	C18	1.51(3)
N1	C2	1.34(2)	C18	C19	1.50(2)
N1	C4	1.48(2)	C21	C22	1.511(19)
N2	C2	1.37(2)	C22	C23	1.50(3)

N2	C3	1.411(19)	C23	C24	1.54(3)
N2	C9	1.46(2)	C25	C26	1.53(3)
N3	C13	1.42(2)	C25	C27	1.57(2)
N3	C14	1.36(2)	C26	C29	1.54(2)
N3	C16	1.45(2)	C27	C28	1.52(2)
N4	C14	1.32(2)	C27	C28S	1.498(15)
N4	C15	1.36(2)	C29	C30	1.56(2)
N4	C21	1.47(2)	C29	C30S	1.57(4)
C1	C3	1.34(2)			
S1	C8	1.676(19)	C2	C8	1.52(2)
S2	C8	1.636(17)	C4	C5	1.54(2)
S3	C20	1.665(16)	C5	C6	1.54(2)
S4	C20	1.659(16)	C6	C7	1.55(2)
P1	C1	1.856(18)	C9	C10	1.53(3)
P1	C13	1.822(15)	C10	C11	1.52(3)
P1	C25	1.915(16)	C11	C12	1.50(3)
P2	C3	1.820(15)	C13	C15	1.33(2)
P2	C15	1.830(16)	C14	C20	1.52(2)
P2	C26	1.888(17)	C16	C17	1.53(2)
N1	C1	1.36(2)	C17	C18	1.51(3)
N1	C2	1.34(2)	C18	C19	1.50(2)
N1	C4	1.48(2)	C21	C22	1.511(19)
N2	C2	1.37(2)	C22	C23	1.50(3)
N2	C3	1.411(19)	C23	C24	1.54(3)
N2	C9	1.46(2)	C25	C26	1.53(3)
N3	C13	1.42(2)	C25	C27	1.57(2)
N3	C14	1.36(2)	C26	C29	1.54(2)
N3	C16	1.45(2)	C27	C28	1.52(2)
N4	C14	1.32(2)	C27	C28S	1.498(15)
N4	C15	1.36(2)	C29	C30	1.56(2)
N4	C21	1.47(2)	C29	C30S	1.57(4)
C1	C3	1.34(2)			

Table 65. Bond angles for 36b.

Atom	Atom	Atom	Angle / °	Atom	Atom	Atom	Angle / °
C1	P1	C25	97.6(8)	C2	C8	S2	114.7(13)
C13	P1	C1	91.4(7)	N2	C9	C10	111.1(14)
C13	P1	C25	93.7(7)	C11	C10	C9	116.5(15)
C3	P2	C15	93.4(7)	C12	C11	C10	113.4(16)
C3	P2	C26	94.3(7)	N3	C13	P1	126.7(12)
C15	P2	C26	98.0(7)	C15	C13	P1	126.1(12)
C1	N1	C4	126.4(14)	C15	C13	N3	106.6(13)
C2	N1	C1	110.0(14)	N3	C14	C20	124.2(14)
C2	N1	C4	123.5(14)	N4	C14	N3	108.9(13)
C2	N2	C3	108.2(14)	N4	C14	C20	126.6(14)
C2	N2	C9	125.3(14)	N4	C15	P2	130.2(12)
C3	N2	C9	126.4(14)	C13	C15	P2	120.7(12)
C13	N3	C16	129.1(13)	C13	C15	N4	109.1(14)
C14	N3	C13	106.5(13)	N3	C16	C17	112.4(14)
C14	N3	C16	124.3(13)	C18	C17	C16	112.7(15)
C14	N4	C15	108.8(13)	C19	C18	C17	113.7(16)
C14	N4	C21	124.9(13)	S4	C20	S3	131.8(9)
C15	N4	C21	126.3(13)	C14	C20	S3	113.5(11)
N1	C1	P1	129.5(13)	C14	C20	S4	114.6(11)
C3	C1	P1	121.7(12)	N4	C21	C22	113.6(13)

C3	C1	N1	108.7(15)	C23	C22	C21	112.0(15)
N1	C2	N2	106.8(15)	C22	C23	C24	114.5(18)
N1	C2	C8	128.5(16)	C26	C25	P1	117.5(12)
N2	C2	C8	124.7(16)	C26	C25	C27	113.8(13)
N2	C3	P2	129.4(12)	C27	C25	P1	104.7(11)
C1	C3	P2	124.4(12)	C25	C26	P2	118.6(11)
C1	C3	N2	106.2(13)	C25	C26	C29	112.4(13)
N1	C4	C5	113.8(13)	C29	C26	P2	104.9(11)
C4	C5	C6	114.1(14)	C28	C27	C25	113.5(14)
C5	C6	C7	112.7(15)	C28S	C27	C25	112(6)
S2	C8	S1	133.8(11)	C26	C29	C30	111.2(14)
C2	C8	S1	111.5(12)	C26	C29	C30S	104(4)

7.4.18 1,3,5,7-Tetrabutyl-9-butyl-1,5-dihydro-4,8-ethano[1,4]diphosphinino[2,3-d:5,6-d']di-2,6-bis(dithiocarboxy)imidazolium 36c

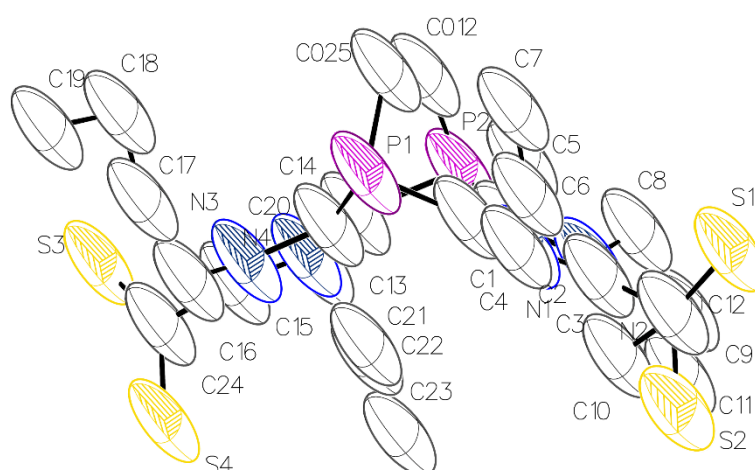


Figure 106. Molecular structure of **36c** in the single crystal. Thermal ellipsoids are set at 50 % probability level. Hydrogen atoms and solvent molecules were omitted for clarity.

Table 66. Crystal data and structure refinements for **36c**.

Identification code	GSTR839, TT-850 // GXray7592
Crystal habitus	clear pink plank
Device type	STOE STADIVARI
Empirical formula	C ₂₆ H ₄₁ N ₄ P ₂ S ₄
Moiety formula	C ₂₆ H ₄₀ N ₄ P ₂ S ₄
Formula weight / g mol ⁻¹	599.81
T / K	100
Crystal system	monoclinic
Space group	P2 ₁ /c
<i>a</i> / Å	14.608(2)
<i>b</i> / Å	17.6133(11)
<i>c</i> / Å	19.3998(16)
α / °	90
β / °	96.956(10)
γ / °	90
<i>V</i> / Å ³	4954.6(9)
<i>Z</i>	4
ρ_{calc} / g cm ⁻³	0.804

μ / mm^{-1}	2.478
$F(000)$	1276.0
Crystal size / mm^3	$0.26 \times 0.1 \times 0.04$
Absorption correction	multi-scan
$T_{\min}; T_{\max}$	1.0000; 1.0000
Radiation	Cu-K α ($\lambda = 1.54186 \text{ \AA}$)
2θ range for data collection / $^\circ$	8.758 to 140.518
Completeness to θ	0.996
Index ranges	$-17 \leq h \leq 17, -9 \leq k \leq 20, -22 \leq l \leq 23$
Reflections collected	74075
Independent reflections	9329 ($R_{\text{int}} = 1.2757, R_{\sigma} = 0.4488$)
Data / restraints / parameters	9329 / 640 / 325
Goodness-of-fit on F^2	1.043
Final R indexes ($I \geq 2\sigma(I)$)	$R_1 = 0.2052, \omega R_2 = 0.4613$
Final R indexes (all data)	$R_1 = 0.4126, \omega R_2 = 0.5850$
Largest diff. peak / hole / $\text{e \AA}^{-3}$	0.58 / -0.56

Due to the extremely poor quality of the single crystal and, consequently, the refinement no details and structural features are provided.

7.4.19 1,3,5,7-Tetrabutyl-4,8-bis(diethylamino)-4,8-dioxo-1,5-dihydro-4,8-[1,4]diphosphinino[2,3-d:5,6-d']di-2,6-bis(trichloroborato)imidazolium 41b

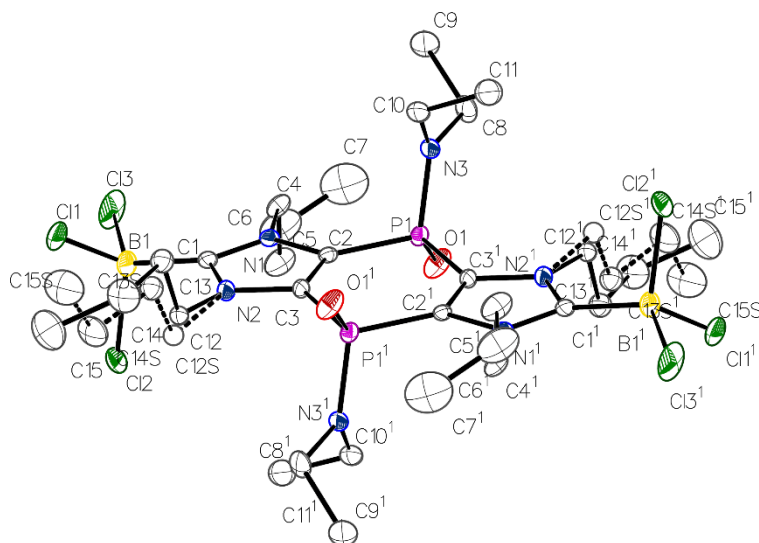


Figure 107. Molecular structure of **41b** in the single crystal. Thermal ellipsoids are set at 50 % probability level. Hydrogen atoms were omitted for clarity.

Table 67. Crystal data and structure refinements for **41b**.

Identification code	TT-274 // GXraycu_6489f
Crystal habitus	clear colourless prism
Device type	Bruker D8 Venture
Empirical formula	$\text{C}_{30}\text{H}_{56}\text{B}_2\text{Cl}_6\text{N}_6\text{O}_2\text{P}_2$
Moiety formula	$\text{C}_{30}\text{H}_{56}\text{B}_2\text{Cl}_6\text{N}_6\text{O}_2\text{P}_2$
Formula weight / g mol^{-1}	829.06
T / K	123
Crystal system	triclinic

Space group	P-1
$a / \text{\AA}$	9.9165(4)
$b / \text{\AA}$	10.3070(4)
$c / \text{\AA}$	11.5166(5)
$\alpha / ^\circ$	115.6440(10)
$\beta / ^\circ$	92.465(2)
$\gamma / ^\circ$	97.618(2)
$V / \text{\AA}^3$	1045.14(7)
Z	1
$\rho_{\text{calc}} / \text{g cm}^{-3}$	1.317
μ / mm^{-1}	4.752
$F(000)$	436.0
Crystal size / mm^3	$0.32 \times 0.16 \times 0.12$
Absorption correction	multi-scan
$T_{\text{min}}; T_{\text{max}}$	0.4836; 0.7535
Radiation	Cu-K α ($\lambda = 1.54178 \text{\AA}$)
2θ range for data collection / $^\circ$	9.054 to 145.154
Completeness to θ	0.983
Index ranges	$-12 \leq h \leq 12, -12 \leq k \leq 12, -14 \leq l \leq 14$
Reflections collected	12580
Independent reflections	4054 ($R_{\text{int}} = 0.0475, R_\sigma = 0.0469$)
Data / restraints / parameters	4054 / 226 / 254
Goodness-of-fit on F^2	1.071
Final R indexes ($I \geq 2\sigma(I)$)	$R_1 = 0.0598, \omega R_2 = 0.1500$
Final R indexes (all data)	$R_1 = 0.0681, \omega R_2 = 0.1584$
Largest diff. peak / hole / $\text{e \AA}^{-3}$	1.39 / -1.03

Table 68. Bond lengths for 41b.

Atom	Atom	Length / $\text{\AA}$	Atom	Atom	Length / $\text{\AA}$
Cl1	B1	1.854(4)	N3	C10	1.469(4)
Cl2	B1	1.874(4)	C1	B1	1.641(5)
Cl3	B1	1.834(4)	C2	C3	1.368(4)
P1	O1	1.466(2)	C3	P1 ¹	1.808(3)
P1	N3	1.638(3)	C4	C5	1.528(4)
P1	C2	1.800(3)	C5	C6	1.526(5)
P1	C3 ¹	1.808(3)	C6	C7	1.502(8)
N1	C1	1.347(4)	C8	C9	1.521(5)
N1	C2	1.390(4)	C10	C11	1.525(5)
N1	C4	1.483(4)	C13	C14	1.528(3)
N2	C1	1.356(4)	C13	C12	1.517(4)
N2	C3	1.390(4)	C14	C15	1.517(4)
N2	C12	1.503(3)	C13S	C14S	1.528(3)
N2	C12S	1.503(3)	C13S	C12S	1.517(4)
N3	C8	1.478(4)	C14S	C15S	1.517(4)

¹1-X,-Y,1-Z

Table 69. Bond angles for 41b.

Atom	Atom	Atom	Angle / $^\circ$	Atom	Atom	Atom	Angle / $^\circ$
O1	P1	N3	113.94(14)	C3	C2	N1	106.7(2)
O1	P1	C2	113.53(14)	N2	C3	P1 ¹	123.6(2)
O1	P1	C3 ¹	114.16(13)	C2	C3	P1 ¹	129.5(2)
N3	P1	C2	106.53(13)	C2	C3	N2	106.6(2)
N3	P1	C3 ¹	107.52(13)	N1	C4	C5	112.2(3)

C2	P1	C3 ¹	99.99(13)	C6	C5	C4	110.4(3)
C1	N1	C2	110.3(2)	C7	C6	C5	114.0(4)
C1	N1	C4	127.7(2)	N3	C8	C9	112.9(3)
C2	N1	C4	121.9(2)	N3	C10	C11	113.8(3)
C1	N2	C3	110.0(2)	C12	C13	C14	113.9(3)
C1	N2	C12	130.4(3)	C15	C14	C13	114.3(4)
C1	N2	C12S	122.6(3)	Cl1	B1	Cl2	110.3(2)
C3	N2	C12	119.0(3)	Cl3	B1	Cl1	106.4(2)
C3	N2	C12S	126.0(3)	Cl3	B1	Cl2	109.3(2)
C8	N3	P1	119.5(2)	C1	B1	Cl1	111.3(2)
C10	N3	P1	120.4(2)	C1	B1	Cl2	103.4(2)
C10	N3	C8	118.8(3)	C1	B1	Cl3	116.2(3)
N1	C1	N2	106.4(2)	C12S	C13S	C14S	107.0(3)
N1	C1	B1	129.3(3)	C15S	C14S	C13S	111.3(3)
N2	C1	B1	123.6(3)	N2	C12	C13	118.4(3)
N1	C2	P1	123.0(2)	N2	C12S	C13S	106.2(2)
C3	C2	P1	130.4(2)				

¹1-X,-Y,1-Z

7.4.20 1,3,5,7-Tetrabutyl-9,10-diethyl-1,5-dihydro-4,8-ethano[1,4]diphosphino[2,3-d:5,6-d']di-2,6-bis(trichloroborato)imidazolium 47b

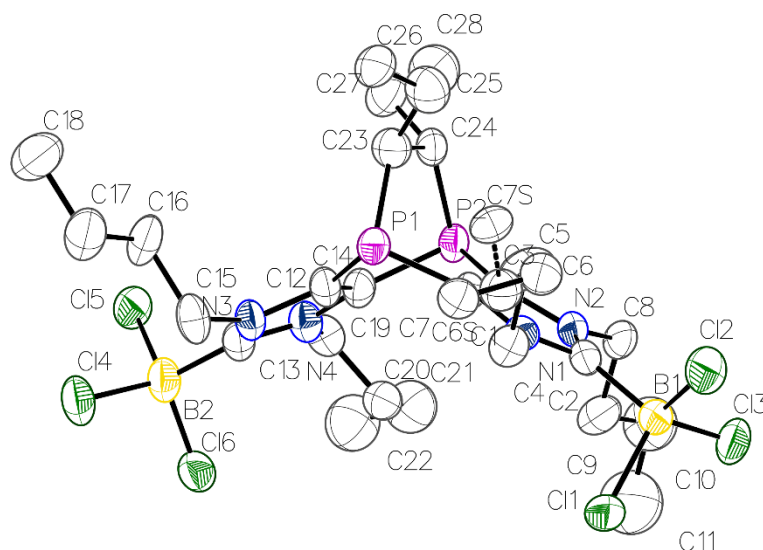


Figure 108. Molecular structure of **47b** in the single crystal. Thermal ellipsoids are set at 50 % probability level. Hydrogen atoms were omitted for clarity.

Table 70. Crystal data and structure refinements for **47b**.

Identification code	GSTR809, TT-763 // GXray7392
Crystal habitus	clear colourless plate
Device type	STOE STADIVARI
Empirical formula	C ₂₈ H ₄₈ B ₂ Cl ₆ N ₄ P ₂
Moiety formula	C ₂₈ H ₄₈ B ₂ Cl ₆ N ₄ P ₂
Formula weight / g mol ⁻¹	736.99
T / K	100
Crystal system	monoclinic

Space group	P2 ₁ /c
<i>a</i> / Å	16.5077(7)
<i>b</i> / Å	12.9269(4)
<i>c</i> / Å	18.8723(8)
α / °	90.00
β / °	113.690(3)
γ / °	90.00
<i>V</i> / Å ³	3687.87(24)
<i>Z</i>	4
ρ_{calc} / g cm ⁻³	1.327
μ / mm ⁻¹	5.26
<i>F</i> (000)	1544.0
Crystal size / mm ³	0.2 × 0.14 × 0.06
Absorption correction	multi-scan
<i>T</i> _{min} ; <i>T</i> _{max}	0.2448; 0.3225
Radiation	Cu-K α (λ = 1.54186 Å)
2 θ range for data collection / °	8.542 to 141.028
Completeness to θ	0.998
Index ranges	-20 ≤ <i>h</i> ≤ 16, -13 ≤ <i>k</i> ≤ 15, -17 ≤ <i>l</i> ≤ 23
Reflections collected	41351
Independent reflections	6990 (<i>R</i> _{int} = 0.1088, <i>R</i> _{σ} = 0.0777)
Data / restraints / parameters	6990 / 56 / 405
Goodness-of-fit on <i>F</i> ²	1.048
Final <i>R</i> indexes (<i>I</i> ≥ 2 σ (<i>I</i>))	<i>R</i> ₁ = 0.0934, ωR ₂ = 0.2248
Final <i>R</i> indexes (all data)	<i>R</i> ₁ = 0.1438, ωR ₂ = 0.2514
Largest diff. peak / hole / e Å ⁻³	0.96 / -0.62

Table 71. Bond lengths for 47b.

Atom	Atom	Length / Å	Atom	Atom	Length / Å
Cl1	B1	1.865(9)	C7S	C6S	1.510(10)
Cl2	B1	1.847(10)	C1	C3	1.342(10)
Cl3	B1	1.854(10)	C2	B1	1.649(11)
Cl4	B2	1.834(9)	C4	C5	1.520(12)
Cl5	B2	1.887(9)	C5	C6	1.484(8)
Cl6	B2	1.861(11)	C5	C6S	1.531(10)
P1	C1	1.822(7)	C6	C7	1.493(7)
P1	C12	1.824(8)	C8	C9	1.505(12)
P1	C23	1.881(8)	C9	C10	1.579(15)
P2	C3	1.828(7)	C10	C11	1.516(17)
P2	C14	1.825(7)	C12	C14	1.360(10)
P2	C24	1.880(8)	C13	B2	1.631(11)
N1	C1	1.392(9)	C15	C16	1.552(12)
N1	C2	1.362(9)	C16	C17	1.494(12)
N1	C4	1.468(9)	C17	C18	1.529(13)
N2	C2	1.345(9)	C19	C20	1.511(11)
N2	C3	1.387(8)	C20	C21	1.525(14)
N2	C8	1.479(9)	C21	C22	1.426(14)
N3	C12	1.393(8)	C23	C24	1.530(10)
N3	C13	1.354(9)	C23	C25	1.492(12)
N3	C15	1.481(9)	C24	C27	1.557(11)
N4	C13	1.359(9)	C25	C26	1.553(12)
N4	C14	1.382(9)	C27	C28	1.527(13)
N4	C19	1.484(9)			

Table 72. Bond angles for 47b.

Atom	Atom	Atom	Angle / °	Atom	Atom	Atom	Angle / °
C1	P1	C12	94.1(3)	N3	C12	P1	129.7(6)
C1	P1	C23	96.9(3)	C14	C12	P1	123.4(5)
C12	P1	C23	92.3(3)	C14	C12	N3	106.9(6)
C3	P2	C24	95.1(3)	N3	C13	N4	105.6(6)
C14	P2	C3	93.8(3)	N3	C13	B2	131.5(6)
C14	P2	C24	95.6(3)	N4	C13	B2	123.0(7)
C1	N1	C4	123.2(6)	N4	C14	P2	130.3(6)
C2	N1	C1	109.2(6)	C12	C14	P2	122.8(6)
C2	N1	C4	127.5(6)	C12	C14	N4	106.6(6)
C2	N2	C3	110.0(6)	N3	C15	C16	109.8(6)
C2	N2	C8	129.3(6)	C17	C16	C15	112.4(7)
C3	N2	C8	120.7(6)	C16	C17	C18	111.6(8)
C12	N3	C15	120.0(6)	N4	C19	C20	112.4(6)
C13	N3	C12	110.1(6)	C19	C20	C21	112.6(7)
C13	N3	C15	129.4(6)	C22	C21	C20	114.5(9)
C13	N4	C14	110.7(6)	C24	C23	P1	119.8(5)
C13	N4	C19	128.4(6)	C25	C23	P1	109.9(6)
C14	N4	C19	120.9(6)	C25	C23	C24	112.7(6)
N1	C1	P1	129.2(5)	C23	C24	P2	118.2(5)
C3	C1	P1	123.6(5)	C23	C24	C27	111.5(6)
C3	C1	N1	107.2(6)	C27	C24	P2	108.8(5)
N1	C2	B1	122.5(7)	C23	C25	C26	116.3(7)
N2	C2	N1	106.3(6)	C28	C27	C24	114.1(7)
N2	C2	B1	131.1(7)	Cl2	B1	Cl1	111.6(5)
N2	C3	P2	129.2(5)	Cl2	B1	Cl3	107.6(4)
C1	C3	P2	123.3(5)	Cl3	B1	Cl1	107.3(5)
C1	C3	N2	107.3(6)	C2	B1	Cl1	106.3(5)
N1	C4	C5	110.8(6)	C2	B1	Cl2	110.0(6)
C4	C5	C6S	104.0(11)	C2	B1	Cl3	114.1(6)
C6	C5	C4	119.4(8)	Cl4	B2	Cl5	106.9(4)
C5	C6	C7	102.3(9)	Cl4	B2	Cl6	108.9(5)
C7S	C6S	C5	122.4(17)	Cl6	B2	Cl5	110.7(5)
N2	C8	C9	110.9(6)	C13	B2	Cl4	115.8(6)
C8	C9	C10	109.7(8)	C13	B2	Cl5	106.2(5)
C11	C10	C9	106.0(10)	C13	B2	Cl6	108.3(5)

7.4.21 (1,3,5,7-Tetrabutyl-1,3,5,7-tetrahydro-2*H*,6*H*-4,8-ethano[1,4]diphosphino[2,3-*d*:5,6-*d'*]diimidazole-2,6-ylidene-2κC,6κC,4κP)tris(borane) 48a

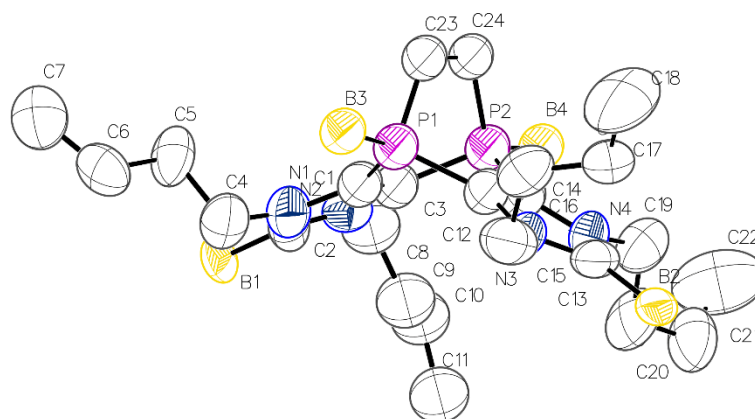


Figure 109. Molecular structure of **48a** in the single crystal. Thermal ellipsoids are set at 50 % probability level. Hydrogen atoms and solvent molecules were omitted for clarity.

Table 73. Crystal data and structure refinements for **48a**.

Identification code	GSTR833, TT-895 // GXray7880_pl
Crystal habitus	clear colourless plate
Device type	STOE Stadivari
Empirical formula	C ₂₅ H ₅₄ B ₄ Cl ₂ N ₄ P ₂
Moiety formula	C ₂₄ H ₅₂ B ₄ N ₄ P ₂ , CH ₂ Cl ₂
Formula weight / g mol ⁻¹	586.80
T / K	100
Crystal system	monoclinic
Space group	P2 ₁ /n
<i>a</i> / Å	9.4532(9)
<i>b</i> / Å	16.1259(19)
<i>c</i> / Å	22.898(3)
α / °	90
β / °	101.770(9)
γ / °	90
<i>V</i> / Å ³	3417.2(7)
<i>Z</i>	4
ρ_{calc} / g cm ⁻³	1.141
μ / mm ⁻¹	2.737
<i>F</i> (000)	1264.0
Crystal size / mm ³	0.24 × 0.157 × 0.01
Absorption correction	multi-scan
<i>T</i> _{min} ; <i>T</i> _{max}	0.2048; 0.8623
Radiation	Cu-Kα (λ = 1.54186 Å)
2 θ range for data collection / °	6.752 to 135.472
Completeness to θ	0.996
Index ranges	-11 ≤ <i>h</i> ≤ 4, -17 ≤ <i>k</i> ≤ 19, -26 ≤ <i>l</i> ≤ 27
Reflections collected	42408
Independent reflections	6175 (<i>R</i> _{int} = 0.2787, <i>R</i> _σ = 0.1059)
Data / restraints / parameters	6175 / 135 / 370
Goodness-of-fit on <i>F</i> ²	2.228
Final <i>R</i> indexes (<i>I</i> ≥ 2σ(<i>I</i>))	<i>R</i> ₁ = 0.3226, ωR_2 = 0.6469
Final <i>R</i> indexes (all data)	<i>R</i> ₁ = 0.3802, ωR_2 = 0.6684

Largest diff. peak / hole / e Å⁻³

1.84 / -0.84

Table 74. Bond lengths for **48a**.

Atom	Atom	Length / Å	Atom	Atom	Length / Å
P1	C1	1.80(2)	C1	C3	1.32(3)
P1	C12	1.816(17)	C2	B1	1.64(2)
P1	C23	1.79(2)	C4	C5	1.49(3)
P1	B3	1.951(9)	C5	C6	1.60(3)
P2	C3	1.82(2)	C6	C7	1.504(10)
P2	C14	1.81(2)	C8	C9	1.53(4)
P2	C24	1.863(18)	C9	C10	1.51(4)
P2	B4	1.957(9)	C10	C11	1.506(10)
N1	C1	1.42(3)	C12	C14	1.33(3)
N1	C2	1.34(3)	C13	B2	1.57(2)
N1	C4	1.51(3)	C15	C16	1.503(10)
N2	C2	1.23(2)	C16	C17	1.498(10)
N2	C3	1.40(3)	C17	C18	1.52(4)
N2	C8	1.467(10)	C19	C20	1.499(10)
N3	C12	1.41(2)	C20	C21	1.497(10)
N3	C13	1.46(3)	C21	C22	1.497(10)
N3	C15	1.465(10)	C23	C24	1.54(3)
N4	C13	1.32(3)	Cl1	C25	1.80(3)
N4	C14	1.41(2)	Cl2	C25	1.69(3)
N4	C19	1.471(10)			

Table 75. Bond angles for **48a**.

Atom	Atom	Atom	Angle / °	Atom	Atom	Atom	Angle / °
C1	P1	C12	96.2(8)	N2	C2	B1	124(2)
C1	P1	B3	128.1(9)	N2	C3	P2	135.1(16)
C12	P1	B3	122.6(9)	C1	C3	P2	117.0(15)
C23	P1	C1	98.0(10)	C1	C3	N2	107.5(16)
C23	P1	C12	96.7(9)	C5	C4	N1	111.1(17)
C23	P1	B3	108.8(9)	C4	C5	C6	109(2)
C3	P2	C24	100.3(9)	C7	C6	C5	113(2)
C3	P2	B4	119.5(9)	N2	C8	C9	114(2)
C14	P2	C3	97.5(9)	C10	C9	C8	113(2)
C14	P2	C24	98.0(9)	C11	C10	C9	102(2)
C14	P2	B4	120.9(8)	N3	C12	P1	129.3(16)
C24	P2	B4	116.2(9)	C14	C12	P1	122.1(14)
C1	N1	C4	126.8(19)	C14	C12	N3	108.2(15)
C2	N1	C1	106.3(18)	N3	C13	B2	122.2(19)
C2	N1	C4	126.9(18)	N4	C13	N3	105.0(13)
C2	N2	C3	109.2(18)	N4	C13	B2	132.7(19)
C2	N2	C8	128(2)	N4	C14	P2	132.8(16)
C3	N2	C8	122.1(19)	C12	C14	P2	119.2(12)
C12	N3	C13	106.7(17)	C12	C14	N4	107.9(16)
C12	N3	C15	126.8(16)	N3	C15	C16	115.2(17)
C13	N3	C15	125.5(15)	C17	C16	C15	114.3(17)
C13	N4	C14	111.9(16)	C16	C17	C18	113(2)
C13	N4	C19	127.4(14)	N4	C19	C20	110.3(16)
C14	N4	C19	120.6(15)	C21	C20	C19	114(2)
N1	C1	P1	129.3(16)	C20	C21	C22	117(3)
C3	C1	P1	125.1(15)	C24	C23	P1	118.7(13)
C3	C1	N1	105.3(17)	C23	C24	P2	114.8(14)

N1	C2	B1	124.5(17)	Cl2	C25	Cl1	111.7(15)
N2	C2	N1	111.5(19)				

7.5 Computational data

Table 76. Computational data for pyridine.

Pyridine			
$E = -248.724611351206$			
$E_{ZPE} = 0.08725663$			
$E_T = 0.00435937$			
$E_S = -0.03275869$			
C	-6.49613	-6.65624	-0.55653
C	-6.92043	-5.39600	-0.97696
C	-4.70645	-4.59767	-0.52171
C	-4.37820	-5.89264	-0.12131
C	-6.00579	-4.34394	-0.95886
N	-5.24787	-6.91734	-0.13214
H	-7.18602	-7.49819	-0.55838
H	-7.94349	-5.24750	-1.30935
H	-3.95875	-3.81081	-0.49002
H	-3.37240	-6.12345	0.22502
H	-6.29907	-3.34801	-1.27877

Table 77. Computational data for phosphinine.

Phosphinine			
$E = -535.543370985924$			
$E_{ZPE} = 0.08297056$			
$E_T = 0.00492275$			
$E_S = -0.03440151$			
C	-6.67368	-6.71563	-0.59421
C	-6.94642	-5.40582	-0.98207
C	-4.68021	-4.58876	-0.51641
C	-4.20319	-5.82482	-0.08621
C	-5.99409	-4.38373	-0.94602
P	-5.13841	-7.28881	-0.01267
H	-7.47889	-7.44583	-0.65625
H	-7.94853	-5.16217	-1.33074
H	-4.00003	-3.73877	-0.51962
H	-3.16374	-5.89005	0.23107
H	-6.28752	-3.38750	-1.26586

Table 78. Computational data for **1^{Me}**.

1^{Me}			
$E = -6097.147735690066$			

$$E_{ZPE} = 0.21546057$$

$$E_T = 0.01970719$$

$$E_S = -0.06819458$$

C	-6.63660	-6.76350	-0.57438
C	-7.01810	-5.46794	-0.98979
C	-4.58926	-4.59093	-0.48861
C	-4.20813	-5.88621	-0.07202
P	-6.11505	-3.97317	-1.07857
P	-5.11074	-7.38130	0.01539
N	-7.76343	-7.56272	-0.71510
N	-8.35413	-5.55730	-1.35753
N	-3.46237	-3.79177	-0.34810
N	-2.87256	-5.79650	0.29726
C	-9.13716	-4.42944	-1.84950
H	-9.15479	-3.64136	-1.09138
H	-8.68712	-4.04651	-2.76985
H	-10.14786	-4.78917	-2.04432
C	-7.79637	-8.98343	-0.38623
H	-7.06122	-9.51543	-0.99657
H	-7.56282	-9.11693	0.67388
H	-8.80108	-9.34835	-0.60113
C	-2.08982	-6.92415	0.79013
H	-2.05535	-7.70533	0.02542
H	-1.08449	-6.55997	1.00360
H	-2.55170	-7.31810	1.69986
C	-3.42922	-2.37115	-0.67734
H	-2.42210	-2.00828	-0.47040
H	-3.67088	-2.23765	-1.73562
H	-4.15839	-1.83731	-0.06143
Se	-0.70978	-3.90794	0.48230
C	-2.40381	-4.51871	0.13232
C	-8.82250	-6.83540	-1.19380
Se	-10.51670	-7.44603	-1.54318

Table 79. Computational data for **2a^{Me}**.

$$\mathbf{2a^{Me}}$$

$$E = -6175.906245036859$$

$$E_{ZPE} = 0.27120048$$

$$E_T = 0.02213321$$

$$E_S = -0.07289518$$

C	-5.37582	-7.63244	0.34730
C	-6.00388	-6.84459	-0.57853
C	-3.86284	-5.22939	-0.65073
C	-3.23837	-6.01434	0.27960

P	-5.66913	-5.06727	-0.75398	C	2.47138	4.56233	7.61084
P	-4.14421	-6.98707	1.51812	C	5.85860	2.96381	4.35889
N	-5.94910	-8.89262	0.27088	C	7.80486	5.56265	7.69861
N	-6.95474	-7.63168	-1.20980	C	6.69715	5.91488	8.72908
N	-2.87343	-4.55403	-1.34895	C	9.06111	6.42320	7.94333
N	-1.87401	-5.81072	0.13958	C	10.26613	6.06245	7.07133
C	-7.85496	-7.21076	-2.27926	C	6.35118	4.69103	9.60001
H	-8.89039	-7.35653	-1.96349	C	5.41758	4.98957	10.77578
H	-7.66639	-6.15564	-2.48089	H	7.75600	8.89411	3.26752
H	-7.66454	-7.80722	-3.17446	H	8.54383	7.46584	4.00748
C	-5.57990	-10.06176	1.06346	H	9.06051	9.12018	4.45946
H	-4.77313	-9.76973	1.73680	H	4.31961	9.42448	8.19089
H	-6.44502	-10.40480	1.63533	H	4.25263	10.59908	6.83935
H	-5.24747	-10.86285	0.39922	H	5.52057	10.74835	8.08111
C	-0.81910	-6.46067	0.91186	H	1.99506	5.52794	7.42659
H	-1.29441	-7.12108	1.63794	H	2.71589	4.46632	8.67140
H	-0.17614	-7.03549	0.24133	H	1.81228	3.74992	7.30208
H	-0.22038	-5.70390	1.42360	H	5.24130	2.94819	3.45800
C	-3.07639	-3.61198	-2.44573	H	5.99972	1.94130	4.71635
H	-2.55019	-3.96840	-3.33401	H	6.82350	3.42699	4.14872
H	-4.14763	-3.54890	-2.64048	H	8.06912	4.50562	7.83510
H	-2.68497	-2.63150	-2.16487	H	7.08491	6.71097	9.37886
C	-1.64151	-4.91219	-0.86810	H	8.79535	7.47929	7.80356
C	-6.92195	-8.90032	-0.69383	H	9.32997	6.30982	9.00146
C	-5.21515	-5.55503	2.12302	H	11.14060	6.65110	7.36745
C	-5.91185	-4.66151	1.07402	H	10.07353	6.26042	6.01106
H	-5.95714	-6.02237	2.77811	H	10.51912	5.00072	7.17266
H	-5.57834	-3.62400	1.17603	H	5.91871	3.91112	8.95922
Se	-7.96161	-10.33376	-1.21020	H	7.29726	4.28661	9.98220
Se	-0.00154	-4.31842	-1.46886	H	5.28903	4.09718	11.39708
H	-6.99619	-4.67496	1.22198	H	4.42529	5.30741	10.43714
H	-4.55069	-4.95579	2.75330	H	5.82762	5.78751	11.40562
				Se	2.84864	2.09798	5.35831
				Se	6.85030	11.33364	5.17318

Table 80. Computational data for **2b^{Me}**.**2b^{Me}**

$$E = -6333.438668717915$$

$$E_{ZPE} = 0.38173882$$

$$E_T = 0.02732074$$

$$E_S = -0.08286413$$

P	7.35624	5.63915	5.84925
P	5.08171	6.67855	8.06455
N	7.23186	8.47598	5.25405
N	5.77154	9.16106	6.73388
N	3.69278	4.46097	6.81641
N	5.19789	3.75775	5.39078
C	6.77444	7.35567	5.92887
C	6.61209	9.59558	5.74371
C	5.86539	7.78200	6.85687
C	4.77085	5.32697	6.89470
C	3.94777	3.48814	5.88244
C	5.71352	4.88779	6.00905
C	8.21379	8.49195	4.17428
C	4.90871	10.04360	7.51322

Table 81. Computational data for **2c^{Me}**.**2c^{Me}**

$$E = -6333.438741870260$$

$$E_{ZPE} = 0.38270019$$

$$E_T = 0.02773531$$

$$E_S = -0.08395965$$

P	7.35325	5.58740	5.87019
P	5.08660	6.62896	8.09260
N	7.29756	8.43586	5.33937
N	5.82306	9.12425	6.80314
N	3.65377	4.46950	6.77571
N	5.16373	3.76151	5.35711
C	6.78953	7.31058	5.96955
C	6.70043	9.55994	5.84596
C	5.87022	7.74043	6.88781
C	4.75819	5.29657	6.90416
C	3.89726	3.51971	5.81793
C	5.70281	4.85488	6.02057

C	8.31032	8.45149	4.28828	C	-7.86910	-7.46331	-2.25010
C	4.96509	10.01089	7.58353	H	-8.89324	-7.64764	-1.91899
C	2.40306	4.57119	7.52190	H	-7.73664	-6.40997	-2.49891
C	5.81555	2.97618	4.31350	H	-7.65144	-8.08924	-3.11833
C	7.81338	5.50304	7.72111	C	-5.43154	-10.05549	1.19326
C	6.69100	5.85957	8.72608	H	-4.62912	-9.70319	1.84243
C	9.04993	6.39400	7.95526	H	-6.27291	-10.41150	1.79171
C	10.24965	6.09303	7.05384	H	-5.07420	-10.86625	0.55461
H	7.90776	8.94325	3.40003	C	-0.86780	-6.25208	0.85338
H	8.57337	7.41728	4.06274	H	-1.30353	-6.86706	1.64135
H	9.19088	8.99718	4.63521	H	-0.21626	-6.85556	0.21745
H	4.33784	9.39176	8.22599	H	-0.29122	-5.43286	1.28789
H	4.34630	10.60540	6.90777	C	-3.27329	-3.72286	-2.65834
H	5.58121	10.67991	8.18880	H	-2.88450	-2.72182	-2.45989
H	1.57435	4.72587	6.82735	H	-2.76898	-4.13964	-3.53293
H	2.48680	5.41759	8.20462	H	-4.35018	-3.68404	-2.82593
H	2.23518	3.64868	8.08241	C	-1.77108	-4.86359	-1.01880
H	5.20393	2.99315	3.40874	C	-6.83883	-9.03935	-0.60429
H	5.93284	1.94322	4.64936	C	-5.32427	-5.44272	1.96109
H	6.79148	3.42282	4.11935	C	-5.96913	-4.74408	1.02169
H	8.09143	4.45187	7.86358	Se	-7.79507	-10.54406	-1.05625
H	7.07602	6.57254	9.46372	Se	-0.16733	-4.25552	-1.68294
H	8.75173	7.44509	7.83788	C	-6.94470	-3.66559	1.37783
H	9.34796	6.27472	9.00564	O	-8.01461	-3.91905	1.90125
H	9.97042	6.22758	5.99962	O	-6.62704	-2.39613	1.07716
H	10.53406	5.03692	7.16335	C	-5.30385	-2.09477	0.54060
H	6.36319	4.96906	9.27173	H	-5.29562	-2.28431	-0.53600
C	11.45563	6.98683	7.36291	H	-5.15783	-1.03295	0.73289
H	11.75487	6.84209	8.40989	H	-4.53977	-2.68162	1.05424
H	11.15431	8.03884	7.26666	C	-5.40316	-5.06761	3.40858
C	12.64655	6.70618	6.44129	O	-4.87631	-4.05721	3.83761
H	13.49619	7.35591	6.67787	O	-6.05210	-5.89481	4.24383
H	12.97963	5.66592	6.53842	C	-6.75180	-7.05519	3.70249
H	12.37498	6.87369	5.39211	H	-6.03518	-7.86037	3.52162
Se	7.00250	11.30512	5.32972	H	-7.45212	-7.34910	4.48282
Se	2.74500	2.19353	5.25433	H	-7.29004	-6.78798	2.79104

Table 82. Computational data for $2e^{Me}$. **$2e^{Me}$** $E = -6631.158166466994$ $E_{ZPE} = 0.33072071$ $E_T = 0.03141271$ $E_S = -0.0917406$

C	-5.36638	-7.64823	0.38052
C	-6.03768	-6.93606	-0.57238
C	-3.97363	-5.24460	-0.74691
C	-3.30862	-5.94548	0.21924
P	-5.78950	-5.15264	-0.82274
P	-4.17054	-6.88354	1.51873
N	-5.86522	-8.93790	0.35890
N	-6.94332	-7.79262	-1.16929
N	-3.02472	-4.57928	-1.50121
N	-1.95825	-5.70309	0.05129

Table 83. Computational data for ethene.

Ethene $E = -78.726416921569$ $E_{ZPE} = 0.050233$ $E_T = 0.00305219$ $E_S = -0.02487869$

C	-2.62830	0.55359	-0.00020
H	-3.71536	0.51851	0.00021
H	-2.11074	-0.40296	-0.00059
C	-1.96480	1.70925	-0.00023
H	-2.48236	2.66580	0.00016
H	-0.87774	1.74433	-0.00064

Table 84. Computational data for 3-hexene.

3-Hexene			
$E = -236.265093679682$			
$E_{ZPE} = 0.16211694$			
$E_T = 0.00817955$			
$E_S = -0.0409027$			
C	-4.80070	-0.48323	0.14402
H	-4.40330	-1.48680	0.33177
H	-4.41536	-0.13519	-0.82071
H	-5.89126	-0.56129	0.06580
C	-4.40093	0.48102	1.27559
H	-4.77204	1.48554	1.02492
H	-3.30796	0.54955	1.33869
C	-4.95555	0.06319	2.60837
H	-6.04548	0.01288	2.68038
C	-4.22454	-0.26596	3.67863
H	-3.13461	-0.21558	3.60665
C	-4.77916	-0.68389	5.01138
H	-4.40800	-1.68839	5.26201
H	-5.87212	-0.75247	4.94826
C	-4.37946	0.28034	6.14300
H	-4.77691	1.28389	5.95529
H	-4.76481	-0.06776	7.10771
H	-3.28891	0.35846	6.22125

Table 85. Computational data for 1-hexene.

1-Hexene			
$E = -236.261309781082$			
$E_{ZPE} = 0.16248643$			
$E_T = 0.00799746$			
$E_S = -0.04057872$			
C	-5.69010	0.90690	0.33080
H	-5.35886	0.26507	1.14573
H	-6.76314	1.02911	0.20651
C	-4.81558	1.51175	-0.47727
H	-5.19001	2.14970	-1.28065
C	-3.32216	1.40836	-0.36716
H	-2.91789	0.99531	-1.30374
H	-3.05663	0.70880	0.43568
C	-2.65043	2.77096	-0.11263
H	-3.02843	3.18785	0.83083
H	-2.94361	3.47318	-0.90561
C	-1.12171	2.67696	-0.05559
H	-0.75228	2.25697	-1.00119
H	-0.83359	1.96854	0.73307
C	-0.45474	4.03199	0.20201
H	-0.78876	4.45688	1.15619
H	0.63645	3.93939	0.23805
H	-0.70663	4.74837	-0.58913

Table 86. Computational data for DMAD.

DMAD			
$E = -533.978341572185$			
$E_{ZPE} = 0.11191978$			
$E_T = 0.01125383$			
$E_S = -0.04927094$			
C	-1.06631	0.37679	-0.13921
C	0.07840	0.65837	-0.42062
C	1.44700	0.89718	-0.81317
C	-2.46374	0.11690	0.11363
O	-3.35904	0.61372	-0.54828
O	2.04297	0.18344	-1.60184
O	-2.62544	-0.72181	1.14682
O	1.94771	1.98111	-0.20376
C	-4.01459	-1.04128	1.46986
H	-4.48592	-1.52296	0.61129
H	-3.94988	-1.71923	2.31847
H	-4.54700	-0.12548	1.73288
C	3.33296	2.29639	-0.54654
H	3.56330	3.18735	0.03407
H	3.97688	1.46132	-0.26494
H	3.40728	2.49039	-1.61806

Table 87. Computational data for $2a^{\text{Me-TS}}$.

$2a^{\text{Me-TS}}$			
$E = -6175.861062308280$			
$E_{ZPE} = 0.26772679$			
$E_T = 0.02197965$			
$E_S = -0.07280527$			
$\text{imf} = -283.83 \text{ cm}^{-1}$			
C	-0.43619	-1.65116	-0.11573
C	-1.05269	-0.84065	-1.06094
C	1.08505	0.73447	-1.09954
C	1.70310	-0.07906	-0.15760
P	-0.64496	0.83599	-1.45275
P	0.91515	-1.21925	0.94158
N	-1.26326	-2.75388	0.06596
N	-2.23436	-1.47936	-1.42220
N	2.03002	1.67339	-1.49804
N	3.00392	0.39329	-0.01675
C	-3.19951	-0.98036	-2.39753
H	-4.00507	-0.44110	-1.89129
H	-2.67656	-0.30921	-3.08124
H	-3.61570	-1.83168	-2.93789
C	-0.99240	-3.85848	0.98106
H	0.07879	-4.07054	0.96266
H	-1.29991	-3.59185	1.99633
H	-1.56238	-4.72382	0.64058
C	4.01804	-0.17080	0.86937

H	3.72634	-1.19447	1.11070
H	4.97897	-0.15796	0.35262
H	4.09045	0.42143	1.78563
C	1.79646	2.73514	-2.47220
H	2.75981	3.02026	-2.89707
H	1.12989	2.35356	-3.24830
H	1.33989	3.60143	-1.98467
C	3.21280	1.46706	-0.83919
C	-2.36872	-2.65684	-0.73682
C	-0.43391	0.64055	1.86171
C	-1.05718	1.45518	0.91451
H	-1.02973	-0.08439	2.40830
H	-0.64516	2.43869	0.70937
H	0.45095	1.00736	2.37348
H	-2.12310	1.34273	0.74018
Se	-3.74677	-3.86910	-0.89253
Se	4.77933	2.41522	-1.03229

Table 88. Computational data for **2b^{Me}-TS**.**2b^{Me}-TS**

$$E = -6333.397572999522$$

$$E_{ZPE} = 0.37861033$$

$$E_T = 0.027709$$

$$E_S = -0.08386964$$

$$imf = -241.86 \text{ cm}^{-1}$$

C	-0.46919	-1.62559	-0.08430
C	-1.05624	-0.82988	-1.05880
C	1.07305	0.75454	-1.05243
C	1.69635	-0.09340	-0.14751
P	-0.65936	0.86535	-1.40429
P	0.88073	-1.19391	0.98031
N	-1.27134	-2.75569	0.04713
N	-2.19550	-1.50328	-1.48914
N	2.03856	1.65754	-1.48745
N	3.02308	0.31953	-0.06537
C	-3.10180	-1.07052	-2.54936
H	-4.09086	-0.86628	-2.13365
H	-2.68882	-0.16550	-2.99757
H	-3.18218	-1.86140	-3.29826
C	-1.02662	-3.86410	0.96410
H	-1.58226	-3.71573	1.89431
H	-1.35836	-4.78715	0.48633
H	0.04387	-3.90251	1.17459
C	4.07490	-0.32278	0.71851
H	3.64725	-1.20525	1.19713
H	4.89328	-0.61209	0.05547
H	4.45112	0.37025	1.47391
C	1.80365	2.73558	-2.44220
H	1.17970	2.35568	-3.25425
H	1.29971	3.57182	-1.94906
H	2.77341	3.06173	-2.82067
Se	4.84585	2.25607	-1.14591

C	3.24050	1.38929	-0.89104
C	-2.32833	-2.68848	-0.81771
Se	-3.65761	-3.93935	-1.05910
H	-0.70234	0.12295	2.62655
C	-0.29653	0.81063	1.88356
C	-1.23072	1.35281	0.97871
C	0.88321	1.65132	2.32565
H	-1.06899	2.39562	0.70351
C	-2.67307	0.89379	1.02903
H	0.48094	2.58052	2.75577
H	1.46221	1.96518	1.44807
H	-3.03661	1.07175	2.05200
H	-2.72255	-0.19329	0.88894
C	1.78881	0.98704	3.36295
H	2.59812	1.66189	3.65839
H	1.21778	0.72320	4.26021
H	2.24122	0.06566	2.98097
C	-3.60392	1.60733	0.04839
H	-4.63242	1.25121	0.16293
H	-3.59385	2.68880	0.22442
H	-3.30313	1.44150	-0.99166

Table 89. Computational data for **2c^{Me}-TS**.**2c^{Me}-TS**

$$E = -6333.395489899107$$

$$E_{ZPE} = 0.37924521$$

$$E_T = 0.02828747$$

$$E_S = -0.0852108$$

$$imf = -293.61 \text{ cm}^{-1}$$

C	-0.52287	-1.79669	-0.27456
C	-1.09328	-0.86704	-1.13278
C	1.06547	0.66161	-0.90266
C	1.65367	-0.29084	-0.07999
P	-0.65479	0.84151	-1.26434
P	0.82933	-1.55951	0.83630
N	-1.37836	-2.89352	-0.24934
N	-2.27699	-1.42816	-1.60040
N	2.04616	1.60815	-1.18636
N	2.97365	0.10792	0.10669
C	-3.20523	-0.79198	-2.53073
H	-2.66107	-0.02150	-3.07985
H	-3.58920	-1.55106	-3.21402
H	-4.03800	-0.34071	-1.98433
C	-1.15406	-4.10599	0.53110
H	-0.09955	-4.38102	0.45613
H	-1.41724	-3.93394	1.57882
H	-1.78737	-4.89136	0.11655
C	3.99498	-0.62798	0.84761
H	3.55368	-1.56569	1.18914
H	4.84373	-0.82731	0.18984
H	4.33223	-0.03828	1.70221
C	1.85312	2.79223	-2.01659

H	2.82676	3.09130	-2.40728	H	4.00001	-1.35159	0.97656
H	1.17197	2.53739	-2.83130	H	5.15262	-0.06997	0.47791
H	1.43019	3.60714	-1.42203	H	4.06936	0.19501	1.87408
C	3.22139	1.26926	-0.57500	C	1.96564	2.59013	-2.51228
C	-2.45709	-2.67449	-1.06435	H	2.92369	2.83160	-2.97394
C	-0.47059	0.41986	1.96963	H	1.26287	2.21269	-3.25761
C	-1.24743	1.11578	1.03664	H	1.55490	3.48138	-2.02963
H	-0.93579	-0.40425	2.50546	C	3.38322	1.33880	-0.86288
H	-1.06246	2.18337	0.93140	C	-2.37968	-2.55286	-0.43272
H	-2.27298	0.80408	0.86021	C	-0.16791	0.68650	1.86665
Se	-3.85881	-3.82147	-1.40070	C	-0.72709	1.42195	1.02233
Se	4.83044	2.16035	-0.65447	Se	-3.84083	-3.66043	-0.42203
C	0.68734	1.12504	2.63623	Se	4.93907	2.28419	-1.07647
H	0.27175	1.96308	3.21799	C	0.22370	0.46209	3.24841
H	1.31721	1.59373	1.86777	O	1.30832	0.80176	3.69246
C	1.54282	0.26997	3.57039	O	-0.66430	-0.16445	4.04604
H	0.90496	-0.16286	4.35349	C	-1.99652	-0.46278	3.52962
H	1.96061	-0.58225	3.01765	H	-1.92884	-1.02838	2.59938
C	2.68449	1.06426	4.21251	H	-2.46494	-1.06268	4.30819
H	3.29313	1.51901	3.41902	H	-2.54751	0.46677	3.37438
H	2.26373	1.89522	4.79478	C	-1.64610	2.52661	0.78689
C	3.57289	0.20002	5.11221	O	-2.83576	2.36085	0.57426
H	4.38063	0.78977	5.55907	O	-1.13042	3.77119	0.79690
H	2.98933	-0.24554	5.92668	C	0.27525	3.95714	1.14346
H	4.02813	-0.61771	4.54076	H	0.91044	3.33364	0.51291
				H	0.46719	5.01208	0.95440
				H	0.42867	3.71957	2.19777

Table 90. Computational data for $2e^{Me-TS}$. **$2e^{Me-TS}$**

$$E = -6631.107281740679$$

$$E_{ZPE} = 0.32826588$$

$$E_T = 0.03185093$$

$$E_S = -0.09285985$$

$$imf = -136.21 \text{ cm}^{-1}$$

C	-0.33299	-1.68294	-0.00066
C	-0.97237	-0.84504	-0.91335
C	1.24615	0.62514	-1.09880
C	1.86798	-0.18480	-0.14918
P	-0.48037	0.76932	-1.43322
P	1.11594	-1.34532	0.94717
N	-1.21244	-2.71794	0.27139
N	-2.21797	-1.39684	-1.15616
N	2.19482	1.54243	-1.51977
N	3.16794	0.27376	-0.02417
C	-3.22972	-0.81883	-2.03784
H	-2.73158	-0.41068	-2.91978
H	-3.91893	-1.61520	-2.31989
H	-3.77150	-0.02652	-1.51437
C	-0.94245	-3.82665	1.18428
H	0.11587	-4.08523	1.11134
H	-1.18556	-3.53674	2.21037
H	-1.56628	-4.66868	0.88257
C	4.16503	-0.27557	0.89190

Table 91. Computational data for 13^{Me} . **13^{Me}**

$$E = -1292.581999195648$$

$$E_{ZPE} = 0.2383914$$

$$E_T = 0.01632579$$

$$E_S = -0.05945547$$

C	-6.60694	-6.77380	-0.55925
C	-7.00010	-5.48893	-1.01040
C	-4.60946	-4.58942	-0.53406
C	-4.21629	-5.87430	-0.08293
P	-6.12867	-3.98288	-1.14165
P	-5.08769	-7.38038	0.04819
N	-7.73642	-7.58772	-0.68421
N	-8.34293	-5.60575	-1.38051
N	-3.48005	-3.77544	-0.40888
N	-2.87351	-5.75743	0.28735
C	-9.18020	-4.52109	-1.91360
H	-10.17065	-4.92536	-2.11678
H	-9.24292	-3.72396	-1.16991
H	-8.72921	-4.14624	-2.83464
C	-7.80510	-9.01347	-0.33114
H	-7.58005	-9.12511	0.73149
H	-7.07843	-9.56232	-0.93349
H	-8.81308	-9.36752	-0.54252
C	-2.03629	-6.84202	0.82066

H	-2.48681	-7.21608	1.74225
H	-1.04555	-6.43797	1.02288
H	-1.97433	-7.63967	0.07747
C	-3.41140	-2.34967	-0.76186
H	-2.40344	-1.99561	-0.55043
H	-4.13811	-1.80088	-0.15950
H	-3.63642	-2.23797	-1.82449
C	-2.47553	-4.50242	0.07986
C	-8.74097	-6.86072	-1.17286
H	-9.73566	-7.23435	-1.37297
H	-1.48088	-4.12875	0.28012

Table 92. Computational data for **11a**^{Me}.**11a**^{Me} $E = -1371.357376534402$ $E_{ZPE} = 0.29364102$ $E_T = 0.01904694$ $E_S = -0.0647613$

C	-5.38710	-7.59867	0.38180
C	-6.00988	-6.81350	-0.55598
C	-3.86093	-5.24737	-0.66417
C	-3.24197	-6.02847	0.27914
P	-5.66896	-5.03353	-0.76704
P	-4.14341	-6.96609	1.55811
N	-5.96696	-8.85396	0.31128
N	-6.95962	-7.60276	-1.18188
N	-2.86334	-4.62528	-1.39559
N	-1.87732	-5.86985	0.10752
C	-7.87218	-7.18589	-2.25931
H	-8.47116	-8.04819	-2.54954
H	-8.51650	-6.38701	-1.88915
H	-7.28060	-6.83324	-3.10518
C	-5.61725	-10.02851	1.12672
H	-4.56521	-10.26839	0.96680
H	-5.79660	-9.79641	2.17754
H	-6.24678	-10.85966	0.81185
C	-0.81487	-6.51937	0.89272
H	-0.91086	-7.60108	0.78939
H	0.14662	-6.18613	0.50444
H	-0.91986	-6.22852	1.93884
C	-3.05234	-3.69119	-2.51758
H	-2.06973	-3.40147	-2.88730
H	-3.61959	-4.19330	-3.30253
H	-3.59468	-2.81441	-2.16088
C	-1.67826	-5.02065	-0.91033
C	-6.90983	-8.82800	-0.64087
C	-5.19775	-5.50560	2.12044
C	-5.87814	-4.61381	1.06127
H	-5.94692	-5.95561	2.77899
H	-5.52022	-3.58300	1.14331
H	-6.96133	-4.59962	1.21487
H	-4.52594	-4.90960	2.74539
H	-0.71414	-4.71097	-1.28574

H	-7.52510	-9.66538	-0.93472

Table 93. Computational data for **11b**^{Me}.**11b**^{Me} $E = -1528.889624617097$ $E_{ZPE} = 0.40448133$ $E_T = 0.02408162$ $E_S = -0.07456163$

P	6.93613	5.23746	5.78001
P	5.57233	7.15454	8.21024
N	7.84033	7.89205	5.02594
N	6.98421	9.12058	6.61838
N	3.25207	5.72379	7.20519
N	4.14415	4.46413	5.65725
C	7.09588	7.05051	5.83339
C	7.75344	9.13493	5.52119
C	6.56125	7.81933	6.83510
C	4.59688	6.04339	7.14549
C	3.00617	4.77054	6.29509
C	5.15870	5.25159	6.17676
C	8.60614	7.50188	3.83137
C	6.65293	10.29684	7.43845
C	2.25372	6.31664	8.10945
C	4.27454	3.46183	4.58722
C	7.53240	5.00598	7.57278
C	6.81632	5.79887	8.70072
C	9.05640	5.24347	7.62114
C	9.87120	4.36657	6.66755
C	6.13565	4.83383	9.69367
C	5.53852	5.50392	10.93284
H	9.06263	8.39731	3.41168
H	7.92567	7.04935	3.10888
H	9.37649	6.78697	4.12391
H	5.56832	10.40868	7.47161
H	7.10943	11.17176	6.97731
H	7.04823	10.15118	8.44482
H	2.20520	7.39080	7.92553
H	2.55273	6.12287	9.14064
H	1.28983	5.85335	7.90313
H	3.28837	3.04321	4.39076
H	4.95837	2.67816	4.91649
H	4.66379	3.95052	3.69293
H	7.33685	3.93852	7.73806
H	7.57689	6.38012	9.23827
H	9.25732	6.30603	7.43016
H	9.37455	5.05202	8.65341
H	10.94182	4.52850	6.82705
H	9.65315	4.59082	5.61718
H	9.65773	3.30500	6.83508
H	5.36544	4.26099	9.16029
H	6.89850	4.10853	10.00261
H	5.16294	4.74631	11.62775
H	4.70270	6.16559	10.67811

H	6.29284	6.10254	11.45559
H	8.22095	10.01083	5.09652
H	2.04119	4.32656	6.10071

H	12.51156	4.94868	7.65663
C	13.04478	3.83720	5.87684
H	12.77311	3.78379	4.81575
H	14.11264	4.07190	5.93998
H	12.89123	2.84291	6.31247

Table 94. Computational data for **11c^{Me}**.**11c^{Me}** $E = -1528.888904687939$ $E_{ZPE} = 0.40486064$ $E_T = 0.02480414$ $E_S = -0.07649762$

P	7.69765	4.92610	5.61398
P	6.29908	7.50458	7.30248
N	8.44603	7.19800	3.96640
N	7.54799	8.86354	5.06098
N	4.02161	5.73692	6.91247
N	4.94415	4.05685	5.86050
C	7.76510	6.65637	5.04323
C	8.29639	8.52963	4.00072
C	7.20342	7.70226	5.73178
C	5.35207	6.06152	6.71354
C	3.80341	4.52272	6.38706
C	5.93215	5.00861	6.05381
C	9.20971	6.45516	2.95138
C	7.16597	10.23524	5.43307
C	3.00881	6.56584	7.58588
C	5.10155	2.75581	5.19074
C	8.35607	5.34428	7.35471
C	7.62239	6.45768	8.14096
C	9.86194	5.65884	7.24429
C	10.70003	4.58706	6.54252
H	9.51979	7.15723	2.17858
H	8.56724	5.68336	2.52605
H	10.08368	6.00223	3.42208
H	6.07859	10.29107	5.49941
H	7.53268	10.91152	4.66213
H	7.61602	10.48095	6.39617
H	3.29637	6.70011	8.62980
H	2.05128	6.05091	7.52239
H	2.95369	7.53145	7.08171
H	4.13833	2.24750	5.20580
H	5.84641	2.16844	5.72943
H	5.42515	2.92467	4.16262
H	8.22511	4.39556	7.88822
H	8.35249	7.18609	8.50984
H	9.98792	6.62561	6.73726
H	10.23537	5.79826	8.26715
H	10.39808	4.50124	5.48886
H	10.50053	3.60869	7.00137
H	2.85538	4.00571	6.38091
H	8.70078	9.22310	3.27839
H	7.11044	6.03991	9.01350
C	12.20186	4.88873	6.60476
H	12.38784	5.87931	6.16769

Table 95. Computational data for **11a^{Me}-TS**.**11a^{Me}-TS** $E = -1371.305807789954$ $E_{ZPE} = 0.29114939$ $E_T = 0.01917415$ $E_S = -0.06503107$ $imf = -155.65 \text{ cm}^{-1}$

C	-0.42047	-1.64614	-0.11258
C	-1.04169	-0.83009	-1.06221
C	1.07071	0.72688	-1.10802
C	1.69382	-0.09213	-0.16206
P	-0.63445	0.81661	-1.53844
P	0.97434	-1.29495	0.90378
N	-1.25928	-2.74517	0.07115
N	-2.22996	-1.46975	-1.41349
N	2.02235	1.66806	-1.50055
N	2.99513	0.38863	-0.02109
C	-3.21469	-0.97947	-2.38950
H	-3.65707	-0.05375	-2.01613
H	-2.70688	-0.80010	-3.33891
H	-3.98455	-1.74061	-2.51022
C	-1.00998	-3.87619	0.97705
H	-0.04277	-4.31711	0.72891
H	-1.00809	-3.51516	2.00749
H	-1.80609	-4.60632	0.83747
C	4.01983	-0.15940	0.88000
H	4.16476	-1.21574	0.64637
H	4.94451	0.39421	0.72201
H	3.68496	-0.04283	1.91265
C	1.81825	2.73968	-2.48627
H	2.76491	3.26041	-2.62365
H	1.48960	2.29420	-3.42697
H	1.06109	3.43099	-2.11076
C	3.15889	1.42908	-0.84205
C	-2.32102	-2.61185	-0.72730
C	-0.45324	0.69382	1.90875
C	-1.08195	1.48361	0.97808
H	-1.00164	-0.08935	2.42340
H	-0.65765	2.44267	0.69666
H	0.47629	1.01898	2.36606
H	-2.13139	1.32865	0.74650
H	-3.12137	-3.33122	-0.82488
H	4.07938	1.98068	-0.96914

Table 96. Computational data for **11b^{Me}-TS**.

11b^{Me}-TS			
$E = -1528.842008476558$			
$E_{ZPE} = 0.40167491$			
$E_T = 0.02517429$			
$E_S = -0.07697483$			
$imf = -139.65 \text{ cm}^{-1}$			
C	-0.42616	-1.62138	-0.11031
C	-1.02316	-0.81842	-1.08559
C	1.05730	0.77073	-1.05792
C	1.69304	-0.08712	-0.15679
P	-0.64754	0.85677	-1.49697
P	0.95988	-1.27435	0.92287
N	-1.21297	-2.76832	-0.00686
N	-2.13922	-1.52121	-1.54349
N	2.02570	1.67616	-1.49107
N	3.02580	0.32465	-0.09588
C	-3.04996	-1.09914	-2.61920
H	-3.62952	-0.23697	-2.28675
H	-2.45396	-0.83927	-3.49570
H	-3.71546	-1.93103	-2.84693
C	-0.96380	-3.90329	0.89315
H	-1.05866	-3.56689	1.92738
H	-1.70154	-4.67588	0.68041
H	0.04426	-4.28042	0.70992
C	4.09863	-0.32288	0.67488
H	3.87046	-0.25321	1.73900
H	4.16493	-1.36907	0.37049
H	5.03243	0.19482	0.45923
C	1.81001	2.77447	-2.44334
H	1.39892	2.36244	-3.36693
H	1.11249	3.49238	-2.00735
H	2.76952	3.25259	-2.63549
C	3.18878	1.36992	-0.91201
C	-2.21395	-2.68202	-0.88595
H	-0.67443	0.06748	2.62945
C	-0.35168	0.86427	1.95844
C	-1.29272	1.36858	1.08317
C	0.85985	1.66175	2.38061
H	-1.12491	2.37712	0.70374
C	-2.71411	0.85779	1.05054
H	0.50672	2.65117	2.70272
H	1.50748	1.86080	1.51784
H	-3.09661	0.89319	2.08023
H	-2.73440	-0.20461	0.77801
C	1.65151	1.01872	3.52014
H	2.51202	1.63670	3.79282
H	1.02016	0.90089	4.40725
H	2.02004	0.02372	3.24472
C	-3.64268	1.67416	0.15036
H	-4.66302	1.28141	0.18718
H	-3.66683	2.72028	0.47364
H	-3.31073	1.66259	-0.89416

H	-2.95865	-3.44536	-1.05940
H	4.12534	1.87821	-1.09048

Table 97. Computational data for **11c^{Me}-TS**.

11c^{Me}-TS			
$E = -1528.840687095591$			
$E_{ZPE} = 0.40243271$			
$E_T = 0.02475636$			
$E_S = -0.07639928$			
$imf = -155.60 \text{ cm}^{-1}$			
C	-0.48912	-1.77349	-0.26670
C	-1.09234	-0.83832	-1.10837
C	1.04080	0.68313	-0.94271
C	1.65772	-0.27288	-0.13268
P	-0.67420	0.86644	-1.31716
P	0.91395	-1.58390	0.78618
N	-1.33227	-2.88408	-0.24461
N	-2.27636	-1.41950	-1.56171
N	2.02353	1.61736	-1.27181
N	2.99174	0.11750	-0.01237
C	-3.24704	-0.80092	-2.47690
H	-2.72691	-0.49644	-3.38683
H	-4.01484	-1.53815	-2.70826
H	-3.69606	0.06711	-1.99009
C	-1.09659	-4.12586	0.50611
H	-0.12144	-4.52605	0.22255
H	-1.11799	-3.90620	1.57539
H	-1.88494	-4.83353	0.25300
C	4.04635	-0.61991	0.70017
H	4.07852	-1.64058	0.31458
H	4.99507	-0.11654	0.51946
H	3.82492	-0.62665	1.76813
C	1.82751	2.81054	-2.10803
H	2.79584	3.28631	-2.25746
H	1.40491	2.50084	-3.06562
H	1.14679	3.49502	-1.59810
C	3.17525	1.24143	-0.71293
C	-2.38141	-2.64237	-1.03558
C	-0.44862	0.48522	2.00869
C	-1.24697	1.16581	1.10623
H	-0.86101	-0.39652	2.49519
H	-1.06137	2.22541	0.94252
H	-2.25472	0.81901	0.90072
H	-3.17994	-3.34078	-1.24036
H	4.11918	1.75464	-0.82586
C	0.74030	1.15025	2.65372
H	0.37485	2.05771	3.15769
H	1.42899	1.51612	1.87973
C	1.48712	0.29002	3.67347
H	0.79173	-0.00706	4.46998
H	1.82098	-0.64406	3.19969
C	2.69373	1.01071	4.28244

H	3.37884	1.30744	3.47596
H	2.35534	1.94009	4.75958
C	3.44364	0.14955	5.30325
H	4.30536	0.68441	5.71637
H	2.78801	-0.12901	6.13645
H	3.80946	-0.77564	4.84180

C	10.70771	4.16009	8.71076
H	11.33271	4.99229	9.06321
H	9.66755	4.50628	8.77590
C	10.90233	2.94472	9.62253
H	11.94266	2.59887	9.59917
H	10.64933	3.18138	10.66191
H	10.26648	2.11066	9.30176

Table 98. Computational data for bridge-deprotonated **11c^{Me}**.bridge-deprotonated **11c^{Me}** $E = -1528.423025325717$ $E_{ZPE} = 0.39058268$ $E_T = 0.02537161$ $E_S = -0.07872518$

P	6.56379	5.93921	3.17718
P	7.25846	7.29093	6.62525
N	6.89371	8.69591	2.89506
N	7.13230	9.52243	4.89215
N	5.90042	4.84472	6.98310
N	5.63315	4.02951	4.98527
C	6.86984	7.60050	3.76546
C	7.05102	9.82815	3.59879
C	7.04152	8.13473	5.04173
C	6.41581	5.79187	6.09142
C	5.44781	3.79967	6.29496
C	6.23483	5.28045	4.80710
C	6.73636	8.61376	1.44354
C	7.32283	10.49367	5.97418
C	5.91726	4.94748	8.44546
C	5.23637	3.13082	3.90195
C	9.44113	5.53508	6.25887
C	9.01169	6.77048	6.54699
C	10.86735	5.07340	6.31258
C	11.05031	3.85952	7.24785
H	6.72215	9.62411	1.03561
H	5.79682	8.10187	1.21844
H	7.57061	8.04969	1.01964
H	6.51211	10.38719	6.69704
H	7.31038	11.49423	5.54216
H	8.28191	10.31043	6.46363
H	6.95201	4.94621	8.79595
H	5.38298	4.09093	8.85579
H	5.42523	5.87480	8.74329
H	4.74219	2.26091	4.33386
H	6.12416	2.82016	3.34573
H	4.55352	3.66201	3.23373
H	8.70962	4.77345	5.98121
H	9.72686	7.54105	6.84234
H	11.18109	4.77931	5.30061
H	11.51703	5.89714	6.63208
H	12.09061	3.51617	7.17818
H	10.42113	3.03315	6.88813
H	5.00474	2.91145	6.71864
H	7.10384	10.82247	3.18283

Table 99. Computational data for **MeO⁻**.**MeO⁻** $E = -115.389230578118$ $E_{ZPE} = 0.0351538$ $E_T = 0.00291789$ $E_S = -0.02612925$

O	-1.70613	1.86329	0.00001
C	-3.06668	1.86328	-0.00002
H	-3.54927	2.34208	0.90423
H	-3.54929	2.40737	-0.86658
H	-3.54903	0.84077	-0.03775

Table 100. Computational data for **MeOH**.**MeOH** $E = -115.918633304544$ $E_{ZPE} = 0.05019229$ $E_T = 0.00338938$ $E_S = -0.02716573$

O	-1.70577	1.86756	0.00879
C	-3.14359	1.85352	-0.01847
H	-3.47600	2.34047	0.90113
H	-3.53672	2.41039	-0.87912
H	-3.53705	0.82880	-0.04177
H	-1.39356	1.43865	-0.80386

Table 101. Computational data for **19^{Me}**.**19^{Me}** $E = -1291.634496370217$ $E_{ZPE} = 0.21141758$ $E_T = 0.016036$ $E_S = -0.05881653$

C	-6.64086	-6.76537	-0.57392
C	-7.02257	-5.46853	-0.99079
C	-4.58525	-4.58888	-0.48811
C	-4.20362	-5.88566	-0.07101
P	-6.11254	-3.98176	-1.07557

P	-5.11353	-7.37252	0.01338
N	-7.78739	-7.54712	-0.72345
N	-8.36499	-5.58457	-1.35468
N	-3.43875	-3.80711	-0.33851
N	-2.86132	-5.76953	0.29328
C	-9.15976	-4.46525	-1.84968
H	-9.20373	-3.67310	-1.09549
H	-8.71449	-4.06422	-2.76571
H	-10.16220	-4.83833	-2.05590
C	-7.83406	-8.96933	-0.39943
H	-7.11171	-9.51817	-1.01187
H	-7.59692	-9.12109	0.65834
H	-8.84317	-9.32202	-0.60889
C	-2.06651	-6.88888	0.78815
H	-2.01937	-7.67947	0.03250
H	-1.06515	-6.51496	0.99804
H	-2.51392	-7.29232	1.70208
C	-3.39211	-2.38487	-0.66241
H	-2.38258	-2.03253	-0.45441
H	-3.63076	-2.23295	-1.71981
H	-4.11338	-1.83584	-0.04886
C	-2.36319	-4.50463	0.13960
C	-8.86308	-6.84950	-1.20110

Table 102. Computational data for **17a**^{Me}.**17a**^{Me}

$$E = -1370.391081703325$$

$$E_{ZPE} = 0.26654919$$

$$E_T = 0.01877921$$

$$E_S = -0.06430423$$

C	-5.39778	-7.62016	0.36742
C	-6.01740	-6.83777	-0.56914
C	-3.83819	-5.25330	-0.68087
C	-3.22100	-6.03346	0.25880
P	-5.64319	-5.07139	-0.77853
P	-4.14061	-6.97555	1.51144
N	-6.01100	-8.86487	0.29941
N	-6.98205	-7.63943	-1.16656
N	-2.82294	-4.61397	-1.38121
N	-1.85607	-5.83633	0.09010
C	-7.87637	-7.19721	-2.23412
H	-8.49409	-8.04871	-2.51849
H	-8.51183	-6.37988	-1.88148
H	-7.29479	-6.85478	-3.09446
C	-5.64667	-10.01145	1.12889
H	-4.59690	-10.27296	0.96947
H	-5.80272	-9.77810	2.18585
H	-6.28520	-10.84446	0.83594
C	-0.82241	-6.49241	0.88784
H	-0.89878	-7.57829	0.78354
H	0.14392	-6.15088	0.51768
H	-0.93160	-6.22376	1.94227
C	-3.04192	-3.68254	-2.48571

H	-2.06378	-3.35941	-2.84114
H	-3.58710	-4.17786	-3.29394
H	-3.61591	-2.81750	-2.14190
C	-1.57360	-4.96132	-0.92963
C	-6.99946	-8.91242	-0.65248
C	-5.18493	-5.51323	2.10658
C	-5.87026	-4.62462	1.04719
H	-5.93161	-5.95733	2.77250
H	-5.51579	-3.59219	1.12874
H	-6.95364	-4.61380	1.20310
H	-4.50764	-4.91524	2.72451

Table 103. Computational data for **17b**^{Me}.**17b**^{Me}

$$E = -1527.922647933374$$

$$E_{ZPE} = 0.37774859$$

$$E_T = 0.02452739$$

$$E_S = -0.07552661$$

P	7.35949	5.64680	5.85609
P	5.08872	6.68523	8.06050
N	7.20329	8.49817	5.24745
N	5.77297	9.16841	6.69548
N	3.71389	4.43456	6.80886
N	5.19143	3.74910	5.41668
C	6.78054	7.36471	5.92778
C	6.58851	9.64095	5.69779
C	5.86992	7.79104	6.85462
C	4.77747	5.32126	6.90501
C	3.93664	3.44524	5.88259
C	5.72330	4.88242	6.02029
C	8.18160	8.49142	4.16233
C	4.89831	10.03153	7.48578
C	2.48527	4.53284	7.59332
C	5.87191	2.96464	4.38910
C	7.81364	5.57131	7.70796
C	6.70665	5.93013	8.73599
C	9.07379	6.42452	7.95549
C	10.28449	6.04457	7.09948
C	6.36537	4.71098	9.61501
C	5.42493	5.01024	10.78529
H	8.28601	9.51628	3.80719
H	7.83535	7.84856	3.34844
H	9.14572	8.12428	4.52502
H	3.85884	9.70795	7.38352
H	5.01033	11.04728	7.10737
H	5.18375	9.99534	8.54086
H	1.98427	5.48388	7.39250
H	2.71364	4.46568	8.66064
H	1.84080	3.70451	7.30010
H	5.20225	2.15654	4.09568
H	6.80297	2.54914	4.78470
H	6.09818	3.59371	3.52379
H	8.07269	4.51318	7.84745

H	7.09366	6.73081	9.38074
H	8.81699	7.48052	7.79915
H	9.33439	6.32362	9.01733
H	11.15970	6.63506	7.39062
H	10.09857	6.22265	6.03467
H	10.53298	4.98384	7.22199
H	5.93820	3.92612	8.97688
H	7.31134	4.31214	10.00433
H	5.29971	4.12147	11.41287
H	4.43253	5.31934	10.43935
H	5.82612	5.81563	11.41164

H	9.35464	6.33842	9.00264
H	10.02507	6.17077	6.01357
H	10.53624	5.00536	7.22687
H	6.40995	5.07054	9.31309
C	11.50833	6.93352	7.37999
H	11.77872	6.82121	8.43896
H	11.24160	7.98961	7.23645
C	12.71277	6.58322	6.50052
H	13.57417	7.22017	6.73005
H	13.01551	5.53974	6.64972
H	12.47044	6.71227	5.43873

Table 104. Computational data for $17c^{Me}$. **$17c^{Me}$**

$$E = -1527.922058263005$$

$$E_{ZPE} = 0.37792906$$

$$E_T = 0.02448722$$

$$E_S = -0.0759203$$

P	7.35041	5.63886	5.86320
P	5.07996	6.65958	8.08092
N	7.21273	8.49811	5.29936
N	5.75777	9.15714	6.72791
N	3.69786	4.42568	6.79830
N	5.17873	3.75059	5.40374
C	6.76540	7.35586	5.95098
C	6.59737	9.63845	5.75419
C	5.83836	7.77680	6.86569
C	4.77094	5.29850	6.91900
C	3.91830	3.45058	5.85617
C	5.71753	4.86824	6.03132
C	8.22098	8.50234	4.24191
C	4.87452	10.01529	7.51432
C	2.46144	4.52420	7.57073
C	5.85956	2.97749	4.36772
C	7.82136	5.56005	7.71565
C	6.70892	5.94236	8.72207
C	9.07535	6.42724	7.94373
C	10.28304	6.06459	7.07609
H	8.32963	9.52973	3.89533
H	7.90163	7.86151	3.41558
H	9.17685	8.13939	4.62993
H	3.83382	9.70736	7.38078
H	5.00811	11.03689	7.15928
H	5.13432	9.95462	8.57496
H	1.97492	5.48551	7.38332
H	2.67529	4.43210	8.63926
H	1.81003	3.71050	7.25276
H	5.18347	2.18263	4.05352
H	6.78240	2.54426	4.76371
H	6.10059	3.61996	3.51630
H	8.08113	4.50480	7.86357
H	7.09214	6.69399	9.42168
H	8.80539	7.48047	7.78354

Table 105. Computational data for $17a^{Me-TS}$. **$17a^{Me-TS}$**

$$E = -1370.347095726705$$

$$E_{ZPE} = 0.26414001$$

$$E_T = 0.01877237$$

$$E_S = -0.06418613$$

$$imf = -266.58 \text{ cm}^{-1}$$

C	-0.44457	-1.64737	-0.10096
C	-1.06492	-0.83522	-1.04259
C	1.08266	0.74753	-1.09069
C	1.70052	-0.06153	-0.14479
P	-0.64580	0.83359	-1.44884
P	0.91760	-1.21554	0.94066
N	-1.28451	-2.75103	0.05427
N	-2.24046	-1.50019	-1.39522
N	2.05286	1.66919	-1.48700
N	3.00448	0.42347	-0.03061
C	-3.20332	-0.98423	-2.36429
H	-3.66015	-0.06266	-1.99075
H	-2.70249	-0.77675	-3.31455
H	-3.97122	-1.74455	-2.50421
C	-1.00320	-3.86255	0.95862
H	-0.02542	-4.29489	0.72635
H	-1.00535	-3.51701	1.99691
H	-1.78499	-4.60843	0.81794
C	4.00507	-0.14621	0.86752
H	4.13090	-1.21282	0.65901
H	4.94232	0.38191	0.69431
H	3.69629	-0.01819	1.90947
C	1.81888	2.71738	-2.47645
H	2.76523	3.23154	-2.64204
H	1.46236	2.27595	-3.41179
H	1.07247	3.42768	-2.10768
C	3.25761	1.47893	-0.86479
C	-2.39147	-2.69812	-0.74993
C	-0.45446	0.64194	1.87234
C	-1.04710	1.47585	0.92405
H	-1.06784	-0.08553	2.39525
H	-0.60803	2.44895	0.72610
H	0.42754	0.98672	2.40351

H	-2.11318	1.39089	0.73638

H	-4.63449	1.41252	0.17591
H	-3.56703	2.81035	0.40679
H	-3.29176	1.70513	-0.94429

Table 106. Computational data for **17b^{Me}-TS**.**17b^{Me}-TS** $E = -1527.881585089444$ $E_{ZPE} = 0.37475281$ $E_T = 0.02472331$ $E_S = -0.07596483$ $imf = -218.93 \text{ cm}^{-1}$

C	-0.43524	-1.63766	-0.10067
C	-1.04138	-0.84835	-1.06804
C	1.06454	0.78628	-1.06431
C	1.70653	-0.05253	-0.16381
P	-0.66859	0.84946	-1.41846
P	0.92082	-1.19007	0.94699
N	-1.22016	-2.78825	-0.00700
N	-2.15205	-1.57425	-1.50314
N	2.03939	1.68300	-1.50494
N	3.03207	0.38522	-0.12279
C	-3.05671	-1.12689	-2.55910
H	-3.58412	-0.22008	-2.25212
H	-2.49093	-0.92177	-3.47271
H	-3.77546	-1.92643	-2.73675
C	-0.92883	-3.89638	0.89770
H	-1.00542	-3.56726	1.93838
H	-1.65993	-4.68104	0.70481
H	0.08245	-4.27184	0.71428
C	4.07886	-0.24803	0.67539
H	3.87588	-0.12450	1.74237
H	4.13141	-1.31524	0.44096
H	5.02148	0.23694	0.42304
C	1.78403	2.74799	-2.47028
H	1.36359	2.32716	-3.38859
H	1.08028	3.47592	-2.05514
H	2.73511	3.23553	-2.68296
C	3.27146	1.44336	-0.95977
C	-2.27362	-2.78891	-0.88067
H	-0.74986	0.05564	2.59202
C	-0.32233	0.77171	1.88922
C	-1.23043	1.34390	0.97938
C	0.84509	1.59001	2.40660
H	-1.04344	2.38517	0.71528
C	-2.68519	0.91577	1.00087
H	0.44795	2.55042	2.76643
H	1.52152	1.84175	1.58052
H	-3.04063	0.99528	2.03873
H	-2.76537	-0.14763	0.74381
C	1.61469	0.91967	3.54641
H	2.44178	1.55238	3.88405
H	0.95442	0.73608	4.40178
H	2.02893	-0.04593	3.23670
C	-3.59762	1.75672	0.10634

Table 107. Computational data for **17c^{Me}-TS**.**17c^{Me}-TS** $E = -1527.881237129213$ $E_{ZPE} = 0.3753264$ $E_T = 0.02446129$ $E_S = -0.07577363$ $imf = -287.63 \text{ cm}^{-1}$

C	-0.50442	-1.77141	-0.27777
C	-1.11154	-0.85094	-1.12056
C	1.05320	0.70203	-0.98258
C	1.67541	-0.23980	-0.17304
P	-0.67794	0.85494	-1.29480
P	0.89084	-1.51016	0.77307
N	-1.36135	-2.87343	-0.24751
N	-2.29738	-1.45237	-1.54472
N	2.04252	1.63227	-1.30788
N	3.00274	0.17921	-0.06402
C	-3.25067	-0.81942	-2.45179
H	-2.74710	-0.52267	-3.37658
H	-4.03187	-1.54742	-2.66862
H	-3.69151	0.06601	-1.98355
C	-1.09567	-4.08334	0.52528
H	-0.12007	-4.49497	0.25001
H	-1.10021	-3.85816	1.59620
H	-1.88278	-4.80135	0.29684
C	4.02879	-0.55366	0.67332
H	4.09344	-1.58027	0.30068
H	4.97656	-0.03934	0.51729
H	3.79260	-0.57428	1.74045
C	1.80752	2.80256	-2.14841
H	2.76718	3.29362	-2.30739
H	1.38029	2.49366	-3.10713
H	1.11699	3.49258	-1.65391
C	3.26339	1.32213	-0.77437
C	-2.46740	-2.71334	-1.03847
C	-0.39376	0.43044	1.95310
C	-1.17763	1.15333	1.04750
H	-0.86645	-0.39509	2.48051
H	-0.97131	2.21624	0.93817
H	-2.21259	0.86315	0.89220
C	0.78321	1.10187	2.62676
H	0.41842	2.02099	3.11075
H	1.49930	1.43771	1.86503
C	1.49697	0.25030	3.67786
H	0.77917	-0.03458	4.45998
H	1.84069	-0.68821	3.22232
C	2.68861	0.97346	4.31277
H	3.39424	1.26276	3.52191

H	2.34112	1.90732	4.77544
C	3.41163	0.11862	5.35811
H	4.26169	0.65521	5.79368
H	2.73322	-0.15830	6.17395
H	3.79072	-0.80790	4.91019

Table 108. Computational data for dimer.

dimer

$$E = -2583.285151033203$$

$$E_{ZPE} = 0.4249873$$

$$E_T = 0.0335555$$

$$E_S = -0.09412817$$

C	-6.81640	-6.10509	-0.41240
C	-6.83201	-5.58717	-1.70119
C	-4.52779	-4.34040	-1.19031
C	-4.54924	-4.84754	0.10940
P	-5.70344	-4.47584	-2.50982
P	-5.70693	-5.88290	0.97581
N	-7.92840	-6.95202	-0.36142
N	-7.94563	-6.16374	-2.34100
N	-3.32683	-3.60804	-1.29950
N	-3.36381	-4.38348	0.68672
C	-8.32418	-5.87906	-3.72045
H	-7.50340	-6.13188	-4.39911
H	-9.19619	-6.48953	-3.95504
H	-8.57719	-4.82054	-3.84157
C	-8.28485	-7.71997	0.82495
H	-7.47310	-8.40557	1.08970
H	-8.46934	-7.04762	1.66930
H	-9.18860	-8.28476	0.59634
C	-2.97870	-4.69622	2.05612
H	-2.89463	-5.78056	2.18616
H	-2.01585	-4.22305	2.24867
H	-3.72897	-4.31444	2.75688
C	-2.91623	-2.90651	-2.50924
H	-1.94762	-2.44766	-2.31076
H	-2.82941	-3.60588	-3.34649
H	-3.64322	-2.12845	-2.76724
C	-2.59422	-3.61584	-0.15584
C	-8.64491	-7.00508	-1.53323
C	-6.59198	-2.77184	-2.39869
N	-6.69811	-1.95293	-3.47220
N	-6.89250	-2.03420	-1.30885
C	-7.08613	-0.67474	-3.07820
C	-6.48752	-2.33924	-4.86976
C	-7.20315	-0.72504	-1.67202
C	-6.89652	-2.51860	0.07390
P	-7.37143	0.62509	-4.21821
H	-6.08182	-3.35014	-4.88773
H	-7.44200	-2.30455	-5.40063
H	-5.78127	-1.64208	-5.32718
P	-7.64882	0.50709	-0.50863
H	-7.77207	-2.10265	0.57778

H	-5.98450	-2.19210	0.57857
H	-6.95198	-3.60611	0.07431
C	-7.83022	1.84421	-3.05904
C	-7.93631	1.79822	-1.64565
N	-8.19114	3.14366	-3.40735
N	-8.35025	3.07464	-1.27212
C	-8.22059	3.62622	-4.78541
C	-8.51614	3.92553	-2.33160
C	-8.58645	3.46637	0.11503
H	-8.53689	4.66817	-4.76170
H	-7.22412	3.54779	-5.23142
H	-8.92772	3.03384	-5.37439
H	-9.37074	2.84028	0.55177
H	-7.66683	3.35271	0.69738
H	-8.90014	4.50935	0.11338

Table 109. Computational data for trimer.

trimer

$$E = -3874.923275315401$$

$$E_{ZPE} = 0.63852235$$

$$E_T = 0.05143788$$

$$E_S = -0.12985629$$

C	-6.89885	-6.39713	-0.13778
C	-6.90918	-5.68796	-1.32005
C	-4.33112	-4.95811	-0.92271
C	-4.32066	-5.66763	0.25935
P	-5.57488	-4.88115	-2.22881
P	-5.65477	-6.47479	1.16789
N	-8.18316	-6.92283	-0.00265
N	-8.19496	-5.83766	-1.83841
N	-3.04702	-4.43191	-1.05762
N	-3.03493	-5.51759	0.77784
C	-8.65427	-5.20659	-3.07516
H	-8.74423	-4.12481	-2.94145
H	-7.94775	-5.41637	-3.88375
H	-9.62888	-5.62991	-3.31603
C	-8.59896	-7.78276	1.10436
H	-8.10862	-8.75789	1.03439
H	-8.33886	-7.31263	2.05754
H	-9.67921	-7.90700	1.03566
C	-2.57550	-6.14898	2.01438
H	-2.48535	-7.23069	1.88032
H	-1.60097	-5.72558	2.25541
H	-3.28206	-5.93958	2.82304
C	-2.63136	-3.57169	-2.16445
H	-1.55133	-3.44610	-2.09479
H	-2.89001	-4.04229	-3.11779
H	-3.12296	-2.59716	-2.09507
C	-2.22092	-4.75778	-0.01714
C	-9.00923	-6.59688	-1.04309
C	-6.09671	-3.15332	-2.24183
N	-6.14438	-2.39148	-3.37597
N	-6.61273	-2.37688	-1.24457

C	-6.68402	-1.14601	-3.11118
C	-5.68880	-2.79366	-4.70354
C	-6.99839	-1.13866	-1.73297
C	-6.76963	-2.77187	0.15205
P	-6.85966	0.09314	-4.36950
H	-5.34088	-3.82539	-4.66112
H	-6.52109	-2.70621	-5.40747
H	-4.87437	-2.13502	-5.01853
P	-7.73595	0.10024	-0.70204
H	-6.57011	-1.89636	0.77562
H	-6.05106	-3.55527	0.38463
H	-7.78860	-3.12554	0.33178
C	-7.56046	1.33959	-3.32100
C	-7.88471	1.34289	-1.95907
N	-7.91447	2.60907	-3.78559
N	-8.41051	2.61376	-1.71001
C	-7.73733	3.02906	-5.17037
C	-8.44172	3.42062	-2.81618
C	-8.87871	3.04190	-0.39725
H	-8.08503	4.05861	-5.25211
H	-6.68046	2.96992	-5.45064
H	-8.31947	2.38580	-5.83849
H	-9.69784	2.39895	-0.05859
H	-8.06217	2.99178	0.33065
H	-9.22916	4.06960	-0.49003
C	-5.13266	-8.20260	1.17974
N	-4.61491	-8.97747	0.18215
N	-5.08363	-8.96488	2.31348
C	-4.22685	-10.21519	0.66999
C	-4.45935	-8.58156	-1.21440
C	-4.54147	-10.20915	2.04816
C	-5.54044	-8.56433	3.64112
P	-3.48668	-11.45223	-0.36136
H	-5.18146	-7.80143	-1.44711
H	-3.44194	-8.22334	-1.39392
H	-4.65474	-9.45798	-1.83800
P	-4.36378	-11.44862	3.30587
H	-6.35420	-9.22427	3.95514
H	-5.88954	-7.53297	3.59940
H	-4.70841	-8.65138	4.34541
C	-3.33624	-12.69533	0.89497
C	-3.66073	-12.69332	2.25685
N	-2.80834	-13.96522	0.64531
N	-3.30480	-13.96249	2.72079
C	-2.33930	-14.39193	-0.66762
C	-2.77605	-14.77264	1.75103
C	-3.48163	-14.38356	4.10529
H	-1.98701	-15.41905	-0.57528
H	-3.15588	-14.34294	-1.39554
H	-1.52129	-13.74738	-1.00594
H	-2.90084	-13.73963	4.77394
H	-4.53870	-14.32645	4.38525
H	-3.13214	-15.41253	4.18657

Table 110. Computational data for cyclic trimer.

cyclic trimer

$$E = -3874.966914606102$$

$$E_{ZPE} = 0.64142936$$

$$E_T = 0.04985092$$

$$E_S = -0.12419502$$

C	-1.90059	-6.53929	6.34213
C	-3.15563	-6.64684	5.75953
C	-2.36655	-5.26392	3.66768
C	-1.10564	-5.09730	4.25220
P	-3.85744	-6.06530	4.21561
P	-0.42415	-5.70725	5.80077
N	-1.98783	-7.19354	7.58582
N	-3.91303	-7.36331	6.69050
N	-2.25228	-4.69348	2.39901
N	-0.30559	-4.44428	3.31777
C	-5.31529	-7.70074	6.47876
H	-5.90666	-6.78890	6.34494
H	-5.42387	-8.32806	5.58776
H	-5.66314	-8.24284	7.35786
C	-0.87079	-7.30894	8.51706
H	-0.04208	-7.85814	8.05719
H	-0.52148	-6.31603	8.81713
H	-1.22675	-7.85233	9.39217
C	1.09719	-4.08805	3.53957
H	1.73318	-4.96419	3.40429
H	1.38575	-3.31861	2.82502
H	1.19548	-3.70862	4.55898
C	-3.36496	-4.63609	1.45497
H	-3.00441	-4.23584	0.50797
H	-3.76308	-5.64546	1.31432
H	-4.14809	-3.99183	1.86388
C	-0.98963	-4.22810	2.17856
C	-3.21707	-7.72243	7.82082
C	0.71459	-7.01971	5.07188
N	0.51024	-7.80037	3.99464
N	2.05547	-7.01112	5.30146
C	1.73159	-8.25434	3.48624
C	-0.80745	-8.28769	3.56722
C	2.72964	-7.77376	4.34818
C	2.73930	-6.31303	6.38727
P	1.89735	-8.91894	1.82255
H	-1.24083	-8.88483	4.37111
H	-1.47284	-7.45619	3.33890
H	-0.66094	-8.91196	2.68624
P	4.47996	-8.04609	4.41760
H	3.23660	-7.05185	7.02234
H	2.00546	-5.75201	6.96468
H	3.48632	-5.63625	5.96339
C	3.57926	-9.44623	2.02033
C	4.52661	-9.10725	2.98118
N	4.24134	-10.28442	1.10256
N	5.68902	-9.76527	2.57907
C	3.59768	-10.87690	-0.06533

C	5.54388	-10.49901	1.42409	C	-10.15645	-3.62272	0.11216
C	6.94409	-9.68346	3.31660	H	-11.08143	-4.02333	0.52605
H	4.35026	-11.46511	-0.59007	H	-9.75851	-2.84636	0.77078
H	2.77098	-11.52413	0.24362	H	-10.33776	-3.20857	-0.88132
H	3.21369	-10.09505	-0.72843	C	-7.78403	-7.95248	0.66939
H	7.28968	-8.64530	3.36069	H	-8.14778	-8.69722	-0.04304
H	6.80693	-10.05600	4.33698	H	-6.69213	-7.99051	0.71392
H	7.67750	-10.29570	2.79233	H	-8.19495	-8.15133	1.65865
P	-0.30764	-4.05267	0.42222	C	-3.42545	-6.06340	-3.27711
C	1.06023	-5.20459	0.56739	H	-3.97303	-6.93865	-3.64194
C	0.68753	-2.57986	0.38146	H	-2.68323	-5.75587	-4.01346
C	2.43034	-4.99700	0.75929	H	-2.93048	-6.32142	-2.33513
N	0.84920	-6.58200	0.64244	C	-5.55847	-1.66696	-3.66726
C	2.06151	-2.40536	0.48564	H	-4.86513	-1.41013	-4.46789
N	0.14782	-1.30154	0.14278	H	-6.58765	-1.58219	-4.02911
N	2.97027	-6.27190	0.95997	H	-5.41291	-0.98140	-2.82597
P	3.42853	-3.52776	0.77840	C	-4.21503	-3.74689	-3.73776
C	2.00043	-7.22436	0.93385	C	-9.26881	-5.91978	0.59389
C	-0.43186	-7.22495	0.33434	C	-6.85532	-2.09223	-0.11994
N	2.25465	-1.03227	0.31134	N	-6.20344	-2.48044	0.99067
C	-1.27800	-1.04800	-0.03215	N	-7.06910	-0.75223	0.00397
C	1.09282	-0.32615	0.10528	C	-6.01641	-1.39503	1.84446
C	4.41560	-6.49251	1.06345	C	-5.72423	-3.83651	1.26803
H	-1.19507	-6.91767	1.04972	C	-6.53483	-0.26828	1.19711
H	-0.29791	-8.30540	0.37343	C	-7.72809	0.11355	-0.97109
H	-0.73306	-6.92648	-0.67208	P	-5.28977	-1.57722	3.47714
C	3.57082	-0.40627	0.34397	H	-5.41059	-4.31097	0.33769
H	-1.40489	0.02247	-0.19274	H	-4.86975	-3.75190	1.94139
H	-1.83339	-1.35378	0.86081	H	-6.51171	-4.42794	1.74002
H	-1.65866	-1.59874	-0.89801	P	-6.50829	1.46922	1.59204
H	4.75036	-6.33542	2.09056	H	-8.52501	0.66706	-0.46743
H	4.65079	-7.50343	0.74031	H	-8.14340	-0.50244	-1.76817
H	4.89909	-5.77103	0.39805	H	-6.99776	0.81846	-1.37876
H	4.03679	-0.55190	1.32426	C	-5.11307	0.16147	3.80356
H	4.21563	-0.84570	-0.42411	C	-5.55267	1.27152	3.09395
H	3.43691	0.65825	0.15265	N	-4.40273	0.66359	4.91193
				N	-5.08670	2.36506	3.82631
				C	-3.76711	-0.18340	5.91472
				C	-4.37813	2.02079	4.95432
				C	-5.32604	3.74654	3.42759
				H	-3.29919	0.47164	6.64941
				H	-4.51154	-0.81697	6.40893
				H	-3.00708	-0.81880	5.44955
				H	-4.90605	3.93007	2.43309
				H	-6.40116	3.95319	3.40259
				H	-4.84238	4.39240	4.16011
				P	-10.74930	-6.44345	1.61323
				C	-10.92615	-8.18213	1.28679
				C	-10.02267	-6.62572	3.24590
				C	-10.48663	-9.29222	1.99639
				N	-11.63654	-8.68418	0.17843
				N	-9.83561	-5.54035	4.09973
				C	-9.50434	-7.75251	3.89323
				N	-10.95268	-10.38572	1.26402
				P	-9.53101	-9.49001	3.49829
				C	-11.66124	-10.04138	0.13603
				C	-12.27212	-7.83714	-0.82434

Table 111. Computational data for cyclic tetramer.

cyclic tetramer

 $E = -5166.650465071047$ $E_{ZPE} = 0.85649269$ $E_T = 0.06683373$ $E_S = -0.15636894$

C	-7.34623	-5.84900	-0.61151
C	-8.00203	-4.61761	-0.73638
C	-6.03819	-3.75894	-2.32377
C	-5.43227	-5.00187	-2.20783
P	-7.50727	-3.09886	-1.55621
P	-5.82762	-6.48470	-1.27980
N	-8.15526	-6.60895	0.23225
N	-9.18576	-4.71473	-0.00767
N	-5.27505	-3.04023	-3.26503
N	-4.34057	-4.94596	-3.07718

C	-10.31484	-4.18427	3.82245	P	5.13183	6.66087	8.11873
C	-9.18368	-5.92860	5.21029	N	7.23460	8.47524	5.28808
N	-8.96996	-7.26861	5.08635	N	5.76693	9.14152	6.73595
C	-10.71343	-11.76722	1.66272	N	3.73994	4.44971	6.84230
H	-13.03211	-7.20169	-0.35915	N	5.20776	3.77987	5.39554
H	-12.74009	-8.49213	-1.55903	C	6.80985	7.34749	5.97436
H	-11.52765	-7.20361	-1.31854	C	6.59441	9.58865	5.74791
H	-9.52738	-3.59280	3.35046	C	5.88147	7.76792	6.88711
H	-11.16934	-4.26885	3.14911	C	4.82576	5.30472	6.94914
H	-10.62845	-3.70985	4.75282	C	3.96331	3.50262	5.88466
C	-8.31095	-8.13444	6.06135	C	5.75073	4.88480	6.03384
H	-11.19714	-12.41304	0.93020	C	8.22973	8.47742	4.21312
H	-9.63833	-11.97395	1.68771	C	4.86939	9.99782	7.51556
H	-11.13342	-11.95074	2.65722	C	2.52929	4.54001	7.66021
H	-7.89556	-7.51848	6.85841	C	5.87080	3.02064	4.33277
H	-9.04130	-8.83931	6.46906	C	7.81690	5.48988	7.72114
H	-7.51410	-8.68798	5.55763	C	6.77655	5.97962	8.75215
C	-6.77023	-2.10099	4.49647	H	7.81430	8.97615	3.33746
N	-6.85325	-3.30608	5.09795	H	8.47092	7.44013	3.97710
N	-7.88377	-1.41185	4.85822	H	9.12951	9.00195	4.53991
C	-8.03691	-3.40324	5.82675	H	4.40836	9.38296	8.28957
C	-5.88258	-4.39809	4.97796	H	4.09824	10.41689	6.86684
C	-8.69275	-2.17186	5.70196	H	5.44381	10.80564	7.96925
C	-8.25503	-0.06830	4.42116	H	2.40229	5.57752	7.97236
P	-8.53161	-4.92203	6.64655	H	2.62242	3.89945	8.54098
H	-4.95757	-3.99743	4.56418	H	1.68208	4.21433	7.05848
H	-5.70131	-4.81241	5.97137	H	5.30331	3.10413	3.40456
H	-6.28050	-5.17432	4.31918	H	5.94301	1.97246	4.62450
P	-10.21136	-1.53624	6.37033	H	6.86779	3.44091	4.19390
H	-9.34692	-0.03029	4.37665	H	8.03510	4.42861	7.87460
H	-7.84413	0.13062	3.43191	H	7.19484	6.78738	9.36042
H	-7.89128	0.67641	5.13363	Fe	6.81307	11.45720	5.10884
C	-10.00061	-4.26199	7.41428	Fe	2.74479	2.03671	5.31814
C	-10.60658	-3.01907	7.29840	C	8.21953	11.45807	6.21330
N	-10.76363	-4.98072	8.35561	C	6.01865	12.80695	5.94458
N	-11.69817	-3.07500	8.16789	C	7.80314	11.84186	3.68638
C	-10.48014	-6.35397	8.75783	C	5.36737	11.07634	4.12701
C	-11.82361	-4.27408	8.82848	C	3.24934	1.28168	6.85963
C	-12.61328	-1.95757	8.36793	C	1.02356	1.93343	5.74087
H	-11.17338	-6.61081	9.55855	C	3.39266	0.72258	4.31465
H	-10.62577	-7.03955	7.91656	C	2.41579	3.11480	3.92893
H	-9.45091	-6.43871	9.11956	O	9.12012	11.40791	6.94151
H	-12.06567	-1.08232	8.73269	O	8.44795	12.12897	2.75969
H	-13.10838	-1.69957	7.42602	O	5.50837	13.71471	6.46657
H	-13.35540	-2.26511	9.10439	O	4.43055	10.78108	3.51166
				O	3.60442	0.83266	7.86741
				O	-0.10661	1.83082	6.00355
				O	3.77170	-0.15592	3.65083
				O	2.23196	3.84732	3.04991

Table 112. Computational data for $23a^{Me}$. $23a^{Me}$ $E = -4807.66747170248$ $E_{ZPE} = 0.33699099$ $E_T = 0.04064892$ $E_S = -0.11072$

P	7.40143	5.63114	5.88382

Table 113. Computational data for $23a^{Me}-Fe(CO)_4$. $23a^{Me}-Fe(CO)_4$ $E = -3089.030039853095$ $E_{ZPE} = 0.30174606$

$$E_T = 0.02973354$$

$$E_S = -0.08794279$$

P	7.40095	5.63774	5.89629
P	5.12001	6.66846	8.11123
N	7.23648	8.48908	5.30311
N	5.77305	9.15026	6.72391
N	3.73611	4.44763	6.83446
N	5.21305	3.77593	5.39881
C	6.82101	7.35467	5.98871
C	6.59858	9.62537	5.73508
C	5.88673	7.77696	6.89571
C	4.81603	5.31147	6.93821
C	3.96797	3.49578	5.88388
C	5.74657	4.89045	6.02947
C	8.23071	8.49006	4.23156
C	4.87582	10.00849	7.49539
C	2.52314	4.53604	7.64839
C	5.88286	3.01687	4.34077
C	7.79706	5.47159	7.73870
C	6.75040	5.96228	8.76223
H	8.32459	9.51446	3.87244
H	7.90513	7.83776	3.41667
H	9.19490	8.13996	4.61063
H	5.14673	9.98285	8.55459
H	3.84211	9.67168	7.37921
H	4.98173	11.02266	7.11136
H	2.38737	5.57546	7.95034
H	2.61882	3.90520	8.53601
H	1.67971	4.19746	7.04826
H	5.34728	3.13598	3.39710
H	5.91115	1.96181	4.61387
H	6.89662	3.40689	4.24020
H	8.00393	4.40694	7.88566
H	7.16910	6.76180	9.38127
Fe	2.75303	2.02551	5.31411
C	3.24650	1.28249	6.86457
C	1.02842	1.91902	5.71939
C	3.40641	0.70658	4.32135
C	2.43883	3.10256	3.92138
O	3.59464	0.84183	7.87864
O	-0.10434	1.81338	5.97044
O	3.78698	-0.17621	3.66369
O	2.26476	3.83505	3.04005
H	6.45951	5.14580	9.43055
H	8.73985	6.01178	7.87027

Table 114. Computational data for $\text{Fe}(\text{CO})_4$.

$$E = -1718.55346037018$$

$$E_{\text{ZPE}} = 0.03233374$$

$$E_T = 0.00962626$$

$$E_S = -0.04589597$$

Fe	6.13422	11.59364	5.30310
C	7.94925	11.52269	5.24827
C	6.18655	12.71133	6.67483
C	6.06569	11.97278	3.57556
C	4.32076	11.51485	5.39156
O	9.09692	11.46779	5.21560
O	6.02247	12.39009	2.49416
O	6.21625	13.57243	7.45142
O	3.17438	11.45439	5.44980

Table 115. Computational data for 23b^{Me} .

$$E = -4965.199753177780$$

$$E_{\text{ZPE}} = 0.44826923$$

$$E_T = 0.04625442$$

$$E_S = -0.12115881$$

P	7.34561	5.65465	5.81560
P	5.08362	6.67822	8.05422
N	7.20114	8.50082	5.24201
N	5.77758	9.16923	6.73182
N	3.69443	4.46158	6.79107
N	5.18393	3.76394	5.38059
C	6.75555	7.36858	5.90446
C	6.60108	9.61919	5.74281
C	5.85834	7.78855	6.84704
C	4.76567	5.33538	6.87670
C	3.94102	3.48443	5.86988
C	5.70700	4.89689	5.98812
C	8.18346	8.50233	4.15572
C	4.91736	10.02945	7.54796
C	2.47740	4.55884	7.59847
C	5.86792	2.97683	4.35216
C	7.81281	5.58920	7.66241
C	6.70039	5.89861	8.70059
C	9.04095	6.49230	7.89813
C	10.24665	6.18376	7.00719
C	6.35666	4.64328	9.52706
C	5.38214	4.88391	10.68268
H	7.76831	9.02111	3.29150
H	8.40260	7.46430	3.90199
H	9.09600	9.00509	4.48091
H	4.43864	9.40428	8.30278
H	4.15911	10.49974	6.91961
H	5.52353	10.79889	8.02663
H	2.35119	5.59885	7.90237
H	2.56272	3.92431	8.48412
H	1.63328	4.23097	6.99353
H	5.28676	2.98457	3.42903
H	5.99073	1.95003	4.69879
H	6.84371	3.43235	4.17785
H	8.11501	4.54189	7.79487
H	7.08147	6.67316	9.37951
H	8.73713	7.53986	7.77326

H	9.32768	6.37795	8.95136
H	11.10270	6.80124	7.29831
H	10.03396	6.38492	5.95133
H	10.53924	5.13105	7.09454
H	5.96102	3.87151	8.85368
H	7.30102	4.24999	9.92471
H	5.25798	3.96981	11.27256
H	4.39210	5.18734	10.32467
H	5.75209	5.67205	11.34865
Fe	6.87495	11.49657	5.15699
Fe	2.75918	1.96608	5.37008
C	8.25688	11.42843	6.28952
C	6.09692	12.84491	6.01032
C	7.90371	11.88924	3.76452
C	5.44027	11.17440	4.13884
C	3.30743	1.29353	6.93414
C	1.04671	1.83374	5.81937
C	3.43095	0.62990	4.41249
C	2.39078	2.98057	3.94395
O	9.13982	11.32954	7.03452
O	8.57402	12.17985	2.85718
O	5.59833	13.75154	6.54548
O	4.50903	10.91544	3.49907
O	3.69196	0.90287	7.95565
O	-0.07667	1.71245	6.10250
O	3.82671	-0.26477	3.78073
O	2.18187	3.67425	3.03927

Table 116. Computational data for **23b^{Me}-TS**.**23b^{Me}-TS**

$$E = -4965.159043632103$$

$$E_{ZPE} = 0.44596688$$

$$E_T = 0.04600367$$

$$E_S = -0.1198402$$

C	-0.47192	-1.61395	-0.05929
C	-1.05457	-0.83335	-1.04658
C	1.06354	0.75934	-1.04099
C	1.68943	-0.08577	-0.13673
P	-0.66339	0.85636	-1.41649
P	0.88602	-1.18953	0.99509
N	-1.27898	-2.74160	0.07414
N	-2.18075	-1.53170	-1.47817
N	2.03694	1.65815	-1.47285
N	3.01970	0.32596	-0.07780
C	-3.06402	-1.08695	-2.55852
H	-4.03393	-0.78816	-2.15755
H	-2.59150	-0.23425	-3.04961
H	-3.19690	-1.90171	-3.26987
C	-1.00574	-3.81585	1.02639
H	-0.92617	-3.39714	2.03254
H	-1.83595	-4.51876	0.97942
H	-0.07007	-4.31468	0.76013
C	4.05712	-0.35047	0.70395

H	3.63387	-1.28043	1.08825
H	4.90775	-0.56679	0.05766
H	4.37968	0.27600	1.53714
C	1.77075	2.73219	-2.42736
H	1.56256	2.30910	-3.41372
H	0.90943	3.31210	-2.08714
H	2.65452	3.36711	-2.46746
C	3.24521	1.38933	-0.90346
C	-2.31959	-2.71012	-0.80429
H	-0.68352	0.15481	2.63888
C	-0.30577	0.84860	1.88724
C	-1.25639	1.35545	0.98630
C	0.87396	1.70479	2.29438
H	-1.11559	2.39262	0.68073
C	-2.68414	0.85600	1.03515
H	0.47087	2.63569	2.72016
H	1.43202	2.01222	1.40160
H	-3.05420	1.02036	2.05794
H	-2.70050	-0.23126	0.89323
C	1.80480	1.06245	3.32244
H	2.60663	1.75222	3.60227
H	1.25068	0.79442	4.22898
H	2.26606	0.14626	2.93870
C	-3.63300	1.54406	0.05400
H	-4.64857	1.14982	0.15645
H	-3.66353	2.62355	0.23929
H	-3.31696	1.39932	-0.98475
Fe	4.97639	2.32270	-1.18888
Fe	-3.74705	-4.06819	-1.07376
C	4.70435	2.92883	0.47210
C	5.16029	3.97021	-1.82731
C	6.49255	1.49190	-0.77805
C	4.88485	1.60912	-2.82842
C	-4.76312	-2.88070	-0.20253
C	-4.14090	-5.36717	0.07221
C	-2.43683	-5.01585	-1.84199
C	-4.74227	-4.02709	-2.54457
O	4.48622	3.30416	1.54635
O	5.32325	5.04406	-2.24672
O	7.51245	0.99592	-0.51645
O	4.78341	1.12892	-3.87745
O	-5.38027	-2.08241	0.36723
O	-4.42976	-6.23610	0.79153
O	-1.55742	-5.59087	-2.32952
O	-5.42554	-4.03704	-3.48696

Table 117. Computational data for **26^{Me}**.**26^{Me}**

$$E = -4728.905746672374$$

$$E_{ZPE} = 0.28163534$$

$$E_T = 0.03773719$$

$$E_S = -0.10438937$$

C	-6.66963	-6.72633	-0.46540

C	-6.97951	-5.50397	-1.09868
C	-4.55665	-4.62782	-0.59615
C	-4.24675	-5.85024	0.03701
P	-6.01482	-4.07659	-1.38275
P	-5.21144	-7.27760	0.32115
N	-7.82178	-7.50249	-0.55881
N	-8.30257	-5.62062	-1.51647
N	-3.40456	-3.85162	-0.50260
N	-2.92369	-5.73357	0.45483
C	-9.00564	-4.54083	-2.20430
H	-8.83613	-3.60625	-1.66264
H	-8.63423	-4.44478	-3.22838
H	-10.06693	-4.78137	-2.21036
C	-7.89386	-8.86417	-0.03471
H	-7.01686	-9.42190	-0.37477
H	-7.91561	-8.84367	1.05849
H	-8.80097	-9.32524	-0.42050
C	-2.22058	-6.81344	1.14250
H	-2.38971	-7.74788	0.60046
H	-1.15936	-6.57268	1.14897
H	-2.59230	-6.90994	2.16643
C	-3.33254	-2.48984	-1.02645
H	-2.42544	-2.02882	-0.64057
H	-3.31079	-2.51013	-2.11966
H	-4.20957	-1.93222	-0.68628
C	-2.39451	-4.51536	0.13461
C	-8.83180	-6.83877	-1.19608
Fe	-10.66350	-7.49639	-1.57192
Fe	-0.56290	-3.85768	0.51053
C	-12.05386	-6.40436	-1.77301
C	-10.85450	-7.52404	0.21038
C	-11.04297	-9.22733	-1.73282
C	-10.19254	-7.36583	-3.29684
C	-0.18308	-2.12686	0.67178
C	-1.03391	-3.98836	2.23545
C	-0.37182	-3.82954	-1.27176
C	0.82742	-4.94983	0.71145
O	-10.94619	-7.52595	1.36364
O	-11.34347	-10.34570	-1.83877
O	-9.85499	-7.27457	-4.39961
O	-12.99191	-5.73294	-1.91978
O	-1.37158	-4.07964	3.33818
O	0.11772	-1.00858	0.77793
O	1.76563	-5.62105	0.85812
O	-0.28012	-3.82739	-2.42502

Table 118. Computational data for $26^{\text{Me}}\text{-Fe}(\text{CO})_4$. **$26^{\text{Me}}\text{-Fe}(\text{CO})_4$**

$$E = -3010.271321338640$$

$$E_{\text{ZPE}} = 0.24653473$$

$$E_{\text{T}} = 0.026873$$

$$E_{\text{S}} = -0.0817632$$

C	-6.68233	-6.73232	-0.47118

C	-6.99676	-5.50507	-1.09148
C	-4.56505	-4.62697	-0.59529
C	-4.25239	-5.85493	0.03546
P	-6.03278	-4.07310	-1.35884
P	-5.21528	-7.28571	0.29906
N	-7.83504	-7.51042	-0.56818
N	-8.32238	-5.62137	-1.50713
N	-3.40174	-3.86382	-0.50139
N	-2.92838	-5.72189	0.45287
C	-9.02831	-4.53843	-2.18609
H	-8.87117	-3.60942	-1.63112
H	-8.64847	-4.42523	-3.20550
H	-10.08748	-4.78761	-2.20532
C	-7.90414	-8.87541	-0.05359
H	-7.03219	-9.43280	-0.40713
H	-7.91293	-8.86288	1.04006
H	-8.81697	-9.33160	-0.43178
C	-2.20045	-6.77393	1.15671
H	-2.14595	-7.67275	0.53443
H	-1.19747	-6.40087	1.36000
H	-2.70711	-7.01614	2.09621
C	-3.28716	-2.50893	-1.03385
H	-2.27854	-2.15643	-0.82231
H	-3.46251	-2.51482	-2.11424
H	-4.02072	-1.85417	-0.55301
C	-2.37794	-4.50924	0.13748
C	-8.84695	-6.84300	-1.19650
Fe	-10.68037	-7.50304	-1.57626
C	-12.06769	-6.41131	-1.79209
C	-10.87330	-7.51506	0.20537
C	-11.05974	-9.23416	-1.72580
C	-10.19498	-7.38353	-3.29731
O	-10.96501	-7.50701	1.35889
O	-11.36067	-10.35343	-1.82523
O	-9.84706	-7.29836	-4.39765
O	-13.00475	-5.73993	-1.94818

Table 119. Computational data for 26^{Me}-CO . **26^{Me}-CO**

$$E = -4615.35270007084$$

$$E_{\text{ZPE}} = 0.2725486$$

$$E_{\text{T}} = 0.03584364$$

$$E_{\text{S}} = -0.10111481$$

C	-6.73905	-6.85096	-0.52724
C	-7.03045	-5.58589	-1.07514
C	-4.57160	-4.80062	-0.58739
C	-4.28181	-6.06903	-0.02677
P	-6.03450	-4.16530	-1.29287
P	-5.27397	-7.49027	0.18220
N	-7.91457	-7.59018	-0.63635
N	-8.36683	-5.64138	-1.46412
N	-3.39528	-4.05767	-0.48061
N	-2.95373	-5.99642	0.37633

C	-9.05652	-4.50252	-2.06462
H	-8.85562	-3.60992	-1.46574
H	-8.70168	-4.34648	-3.08730
H	-10.12308	-4.71889	-2.06581
C	-8.00972	-8.97834	-0.19163
H	-7.16541	-9.54076	-0.60010
H	-7.98701	-9.02300	0.90099
H	-8.94596	-9.38910	-0.56471
C	-2.18582	-7.05658	1.02123
H	-2.10411	-7.92335	0.36048
H	-1.17975	-6.66367	1.22626
H	-2.65537	-7.34453	1.96528
C	-3.25125	-2.67844	-0.93959
H	-2.23344	-2.35917	-0.71817
H	-3.43401	-2.62759	-2.01665
H	-3.96640	-2.03954	-0.41385
C	-2.40725	-4.77926	0.10716
C	-8.92180	-6.86203	-1.20441
Fe	-10.78308	-7.44297	-1.56634
Fe	-0.56834	-4.44596	0.59685
C	-12.15177	-6.31050	-1.66167
C	-10.92184	-7.56657	0.21631
C	-11.21005	-9.15148	-1.81868
C	-10.35685	-7.21789	-3.29301
C	-1.00227	-3.19710	1.75163
C	-0.06192	-4.18637	-1.06373
C	1.11311	-4.53284	1.18456
O	-10.97699	-7.63136	1.37027
O	-11.54230	-10.25378	-1.98346
O	-10.04756	-7.06667	-4.39761
O	-13.07753	-5.61084	-1.73980
O	-1.25795	-2.24545	2.37903
O	2.20064	-4.62692	1.57731
O	0.25118	-3.83091	-2.13153

Table 120. Computational data for CO.

CO $E = -113.501002376153$ $E_{ZPE} = 0.00487035$ $E_T = 0.00236077$ $E_S = -0.02243842$

C	6.09033	12.85685	6.01736
O	5.60487	13.73955	6.53844

Table 121. Computational data for 27'a^{Me}.**27'a^{Me}** $E = -2828.09070105005$ $E_{ZPE} = 0.4867384$ $E_T = 0.03859134$ $E_S = -0.10546748$

Rh	5.15560	7.08589	14.99674
Rh	4.32358	15.15326	8.40848
Cl	7.36998	7.12961	15.89430
Cl	6.39321	16.34310	8.39235
P	6.36950	12.65984	13.38871
P	7.40668	10.71387	10.86650
N	5.58364	10.01977	14.31729
N	6.25250	8.75931	12.68811
N	5.20018	13.99909	11.08882
N	5.87015	12.74211	9.45752
C	6.08952	10.86530	13.34059
C	5.67854	8.71823	13.92368
C	6.51175	10.07008	12.31154
C	5.05511	10.44063	15.61477
C	3.11096	7.57095	14.68640
C	3.55854	6.73727	13.63928
C	4.95981	4.98262	15.67863
C	4.53291	5.80955	16.70128
C	6.58432	7.56923	11.90524
C	5.89808	12.94395	11.65848
C	5.17461	13.88198	9.73098
C	6.32142	12.15040	10.62918
C	4.60163	15.11578	11.81931
C	2.84937	13.68294	7.98057
C	2.42081	14.47449	9.06751
C	3.31582	16.93010	7.53820
C	3.79019	16.15125	6.49898
C	6.12945	12.25217	8.10397
C	8.22667	12.54683	13.03972
C	8.70421	11.64700	11.88094
H	4.19376	11.09705	15.47071
H	4.75768	9.53612	16.14931
H	2.99322	8.63947	14.51924
H	3.78423	7.16271	12.66387
H	5.98033	4.61060	15.65606
H	5.21070	6.10078	17.49872
H	6.25762	6.70203	12.48249
H	6.06835	7.60067	10.94282
H	3.85864	14.74262	12.52805
H	4.12793	15.76561	11.08068
H	3.24036	12.68321	8.15721
H	2.48170	14.08373	10.08097
H	3.89715	17.76705	7.91483
H	4.75337	16.36215	6.04322
H	5.73150	11.24095	7.99187
H	5.63063	12.93485	7.41302
H	8.66700	12.21566	13.98530
H	8.54076	13.58178	12.87267
H	9.26043	12.23668	11.14571
H	9.37405	10.86667	12.25517
H	5.83150	10.96574	16.17617
H	5.37924	15.66638	12.35404
H	7.20502	12.24973	7.91203
H	7.66403	7.52269	11.74463
H	3.47468	5.95766	16.89471

H	4.24673	4.46236	15.04628
H	2.48421	7.16578	15.47670
H	3.27869	5.68700	13.61873
H	3.12311	15.50821	5.93299
H	2.26483	16.91646	7.81074
H	1.65771	15.23524	8.92416
H	2.41738	13.82932	6.99381

Table 122. Computational data for $27''\mathbf{a}^{\text{Me}}$. $27''\mathbf{a}^{\text{Me}}$ $E = -2828.090984308466$ $E_{\text{ZPE}} = 0.48712227$ $E_{\text{T}} = 0.03841561$ $E_{\text{S}} = -0.10468178$

Rh	7.05737	10.55640	16.82790
Rh	2.64957	12.40710	7.62481
Cl	9.39856	10.19631	16.50798
Cl	1.23831	12.48872	9.54984
P	7.26403	12.79499	11.33745
P	6.60534	9.52798	10.99944
N	7.10132	11.93406	14.11007
N	6.68741	9.81947	13.89167
N	4.99380	12.83388	9.51895
N	4.56109	10.72215	9.30812
C	6.97158	11.69096	12.75005
C	6.92607	10.78573	14.82309
C	6.70883	10.35644	12.61237
C	7.41630	13.22734	14.71589
C	5.20262	11.57084	17.03626
C	4.96544	10.18814	16.88353
C	7.21464	9.62403	18.83557
C	7.46077	10.97808	18.96872
C	6.48585	8.40770	14.21709
C	5.88132	12.15990	10.34557
C	4.17038	11.95573	8.87959
C	5.60921	10.82702	10.21184
C	4.89311	14.28707	9.38594
C	3.78715	11.58246	6.03383
C	4.07317	12.95990	6.14727
C	1.13376	13.59096	6.52089
C	0.84720	12.25101	6.33601
C	3.90612	9.47667	8.90885
C	8.57100	11.68874	10.53068
C	8.26560	10.18451	10.37042
H	6.65467	13.96096	14.44186
H	7.43034	13.08130	15.79800
H	5.03860	12.24667	16.19961
H	4.61869	9.79889	15.92884
H	8.03409	8.91891	18.72698
H	8.47781	11.35990	18.96566
H	6.55242	8.31557	15.30302
H	5.50370	8.08021	13.86812
H	4.65177	14.72948	10.35532

H	4.09101	14.49033	8.67325
H	1.62415	14.17073	5.74474
H	1.10630	11.74792	5.40916
H	3.50437	8.97393	9.79163
H	3.09364	9.74222	8.22956
H	9.46885	11.83225	11.13978
H	8.75754	12.14567	9.55382
H	8.29511	9.89958	9.31408
H	9.01653	9.58563	10.89511
H	8.39722	13.56704	14.37484
H	5.83780	14.69435	9.01819
H	4.62139	8.82269	8.40440
H	7.26597	7.80634	13.74429
H	6.69850	11.64919	19.35287
H	6.25393	9.20146	19.11434
H	5.11335	12.03567	18.01496
H	4.69348	9.58081	17.74310
H	0.12148	11.74677	6.96794
H	0.63810	14.16081	7.30175
H	3.65335	13.66530	5.43449
H	3.14646	11.21864	5.23447
H	4.49558	10.84757	6.41036
H	5.00199	13.28586	6.61065

Table 123. Computational data for $27''' \mathbf{a}^{\text{Me}}$. $27''' \mathbf{a}^{\text{Me}}$ $E = -2828.089934700439$ $E_{\text{ZPE}} = 0.486704$ $E_{\text{T}} = 0.03858946$ $E_{\text{S}} = -0.10537186$

Rh	5.20477	7.07417	14.96880
Rh	4.33371	15.17612	8.44112
Cl	3.08300	7.26003	13.89298
Cl	2.31350	13.94790	8.76252
P	6.39399	12.67850	13.41590
P	7.44897	10.75516	10.88373
N	5.65330	10.02424	14.34049
N	6.34657	8.77865	12.70989
N	5.23187	14.03028	11.12050
N	5.90042	12.77735	9.48536
C	6.13937	10.88069	13.36272
C	5.77394	8.72503	13.94562
C	6.57567	10.09440	12.33273
C	5.03461	10.43555	15.60064
C	6.79219	7.44461	16.33202
C	7.25603	6.61919	15.28549
C	4.72604	4.96593	15.46997
C	4.27367	5.76809	16.50131
C	6.62352	7.59922	11.89028
C	5.92145	12.96800	11.68739
C	5.21059	13.92023	9.76207
C	6.34480	12.17783	10.65561
C	4.56956	15.10483	11.85943

C	6.25790	15.76137	7.75660	N	-3.60553	3.97291	-1.37736
C	5.88696	16.56304	8.85736	N	-2.50647	2.37383	-0.48826
C	3.16652	16.85294	7.56892	N	-6.82113	-0.85784	-0.97822
C	3.48389	15.97212	6.55166	N	-7.91983	0.74108	-1.86815
C	6.07844	12.23949	8.13653	N	-5.39708	2.19589	-3.79148
C	8.25343	12.58723	13.06478	N	-5.02718	0.91986	1.43490
C	8.73759	11.70984	11.89148	P	-4.37716	0.27674	-0.10246
H	4.14808	11.04020	15.39543	C	-3.97671	5.32187	-1.80788
H	4.75083	9.52413	16.13075	H	-3.08214	5.93989	-1.73713
H	7.04733	8.50200	16.34306	H	-4.34169	5.31664	-2.83676
H	7.86811	7.04183	14.49159	H	-4.75703	5.71877	-1.15272
H	5.64755	4.39955	15.56523	C	-1.38116	1.58928	0.02271
H	4.82963	5.85058	17.43039	H	-0.54445	2.27484	0.15374
H	6.31750	6.72542	12.46920	H	-1.62960	1.12422	0.97860
H	6.04944	7.65216	10.96228	H	-1.11532	0.81060	-0.69736
H	3.81969	14.68071	12.53114	C	-3.96995	1.38538	2.34956
H	4.08835	15.75260	11.12387	H	-3.40822	2.20104	1.89007
H	6.97546	14.95422	7.88730	H	-4.45736	1.77462	3.24963
H	6.31488	16.37154	9.83903	H	-3.27154	0.58787	2.65645
H	3.71784	17.77991	7.69550	C	-5.90138	-0.04009	2.13136
H	4.29041	16.18648	5.85679	H	-6.76604	-0.28029	1.50973
H	5.64326	11.23904	8.08162	H	-5.38795	-0.97322	2.42066
H	5.55891	12.91131	7.45008	H	-6.26427	0.44405	3.04411
H	8.69621	12.24483	14.00528	C	-4.52922	3.16054	-4.48954
H	8.55973	13.62715	12.91438	H	-5.04894	4.08978	-4.78016
H	9.26903	12.31937	11.15395	H	-3.66612	3.40758	-3.86844
H	9.43252	10.94374	12.24939	H	-4.16314	2.67748	-5.40160
H	5.74651	11.01258	16.19556	C	-6.45174	1.72322	-4.70539
H	5.30534	15.67084	12.43574	H	-7.00939	0.90546	-4.24470
H	7.14142	12.19467	7.88782	H	-7.15411	2.51665	-5.01385
H	7.69074	7.54568	11.66266	H	-5.96209	1.33507	-5.60472
H	3.24113	6.10455	16.52969	C	-9.04469	1.52530	-2.38059
H	4.05576	4.65833	14.67232	H	-8.79866	1.98269	-3.34081
H	6.58193	7.02181	17.31118	H	-9.88383	0.84119	-2.50349
H	7.40623	5.55573	15.45326	H	-9.30545	2.30990	-1.66514
H	2.78113	15.20208	6.24645	C	-6.45144	-2.20563	-0.54283
H	2.20760	16.79338	8.07596	H	-6.11361	-2.20216	0.49536
H	5.55514	17.58660	8.70315	H	-7.33965	-2.82936	-0.63914
H	6.21445	16.16643	6.74853	H	-5.65163	-2.59431	-1.17900

Table 124. Computational data for **31a**^{Me}.**31a**^{Me} $E = -1561.223420154035$ $E_{ZPE} = 0.37508751$ $E_T = 0.02563652$ $E_S = -0.07729428$

C	-8.05401	-0.57169	-1.50079
C	-5.95317	0.23473	-0.99877
C	-6.64951	1.25414	-1.60327
C	-4.47329	2.88017	-1.35732
C	-3.77656	1.86052	-0.75373
C	-2.37251	3.68674	-0.85512
P	-6.04904	2.83793	-2.25441

Table 125. Computational data for **35b**^{Me}.**35b**^{Me} $E = -3139.317756536563$ $E_{ZPE} = 0.74493356$ $E_T = 0.04818169$ $E_S = -0.12269537$

P	7.38361	5.71599	5.79459
P	5.04561	6.65745	8.04746
N	7.09963	8.54015	5.21730
N	5.63187	9.15510	6.71466
N	3.74106	4.43871	6.72392
N	5.27245	3.80357	5.29983
C	6.71367	7.40656	5.89462

C	6.43621	9.61471	5.71990
C	5.79532	7.79294	6.83834
C	4.78988	5.32160	6.83769
C	4.03525	3.50620	5.77946
C	5.75538	4.91819	5.95007
C	8.04494	8.56440	4.09049
C	4.73406	9.96920	7.54682
C	2.47844	4.53063	7.47284
C	5.99258	3.07189	4.24711
C	7.81193	5.64081	7.64755
C	6.69067	5.93763	8.68106
C	9.04222	6.53501	7.90841
C	10.27093	6.19509	7.06236
C	6.38728	4.68900	9.53484
C	5.43420	4.93250	10.70701
H	8.38294	9.59071	3.94933
H	7.53829	8.20710	3.19210
H	8.88698	7.91599	4.33248
H	3.92765	9.32158	7.89110
H	4.33202	10.78200	6.94574
H	5.28816	10.36722	8.39837
H	2.70670	4.82697	8.49643
H	1.99917	3.55192	7.45628
H	1.83446	5.27304	6.99778
H	5.27708	2.72266	3.50553
H	6.52445	2.22621	4.68596
H	6.69780	3.76576	3.78979
H	8.10823	4.59043	7.76681
H	7.04690	6.73912	9.34154
H	8.75600	7.58527	7.76392
H	9.29137	6.42780	8.97141
H	11.12215	6.81164	7.36755
H	10.09643	6.37365	5.99534
H	10.55024	5.14267	7.18477
H	5.99685	3.89625	8.88260
H	7.34903	4.32574	9.91758
H	5.34384	4.02716	11.31534
H	4.42887	5.20718	10.36835
H	5.80333	5.73989	11.34925
P	2.93630	2.08271	5.42915
P	6.76707	11.33153	5.16968
C	2.35642	2.46570	3.74083
C	1.47026	1.53946	3.16543
C	2.67213	3.63759	3.04049
C	0.94386	1.76469	1.89566
H	1.19326	0.64022	3.71049
C	2.12770	3.86711	1.77644
H	3.33380	4.38178	3.47403
C	1.27126	2.92974	1.19836
H	0.26958	1.03536	1.45633
H	2.37862	4.77952	1.24297
H	0.85387	3.10919	0.21190
C	4.19391	0.76549	5.22895
C	4.93061	0.41960	6.37271
C	4.39245	0.05799	4.03858
C	5.88024	-0.59814	6.31255
H	4.76624	0.95090	7.30786

C	5.32936	-0.97451	3.98945
H	3.82908	0.31720	3.14757
C	6.07908	-1.29974	5.12091
H	6.45566	-0.85117	7.19847
H	5.47799	-1.51963	3.06163
H	6.81166	-2.10040	5.07702
C	5.16627	11.79615	4.42636
C	5.04926	13.11741	3.96240
C	4.11582	10.89626	4.20198
C	3.88469	13.53746	3.32382
H	5.86932	13.81775	4.10135
C	2.95874	11.31768	3.54602
H	4.19240	9.86240	4.52625
C	2.83679	12.63832	3.11355
H	3.80142	14.56444	2.98031
H	2.15137	10.61090	3.37682
H	1.93304	12.96465	2.60736
C	6.81735	12.14781	6.81079
C	7.87266	11.77171	7.65691
C	5.92641	13.14571	7.21957
C	8.01158	12.36383	8.91025
H	8.58247	11.01139	7.33758
C	6.08255	13.75050	8.46734
H	5.10473	13.44511	6.57619
C	7.11820	13.35799	9.31661
H	8.82343	12.05804	9.56397
H	5.38666	14.52495	8.77732
H	7.23230	13.82802	10.28906

Table 126. Computational data for $^{36}\text{b}^{\text{Me}}$. $^{36}\text{b}^{\text{Me}}$ $E = -3198.536145627476$ $E_{\text{ZPE}} = 0.39823083$ $E_{\text{T}} = 0.0324897$ $E_{\text{S}} = -0.09342132$

P	6.90161	5.25258	5.76284
P	5.56922	7.17211	8.17676
N	7.85241	7.88872	5.00634
N	7.02946	9.12375	6.61330
N	3.23629	5.73361	7.21784
N	4.11620	4.45848	5.67352
C	7.08276	7.05931	5.80624
C	7.81174	9.14158	5.51260
C	6.56880	7.82983	6.81350
C	4.57799	6.06802	7.12737
C	2.97176	4.75053	6.32886
C	5.13171	5.26650	6.16641
C	8.61716	7.49731	3.81778
C	6.75277	10.29184	7.45572
C	2.25248	6.30483	8.14328
C	4.24314	3.42424	4.64140
C	7.52578	5.02810	7.54966
C	6.78662	5.79333	8.68047

C	9.03911	5.32493	7.58710
C	9.87551	4.51189	6.59634
C	6.06498	4.81111	9.62482
C	5.41933	5.45968	10.85129
H	8.39083	8.19400	3.00947
H	8.31412	6.48702	3.54437
H	9.68424	7.52087	4.04807
H	5.83428	10.09753	8.00928
H	6.62765	11.16532	6.81534
H	7.58463	10.44985	8.14522
H	2.65235	7.24773	8.51555
H	2.08611	5.61070	8.96942
H	1.31957	6.47761	7.60557
H	3.36082	3.46019	4.00152
H	4.32578	2.44356	5.11495
H	5.13995	3.63781	4.06031
H	7.37267	3.95380	7.71616
H	7.53823	6.34911	9.25642
H	9.19471	6.39922	7.42318
H	9.38025	5.11718	8.60913
H	10.94168	4.70633	6.75083
H	9.63784	4.76595	5.55718
H	9.70120	3.43772	6.72642
H	5.31356	4.25311	9.05106
H	6.81075	4.07522	9.95118
H	5.01027	4.69161	11.51547
H	4.59901	6.13112	10.57350
H	6.15363	6.04510	11.41627
C	8.50411	10.32712	4.95988
C	1.65675	4.10314	6.12285
S	0.77116	4.71308	4.83196
S	1.32833	2.88796	7.23709
S	9.93761	10.70343	5.75302
S	7.71671	11.04694	3.66132

$$E_T = 0.0360935$$

$$E_S = -0.09914472$$

C	-8.01249	-0.52527	-1.52121
C	-5.96264	0.26159	-1.00230
C	-6.65024	1.26922	-1.63053
C	-4.48790	2.89130	-1.37944
C	-3.80106	1.87918	-0.75762
C	-2.42762	3.66510	-0.88475
P	-6.06822	2.86641	-2.28137
N	-3.63241	3.98749	-1.41863
N	-2.53085	2.36846	-0.49213
N	-6.80804	-0.83741	-0.97635
N	-7.91710	0.76971	-1.91422
N	-5.42096	2.24482	-3.81315
N	-5.01053	0.89725	1.42960
P	-4.37864	0.27893	-0.10942
C	-4.05054	5.30380	-1.93431
H	-3.98563	6.03923	-1.13452
H	-3.41885	5.59965	-2.76943
H	-5.08700	5.20910	-2.26173
C	-1.44274	1.54783	0.06623
H	-0.53181	1.75129	-0.49479
H	-1.29195	1.78484	1.11799
H	-1.72955	0.50187	-0.05064
C	-3.93562	1.34296	2.33991
H	-3.40569	2.19413	1.90859
H	-4.41172	1.68007	3.26537
H	-3.21390	0.54911	2.59022
C	-5.88661	-0.07454	2.11551
H	-6.77765	-0.26716	1.51546
H	-5.38731	-1.02822	2.35013
H	-6.20856	0.38497	3.05466
C	-4.57139	3.23431	-4.50741
H	-5.10268	4.16429	-4.76592
H	-3.69578	3.47222	-3.90123
H	-4.22061	2.76958	-5.43366
C	-6.47781	1.76277	-4.72592
H	-7.00170	0.91356	-4.28364
H	-7.20688	2.54090	-5.00276
H	-5.98491	1.41343	-5.63806
C	-8.97887	1.59332	-2.52000
H	-9.30819	1.15169	-3.45825
H	-9.81428	1.67019	-1.82657
H	-8.55732	2.58372	-2.69771
C	-6.39969	-2.16527	-0.48801
H	-6.78899	-2.33622	0.51431
H	-6.78613	-2.92007	-1.17097
H	-5.30892	-2.18945	-0.48135
B	-1.06726	4.53867	-0.75819
B	-9.23145	-1.58327	-1.67559
Cl	-0.43959	4.42378	1.00766
Cl	-1.25459	6.33798	-1.17927
Cl	0.17564	3.77427	-1.95604
Cl	-10.83682	-0.84517	-2.24866
Cl	-9.53557	-2.39409	-0.00887
Cl	-8.67591	-2.86408	-2.94561

Table 127. Computational data for BCl_3 .

BCl_3

$$E = -1406.774558275043$$

$$E_{\text{ZPE}} = 0.007326$$

$$E_T = 0.00444425$$

$$E_S = -0.03404358$$

B	0.84887	-0.06810	0.00071
Cl	-0.02568	1.44555	0.00076
Cl	2.59712	-0.06760	0.00106
Cl	-0.02481	-1.58225	0.00037

Table 128. Computational data for 41a^{Me} .

41a^{Me}

$$E = -4374.934386266487$$

$$E_{\text{ZPE}} = 0.39746753$$

Table 129. Computational data for 42^{Me} .

42^{Me}			
$E = -4105.331649950909$			
$E_{\text{ZPE}} = 0.23292046$			
$E_{\text{T}} = 0.027143$			
$E_{\text{S}} = -0.08314802$			
C	-6.61914	-6.78161	-0.54561
C	-7.00565	-5.50266	-0.99622
C	-4.60714	-4.57362	-0.51250
C	-4.21815	-5.85425	-0.06901
P	-6.13858	-3.99262	-1.11646
P	-5.09047	-7.36020	0.06791
N	-7.74934	-7.59177	-0.67489
N	-8.33907	-5.61775	-1.37210
N	-3.47791	-3.76249	-0.38158
N	-2.88175	-5.74099	0.29734
C	-9.09164	-4.47355	-1.90145
H	-10.00167	-4.82718	-2.37484
H	-9.32850	-3.78905	-1.08383
H	-8.46288	-3.97211	-2.64144
C	-7.72869	-9.01980	-0.31650
H	-8.38084	-9.19701	0.53725
H	-6.70095	-9.27557	-0.05515
H	-8.04748	-9.61660	-1.16827
C	-2.12864	-6.88641	0.82334
H	-2.45201	-7.08853	1.84696
H	-1.06672	-6.66505	0.79832
H	-2.34000	-7.74815	0.18524
C	-3.49347	-2.34020	-0.76227
H	-2.73553	-2.15289	-1.52028
H	-3.31527	-1.72061	0.11478
H	-4.48116	-2.12303	-1.17121
C	-2.43723	-4.47360	0.11432
C	-8.79059	-6.87929	-1.16770
B	-0.91839	-4.00351	0.46068
B	-10.32076	-7.33795	-1.47837
Cl	-11.44517	-6.19047	-0.50368
Cl	-10.58547	-7.13813	-3.33024
Cl	-10.73066	-9.08346	-1.00769
Cl	-0.57514	-2.19964	0.20476
Cl	-0.61529	-4.40808	2.26977
Cl	0.22545	-4.99230	-0.65928

Table 130. Computational data for 45^{Me} .

45^{Me}			
$E = -4257.30575053327$			
$E_{\text{ZPE}} = 0.26066158$			
$E_{\text{T}} = 0.03012508$			

$$E_{\text{S}} = -0.08855081$$

C	-6.65416	-6.82552	-0.66071
C	-7.00783	-5.57784	-1.11147
C	-4.51801	-4.63147	-0.60001
C	-4.13416	-5.86907	-0.14744
P	-6.02211	-4.09770	-1.45666
P	-5.05458	-7.40001	-0.12149
N	-7.79596	-7.61567	-0.72010
N	-8.34840	-5.64557	-1.43302
N	-3.42808	-3.79346	-0.43143
N	-2.82482	-5.74549	0.28944
C	-9.08394	-4.49869	-1.98446
H	-9.91858	-4.86101	-2.57896
H	-9.44093	-3.86428	-1.17215
H	-8.39293	-3.94378	-2.62585
C	-7.78084	-9.04816	-0.36423
H	-8.21946	-9.18794	0.62350
H	-6.74093	-9.37456	-0.37100
H	-8.34038	-9.60724	-1.10905
C	-2.04979	-6.87754	0.82580
H	-2.24598	-6.97878	1.89402
H	-0.99248	-6.69489	0.65204
H	-2.36331	-7.77407	0.28873
C	-3.45785	-2.38512	-0.85927
H	-2.54677	-2.14886	-1.40245
H	-3.56564	-1.73279	0.00680
H	-4.31589	-2.26532	-1.52576
C	-2.39675	-4.46980	0.14134
C	-8.84267	-6.88617	-1.16828
B	-0.92925	-3.94837	0.60188
B	-10.40292	-7.28851	-1.36945
Cl	-11.44307	-5.99351	-0.48902
Cl	-10.74115	-7.26886	-3.22025
Cl	-10.86642	-8.94775	-0.67941
Cl	-0.72290	-2.10346	0.54419
Cl	-0.64567	-4.49437	2.37759
Cl	0.32267	-4.74994	-0.55013
H	-6.55575	-3.27621	-0.43140
O	-5.29028	-7.73312	1.43147
H	-4.84258	-8.55392	1.71318
O	-4.44864	-8.51347	-0.89693

Table 131. Computational data for 47^{bMe} .

47^{bMe}			
$E = -4341.638374465062$			
$E_{\text{ZPE}} = 0.40004788$			
$E_{\text{T}} = 0.03503724$			
$E_{\text{S}} = -0.09767531$			
P	6.92985	5.22392	5.77345
P	5.57994	7.14797	8.17263
N	7.86009	7.86577	5.00213
N	7.01688	9.09329	6.58902

N	3.26086	5.71186	7.18997
N	4.14009	4.43859	5.65960
C	7.10266	7.03317	5.80505
C	7.81231	9.13804	5.48482
C	6.57802	7.80300	6.80403
C	4.59912	6.03219	7.12333
C	2.97110	4.72836	6.29237
C	5.15542	5.23226	6.16557
C	8.55938	7.37303	3.80381
C	6.64487	10.22307	7.45322
C	2.32565	6.35910	8.12136
C	4.36749	3.46946	4.57450
C	7.54528	5.00988	7.56095
C	6.80629	5.78494	8.68642
C	9.05948	5.30268	7.60166
C	9.89858	4.47591	6.62458
C	6.09542	4.80960	9.64602
C	5.46051	5.46814	10.87275
H	8.24205	7.94156	2.93180
H	8.28212	6.32461	3.68872
H	9.63623	7.46310	3.93803
H	5.67259	9.99187	7.89002
H	6.58164	11.12749	6.85238
H	7.39089	10.34498	8.23965
H	2.72234	7.35052	8.34278
H	2.25298	5.76885	9.03549
H	1.34906	6.44016	7.64902
H	3.70396	3.68842	3.74012
H	4.19135	2.45806	4.93723
H	5.40764	3.58189	4.26669
H	7.38910	3.93714	7.73465
H	7.55735	6.35159	9.25241
H	9.21846	6.37467	7.42595
H	9.39509	5.10595	8.62769
H	10.96450	4.66842	6.78317
H	9.66787	4.71922	5.58133
H	9.71988	3.40388	6.76582
H	5.33961	4.24543	9.08401
H	6.84574	4.07804	9.97171
H	5.05598	4.70565	11.54607
H	4.63906	6.13870	10.59640
H	6.20040	6.05658	11.42722
B	8.49379	10.49649	4.92845
B	1.48666	4.11667	6.08708
Cl	9.43973	11.30247	6.34248
Cl	7.10133	11.62868	4.34525
Cl	9.68220	10.24188	3.52296
Cl	0.85738	3.53587	7.76334
Cl	0.38952	5.50040	5.42055
Cl	1.39952	2.67788	4.91407

$$E_{ZPE} = 0.39670242$$

$$E_T = 0.03550312$$

$$E_S = -0.09874674$$

$$imf = -148.68 \text{ cm}^{-1}$$

C	-0.43385	-1.61432	-0.15449
C	-1.02447	-0.80887	-1.11972
C	1.07335	0.79326	-1.07084
C	1.69960	-0.07043	-0.18072
P	-0.64124	0.87793	-1.48202
P	0.94029	-1.25064	0.89200
N	-1.23759	-2.74019	-0.03933
N	-2.16065	-1.48760	-1.55783
N	2.03931	1.71465	-1.47235
N	3.01958	0.35169	-0.09022
C	-3.00309	-0.97877	-2.65348
H	-3.99388	-0.72684	-2.28018
H	-2.51206	-0.08618	-3.04447
H	-3.07793	-1.73036	-3.43694
C	-0.93332	-3.82918	0.89784
H	-1.32234	-3.57954	1.88676
H	-1.38200	-4.75119	0.53837
H	0.15324	-3.93269	0.93773
C	4.03232	-0.36019	0.70351
H	4.12441	0.09573	1.68876
H	3.70170	-1.39644	0.79468
H	4.98702	-0.31857	0.18292
C	1.74626	2.77364	-2.45190
H	0.76166	2.55769	-2.86942
H	1.73565	3.74534	-1.95912
H	2.49367	2.76063	-3.24170
C	3.22513	1.44126	-0.87550
C	-2.28712	-2.66574	-0.89621
H	-0.66126	0.06231	2.58891
C	-0.33773	0.83944	1.89616
C	-1.29326	1.33483	1.02039
C	0.85751	1.66652	2.30781
H	-1.16021	2.36172	0.67875
C	-2.70263	0.79024	1.01189
H	0.47961	2.62746	2.68548
H	1.46002	1.92379	1.42825
H	-3.10741	0.92047	2.02615
H	-2.68557	-0.29426	0.84985
C	1.72087	1.01559	3.38852
H	2.57701	1.64971	3.63683
H	1.13650	0.85312	4.30077
H	2.10207	0.03994	3.06700
C	-3.64078	1.47803	0.02051
H	-4.64536	1.04824	0.07536
H	-3.71275	2.54909	0.23909
H	-3.28616	1.37983	-1.01139
B	4.65746	2.19013	-1.00563
B	-3.42299	-3.81716	-1.01705
Cl	4.60720	3.80412	-1.92402
Cl	5.28298	2.54584	0.73218
Cl	5.82144	1.01227	-1.90298

Table 132. Computational data for 47b^{Me}-TS.

47b^{Me}-TS

$$E = -4341.591909852037$$

Cl	-4.84179	-3.39770	-2.13826
Cl	-4.11914	-4.10014	0.70912
Cl	-2.58385	-5.37550	-1.66185

C	-1.39498	1.10665	5.81440
C	-1.98254	-2.59176	4.79479
H	-1.99871	-2.35195	3.72407
C	-0.67590	-3.36565	5.06325
H	0.20902	-2.81541	4.73473
H	-0.56982	-3.58624	6.13092
H	-0.69748	-4.31407	4.51640
C	-3.18701	-3.49897	5.08003
H	-4.13377	-2.96726	4.94631
H	-3.16921	-4.35082	4.39382
H	-3.15362	-3.89478	6.10075
C	-0.67573	2.34372	5.30793
H	-0.03066	2.06182	4.47095
C	0.22568	2.96287	6.38963
H	-0.36633	3.32842	7.23517
H	0.77475	3.81204	5.96960
H	0.94972	2.23409	6.76677
C	-1.69385	3.36920	4.77207
H	-2.29836	2.93624	3.96859
H	-1.16880	4.24628	4.37885
H	-2.36681	3.69991	5.57040
C	1.73164	-0.23781	4.98735
C	1.35566	-0.80687	6.22036
H	0.37979	-1.24956	6.35189
C	2.24585	-0.82316	7.28602
H	1.94117	-1.27486	8.22473
C	3.51912	-0.26717	7.15218
H	4.20978	-0.27805	7.99002
C	3.89988	0.30283	5.93668
H	4.88465	0.74468	5.82211
C	3.02016	0.31468	4.86231
H	3.33587	0.76680	3.93448
P	-2.84299	-0.02512	2.43712
N	-3.91914	0.06276	-0.08904
N	-2.24326	0.14892	-1.48353
C	-3.59901	0.14180	-1.40426
C	-2.76131	0.02358	0.69146
C	-1.68054	0.05215	-0.20884
C	-5.22327	0.09380	0.54061
C	-5.78331	1.34910	0.81606
C	-7.00861	1.35635	1.49072
H	-7.48380	2.30558	1.71964
C	-7.61982	0.16737	1.87735
H	-8.56815	0.19662	2.40626
C	-7.02805	-1.06054	1.58943
H	-7.52064	-1.97965	1.89201
C	-5.81139	-1.13002	0.90591
C	-5.11920	2.64908	0.40290
H	-4.13467	2.42114	-0.01660
C	-5.94012	3.35383	-0.69395
H	-6.93295	3.62598	-0.31964
H	-5.42955	4.26932	-1.01053
H	-6.06767	2.70761	-1.56819
C	-4.89553	3.57160	1.61378
H	-4.29722	3.07071	2.38183
H	-4.36678	4.47695	1.29754
H	-5.84781	3.87417	2.06171

Table 133. Computational data for XXXVII.

XXXVII

 $E = -3469.113732200630$ $E_{\text{ZPE}} = 1.26824462$ $E_{\text{T}} = 0.07373852$ $E_{\text{S}} = -0.16865406$

P	0.04937	-0.03435	0.02538
N	1.12552	-0.12197	2.55155
N	-0.55035	-0.20827	3.94604
C	0.80539	-0.20100	3.86677
C	-0.03232	-0.08297	1.77104
C	-1.11308	-0.11160	2.67134
C	2.42963	-0.15271	1.92185
C	2.98977	-1.40789	1.64605
C	4.21503	-1.41488	0.97132
H	4.69030	-2.36401	0.74216
C	4.82610	-0.22575	0.58492
H	5.77439	-0.25477	0.05595
C	4.23422	1.00204	0.87316
H	4.72670	1.92126	0.57074
C	3.01760	1.07125	1.55678
C	2.32581	-2.70802	2.05898
H	1.34118	-2.48025	2.47833
C	3.14668	-3.41275	3.15586
H	4.13960	-3.68470	2.78165
H	2.63621	-4.32835	3.47230
H	3.27402	-2.76659	4.03019
C	2.10244	-3.63046	0.84798
H	1.50425	-3.12956	0.07984
H	1.57370	-4.53587	1.16404
H	3.05483	-3.93294	0.40021
C	2.39606	2.41794	1.89190
H	1.53598	2.25119	2.54849
C	3.38189	3.33737	2.63608
H	2.87699	4.27121	2.90425
H	3.75705	2.87742	3.55481
H	4.23973	3.58685	2.00325
C	1.88539	3.11584	0.61996
H	1.39471	4.05977	0.87940
H	2.71450	3.33348	-0.06170
H	1.16494	2.48757	0.08803
C	-1.35178	-0.12649	5.14796
C	-2.04937	-1.27680	5.56304
C	-2.80249	-1.15513	6.73325
H	-3.35747	-2.00972	7.10331
C	-2.85504	0.04795	7.43605
H	-3.44649	0.11257	8.34488
C	-2.16875	1.16656	6.97827
H	-2.23428	2.10166	7.52636

C	-5.19000	-2.47684	0.57106
H	-4.32969	-2.31027	-0.08528
C	-6.17577	-3.39611	-0.17340
H	-5.67102	-4.33014	-0.44122
H	-6.55040	-2.93620	-1.09236
H	-7.03395	-3.64525	0.45911
C	-4.67989	-3.17477	1.84319
H	-4.18916	-4.11874	1.58396
H	-5.50929	-3.39237	2.52452
H	-3.95962	-2.54655	2.37542
C	-1.44192	0.06704	-2.68550
C	-0.74429	1.21728	-3.10066
C	0.00864	1.09557	-4.27099
H	0.56362	1.95013	-4.64112
C	0.06099	-0.10751	-4.97380
H	0.65231	-0.17217	-5.88272
C	-0.62531	-1.22607	-4.51592
H	-0.55993	-2.16118	-5.06402
C	-1.39892	-1.16611	-3.35195
C	-0.81094	2.53226	-2.33243
H	-0.79519	2.29246	-1.26170
C	-2.11724	3.30656	-2.60130
H	-3.00242	2.75666	-2.27288
H	-2.22302	3.52702	-3.66903
H	-2.09545	4.25506	-2.05458
C	0.39396	3.43901	-2.61731
H	1.34046	2.90687	-2.48339
H	0.37637	4.29083	-1.93106
H	0.36101	3.83489	-3.63802
C	-2.11822	-2.40312	-2.84539
H	-2.76317	-2.12116	-2.00834
C	-3.01980	-3.02217	-3.92701
H	-2.42790	-3.38778	-4.77260
H	-3.56893	-3.87129	-3.50692
H	-3.74381	-2.29332	-4.30408
C	-1.10015	-3.42869	-2.30965
H	-0.49555	-2.99581	-1.50619
H	-1.62524	-4.30575	-1.91642
H	-0.42728	-3.75944	-3.10803
C	-4.52526	0.17877	-2.52482
C	-4.14924	0.74778	-3.75784
H	-3.17331	1.19031	-3.88940
C	-5.03946	0.76421	-4.82347
H	-4.73475	1.21588	-5.76218
C	-6.31280	0.20840	-4.68960
H	-7.00349	0.21940	-5.52742
C	-6.69361	-0.36157	-3.47410
H	-7.67843	-0.80329	-3.35950
C	-5.81385	-0.37356	-2.39976
H	-6.12959	-0.82565	-1.47192

Table 134. Computational data for $[BCl_4]^-$. $[BCl_4]^-$ $E = -1867.562064428615$ $E_{ZPE} = 0.00778417$ $E_T = 0.00620515$ $E_S = -0.03888708$

B	0.84852	-0.06808	0.00079
Cl	-0.03479	1.46166	-0.61988
Cl	2.61342	-0.06672	-0.62562
Cl	-0.03417	-1.59616	-0.62488
Cl	0.85152	-0.07111	1.87309

Table 135. Computational data for $(Me_2N)BCl_2$. $(Me_2N)BCl_2$ $E = -1081.006494325866$ $E_{ZPE} = 0.08853845$ $E_T = 0.00773965$ $E_S = -0.04127873$

B	0.82133	-0.01391	0.08734
Cl	-0.13139	0.09847	1.59532
Cl	-0.01970	-0.73589	-1.31498
N	2.13358	0.43114	0.00932
C	2.86377	1.02963	1.13331
H	3.75447	0.42974	1.35372
H	3.18408	2.04278	0.86395
H	2.22946	1.07351	2.01712
C	2.95294	0.35718	-1.20642
H	3.84207	-0.25413	-1.01296
H	2.38168	-0.08299	-2.02208
H	3.27760	1.36467	-1.49114

Table 136. Computational data for $[(Me_2N)BCl_3]^-$. $[(Me_2N)BCl_3]^-$ $E = -1541.756384518004$ $E_{ZPE} = 0.08798312$ $E_T = 0.00940597$ $E_S = -0.04499035$

B	0.81914	-0.15117	-0.02587
Cl	-0.13295	1.31410	-0.75907
Cl	2.59699	-0.08342	-0.67722
Cl	0.01609	-1.76691	-0.83593
N	0.76742	-0.16906	1.44266
C	-0.55375	-0.07911	2.06588
H	-1.12027	-1.02423	1.97961
H	-0.43855	0.14910	3.13324
H	-1.13571	0.71547	1.59522
C	1.57937	-1.17604	2.12701
H	2.58841	-1.19121	1.71039
H	1.64037	-0.93001	3.19486
H	1.14985	-2.19052	2.03633

Table 137. Computational data for 50^{Me} .

50^{Me}			
$E = -1562.18162509977$			
$E_{\text{ZPE}} = 0.40218526$			
$E_{\text{T}} = 0.0260906$			
$E_{\text{S}} = -0.07836272$			
C	-7.95853	-0.52259	-1.51777
C	-5.92982	0.22689	-1.03105
C	-6.63377	1.25176	-1.62523
C	-4.47406	2.86696	-1.38640
C	-3.76958	1.84102	-0.79481
C	-2.44700	3.61750	-0.89484
P	-6.05945	2.85353	-2.29081
N	-3.63056	3.97371	-1.40275
N	-2.49483	2.33274	-0.53059
N	-6.77496	-0.87860	-1.01020
N	-7.90988	0.76117	-1.88570
N	-5.40327	2.19683	-3.80256
N	-4.99795	0.90219	1.38412
P	-4.34436	0.24005	-0.12680
C	-3.96927	5.34074	-1.84163
H	-3.19886	6.01140	-1.46361
H	-4.00312	5.38677	-2.93027
H	-4.93922	5.60655	-1.42082
C	-1.33878	1.57142	-0.02045
H	-0.47215	2.23094	-0.03885
H	-1.53235	1.23941	0.99906
H	-1.17588	0.71366	-0.67386
C	-3.94077	1.36410	2.30860
H	-3.39628	2.20276	1.87002
H	-4.43711	1.72835	3.21248
H	-3.23265	0.57176	2.59781
C	-5.90447	-0.03487	2.08063
H	-6.79071	-0.22470	1.47210
H	-5.42714	-0.98956	2.35163
H	-6.23325	0.45742	3.00017
C	-4.51025	3.14632	-4.49997
H	-4.99865	4.09732	-4.76406
H	-3.62334	3.34282	-3.89458
H	-4.18052	2.66142	-5.42305
C	-6.45667	1.72139	-4.72440
H	-6.98596	0.87273	-4.28635
H	-7.17841	2.50323	-5.00826
H	-5.95810	1.36793	-5.63128
C	-9.06391	1.51951	-2.40519
H	-8.91122	1.75786	-3.45755
H	-9.94976	0.89655	-2.28861
H	-9.16536	2.43393	-1.82012
C	-6.43554	-2.24530	-0.57123
H	-6.33040	-2.27394	0.51323
H	-7.24348	-2.90510	-0.88430
H	-5.50114	-2.53882	-1.05043

H	-1.58873	4.26509	-0.79361
H	-8.81792	-1.16936	-1.61456

Table 138. Computational data for 51^{Me} .

51^{Me}			
$E = -2213.801930881009$			
$E_{\text{ZPE}} = 0.24145787$			
$E_{\text{T}} = 0.01997929$			
$E_{\text{S}} = -0.06767337$			
C	-7.94005	-0.51423	-1.52360
C	-5.90861	0.22748	-1.05045
C	-6.62617	1.26547	-1.61156
C	-4.49568	2.86678	-1.36571
C	-3.77830	1.82882	-0.80427
C	-2.46346	3.60771	-0.89474
P	-6.21142	2.99881	-1.92163
N	-3.64667	3.96518	-1.40065
N	-2.51002	2.32392	-0.52995
N	-6.75709	-0.87143	-1.01703
N	-7.89395	0.76995	-1.88721
P	-4.19372	0.09610	-0.49185
C	-3.96541	5.29643	-1.94819
H	-3.16963	5.98027	-1.65708
H	-4.02994	5.22810	-3.03516
H	-4.91652	5.62773	-1.52756
C	-1.39807	1.58080	0.09061
H	-0.49813	2.18799	0.00464
H	-1.63314	1.39535	1.13974
H	-1.26755	0.63970	-0.44656
C	-9.00578	1.51292	-2.50814
H	-8.77113	1.69703	-3.55760
H	-9.90603	0.90637	-2.42092
H	-9.13550	2.45473	-1.97201
C	-6.43789	-2.20307	-0.47065
H	-6.37054	-2.13501	0.61617
H	-7.23502	-2.88618	-0.75974
H	-5.48815	-2.53501	-0.89382
H	-1.60378	4.25482	-0.79728
H	-8.79927	-1.16175	-1.62239
Cl	-5.91441	2.92382	-3.99582
Cl	-4.49416	0.17480	1.58220

Table 139. Computational data for 52^{Me} .

52^{Me}			
$E = -1753.376751453617$			
$E_{\text{ZPE}} = 0.23874442$			
$E_{\text{T}} = 0.01843942$			
$E_{\text{S}} = -0.06400639$			

C	-7.88905	-0.52573	-1.56205
C	-5.88067	0.25231	-1.00261
C	-6.61864	1.31388	-1.55218
C	-4.55222	2.86462	-1.31898
C	-3.81558	1.80116	-0.77099
C	-2.45887	3.55602	-0.94852
P	-6.22520	3.00676	-1.86540
N	-3.65708	3.93592	-1.41047
N	-2.51534	2.28869	-0.55694
N	-6.72303	-0.87200	-1.02998
N	-7.86472	0.77335	-1.88691
P	-4.29318	0.18792	-0.23236
C	-3.98467	5.26206	-1.93950
H	-3.09301	5.88610	-1.88713
H	-4.31378	5.16147	-2.97666
H	-4.78488	5.69895	-1.33745
C	-1.40109	1.52824	0.02027
H	-0.52296	2.17279	0.04323
H	-1.66622	1.21881	1.03357
H	-1.20780	0.65173	-0.60112
C	-8.96466	1.51728	-2.50512
H	-8.62623	1.92359	-3.46137
H	-9.79967	0.83496	-2.66099
H	-9.26294	2.33165	-1.84060
C	-6.37759	-2.20911	-0.53407
H	-6.15427	-2.14682	0.53317
H	-7.22992	-2.86697	-0.70071
H	-5.50596	-2.57768	-1.07834
H	-1.58097	4.18377	-0.90824
H	-8.72684	-1.18950	-1.71693
Cl	-4.85368	0.61637	1.97290

Table 140. Computational data for 53^{Me} .

53^{Me}			
$E = -1752.908286468929$			
$E_{\text{ZPE}} = 0.23996775$			
$E_{\text{T}} = 0.01809514$			
$E_{\text{S}} = -0.0633584$			
C	-7.96726	-0.46718	-1.48940
C	-5.91440	0.19269	-1.02011
C	-6.59300	1.25453	-1.65093
C	-4.49946	2.84808	-1.39074
C	-3.74878	1.82344	-0.78198
C	-2.50798	3.64583	-0.86387
P	-6.13753	2.90661	-1.99504
N	-3.66864	3.97397	-1.40741
N	-2.52102	2.34514	-0.48932
N	-6.78871	-0.85413	-0.94733
N	-7.88126	0.78021	-1.92060
P	-4.15688	0.07713	-0.67296
C	-4.01549	5.30879	-1.94590
H	-3.15329	5.95797	-1.80229
H	-4.24250	5.20552	-3.00815

H	-4.87616	5.69113	-1.39471
C	-1.37198	1.64508	0.12623
H	-0.49084	2.26823	-0.01699
H	-1.57243	1.49767	1.18780
H	-1.24384	0.68815	-0.38522
C	-8.96994	1.53802	-2.57698
H	-8.61886	1.86827	-3.55574
H	-9.82107	0.86781	-2.68439
H	-9.23043	2.38778	-1.94376
C	-6.54658	-2.19162	-0.36392
H	-6.53417	-2.10438	0.72315
H	-7.35514	-2.84460	-0.68772
H	-5.58914	-2.56294	-0.73647
H	-1.66497	4.31145	-0.73071
H	-8.84688	-1.09480	-1.55129
Cl	-4.02206	-0.38326	1.29426

Table 141. Computational data for 54^{Me} .

54^{Me}			
$E = -2213.775404717578$			
$E_{\text{ZPE}} = 0.24171947$			
$E_{\text{T}} = 0.01970383$			
$E_{\text{S}} = -0.06672019$			
C	-7.93138	-0.51514	-1.49990
C	-5.89213	0.17464	-1.01451
C	-6.57422	1.26053	-1.60679
C	-4.50607	2.81729	-1.37154
C	-3.73700	1.79432	-0.77435
C	-2.46653	3.59567	-0.88021
P	-6.14808	2.92409	-1.99451
N	-3.64943	3.92092	-1.40905
N	-2.47033	2.32735	-0.48656
N	-6.78043	-0.91211	-0.96974
N	-7.84817	0.75995	-1.88851
P	-4.26005	0.18461	-0.47765
C	-4.00923	5.23803	-1.95332
H	-3.15093	5.89943	-1.84325
H	-4.26761	5.12468	-3.00838
H	-4.86258	5.62882	-1.39487
C	-1.32771	1.64085	0.14050
H	-0.50446	2.35180	0.19378
H	-1.60813	1.31838	1.14412
H	-1.04110	0.78636	-0.47424
C	-8.92933	1.53221	-2.51621
H	-8.58925	1.88367	-3.49268
H	-9.79301	0.87850	-2.62990
H	-9.17645	2.37985	-1.87338
C	-6.53142	-2.25779	-0.42447
H	-6.32146	-2.17946	0.64315
H	-7.43086	-2.85043	-0.58522
H	-5.68922	-2.70933	-0.95070
H	-1.62441	4.26643	-0.78381
H	-8.80920	-1.13798	-1.59931

Cl	-4.05576	-0.38159	1.45377
Cl	-3.09945	-1.21415	-1.37997

Table 142. Computational data for **13**.**13**

$$E = -1765.186981251655$$

$$E_{\text{ZPE}} = 0.5738885$$

$$E_{\text{T}} = 0.03305231$$

$$E_{\text{S}} = -0.09441231$$

C	-6.60579	-6.77559	-0.55980
C	-7.00026	-5.49285	-1.01256
C	-4.61057	-4.58766	-0.53375
C	-4.21610	-5.87041	-0.08099
P	-6.13042	-3.98575	-1.14483
P	-5.08589	-7.37756	0.05109
N	-7.73290	-7.59251	-0.68496
N	-8.34269	-5.61064	-1.38385
N	-3.48352	-3.77068	-0.40836
N	-2.87374	-5.75255	0.29055
C	-9.16672	-4.50024	-1.91969
H	-9.15533	-3.71020	-1.16164
H	-8.65023	-4.13230	-2.81221
C	-7.77591	-9.02978	-0.32235
H	-7.48988	-9.09338	0.73272
H	-7.00587	-9.52651	-0.92155
C	-2.04977	-6.86291	0.82654
H	-2.56635	-7.23081	1.71903
H	-2.06106	-7.65300	0.06854
C	-3.44054	-2.33339	-0.77089
H	-4.21069	-1.83674	-0.17178
H	-3.72641	-2.26975	-1.82600
C	-2.47787	-4.49622	0.08247
C	-8.73860	-6.86694	-1.17565
H	-9.72902	-7.24236	-1.37575
H	-1.48751	-4.12075	0.28276
C	-2.07448	-1.70417	-0.53510
H	-1.79569	-1.80598	0.52142
H	-1.31659	-2.22462	-1.13428
C	-2.09319	-0.21712	-0.91497
H	-2.86092	0.29613	-0.32222
H	-2.38514	-0.11743	-1.96810
C	-0.73224	0.44747	-0.68852
H	-0.76502	1.50616	-0.96444
H	-0.43435	0.38031	0.36409
H	0.04466	-0.03631	-1.29148
C	-0.62422	-6.44228	1.15529
H	-0.12903	-6.06442	0.25187
H	-0.63619	-5.63251	1.89567
C	0.17080	-7.63152	1.71279
H	-0.33364	-8.01246	2.60974
H	0.16662	-8.44488	0.97613
C	1.61363	-7.24696	2.05237
H	2.16264	-8.10665	2.44932

H	2.14297	-6.88845	1.16217
H	1.63955	-6.45082	2.80514
C	-9.14204	-9.65894	-0.55789
H	-9.42099	-9.55717	-1.61437
H	-9.89981	-9.13842	0.04139
C	-9.12335	-11.14598	-0.17795
H	-8.35575	-11.65930	-0.77080
H	-8.83123	-11.24563	0.87514
C	-10.48437	-11.81050	-0.40415
H	-10.78243	-11.74337	-1.45671
H	-10.45161	-12.86918	-0.12818
H	-11.26115	-11.32664	0.19891
C	-10.59231	-4.92084	-2.24830
H	-10.58042	-5.73058	-2.98872
H	-11.08740	-5.29875	-1.34485
C	-11.38739	-3.73156	-2.80562
H	-11.38308	-2.91824	-2.06892
H	-10.88308	-3.35058	-3.70263
C	-12.83028	-4.11608	-3.14499
H	-13.37930	-3.25639	-3.54192
H	-12.85634	-4.91227	-3.89771
H	-13.35952	-4.47451	-2.25470

Table 143. Computational data for **54^{Me}**.**54^{Me}**

$$E = -1833.061234285305$$

$$E_{\text{ZPE}} = 0.42912529$$

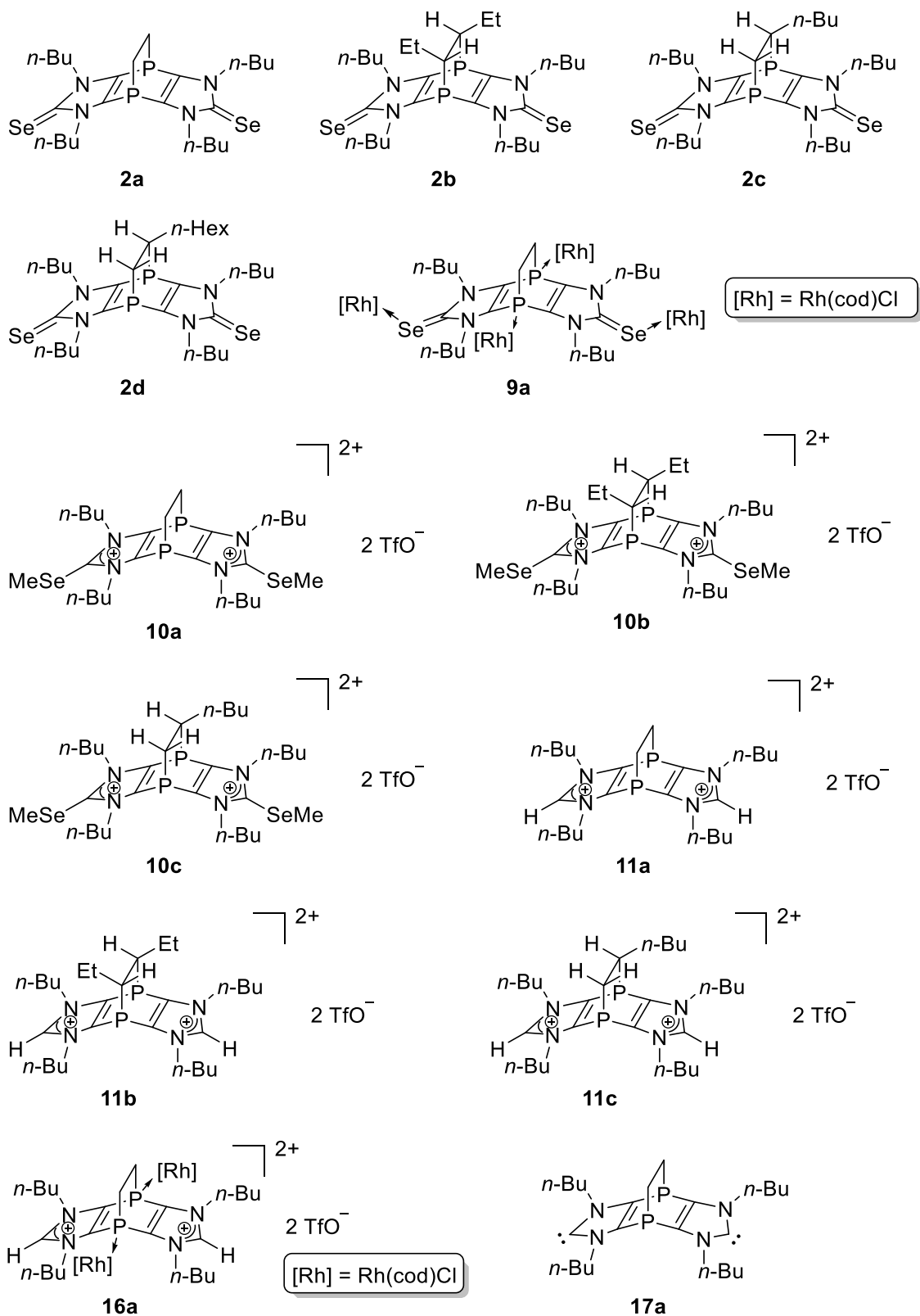
$$E_{\text{T}} = 0.02850905$$

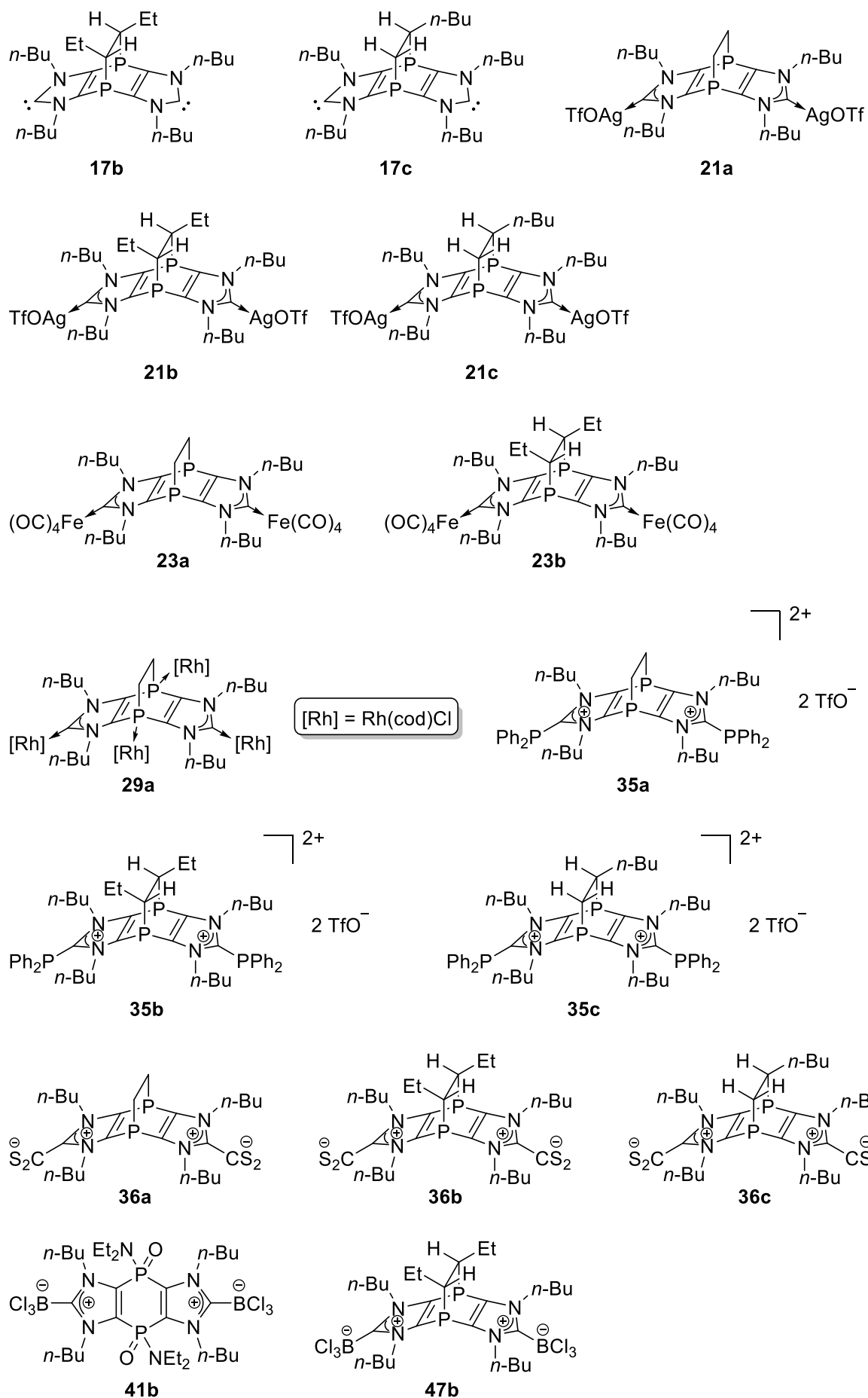
$$E_{\text{S}} = -0.08382878$$

C	-5.53803	-7.56184	0.66298
C	-6.18192	-6.81210	-0.28492
C	-3.99368	-5.35162	-0.58551
C	-3.35524	-6.08784	0.37643
P	-5.79597	-5.04696	-0.56735
P	-4.24905	-6.87504	1.76343
N	-6.13244	-8.80943	0.66913
N	-7.15921	-7.61132	-0.84624
N	-3.01950	-4.84536	-1.42477
N	-2.00080	-6.02105	0.11346
C	-8.10345	-7.22757	-1.90845
H	-8.72825	-8.09027	-2.13548
H	-8.71778	-6.39910	-1.55273
H	-7.53702	-6.92726	-2.79104
C	-5.77654	-9.94585	1.53442
H	-4.73698	-10.21915	1.34876
H	-5.91032	-9.65096	2.57630
H	-6.43548	-10.77796	1.29035
C	-0.92483	-6.65089	0.89617
H	-1.08312	-7.73012	0.90876
H	0.02571	-6.41365	0.42057
H	-0.94885	-6.25259	1.91151
C	-3.23756	-3.99074	-2.60322
H	-2.26712	-3.75972	-3.04008

H	-3.85714	-4.53068	-3.32053
H	-3.73673	-3.07405	-2.28576
C	-1.82486	-5.26607	-0.98245
C	-7.10683	-8.81409	-0.25291
C	-5.19856	-5.30474	2.19773
C	-5.89087	-4.61129	1.26506
C	-5.04650	-4.91349	3.61143
C	-5.13045	-5.87100	4.63515
C	-4.78075	-3.57528	3.95136
C	-4.99574	-5.49379	5.96952
H	-5.32286	-6.91179	4.38624
C	-4.62834	-3.20510	5.28324
H	-4.68726	-2.83373	3.16439
C	-4.74450	-4.16025	6.29767
H	-5.08114	-6.24197	6.75221
H	-4.41378	-2.16976	5.53227
H	-4.62838	-3.86772	7.33717
C	-6.82532	-3.50512	1.54368
C	-7.72747	-3.59212	2.61873
C	-6.85694	-2.36719	0.72135
C	-8.61913	-2.55593	2.87416
H	-7.72971	-4.47950	3.24359
C	-7.73921	-1.32310	0.99049
H	-6.17465	-2.29099	-0.12187
C	-8.62279	-1.41398	2.06745
H	-9.31762	-2.64005	3.70182
H	-7.74037	-0.44161	0.35598
H	-9.31842	-0.60524	2.27149
H	-7.74485	-9.65354	-0.48588
H	-0.87249	-5.03616	-1.43645

7.6 Overview of isolated novel compounds in this work





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