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## Nitrogen- and oxygen-bridged bidentate phosphalkene ligands

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## ABSTRACT

An overview is given on synthesis and structures of new bidentate phosphalkene ligands [(RMe<sub>2</sub>Si)<sub>2</sub>C=P]<sub>2</sub>E (E = O, NR, N<sup>-</sup>) and (RMe<sub>2</sub>Si)<sub>2</sub>C=P–N(R')–PR''<sub>2</sub>. Exceptional properties of these ligands, extending beyond predictable properties of phosphalkenes are: (i) the N–Si bond cleavage of [(iPrMe<sub>2</sub>Si)<sub>2</sub>C=P]<sub>2</sub>NSiMe<sub>3</sub> with Au<sup>I</sup> and Rh<sup>I</sup> chloro complexes under mild conditions leading to binuclear complexes of the 6π-delocalised imidobisphosphalkene anion [(iPrMe<sub>2</sub>Si)<sub>2</sub>C=P]<sub>2</sub>N<sup>-</sup>, and (ii) the chlorotropic formation of molecular 1:2 Pd<sup>II</sup> and Pt<sup>II</sup> *metallochloroylid* complexes with novel ylid-type ligands [(RMe<sub>2</sub>Si)<sub>2</sub>C=P(Cl)–N(R)–PR<sub>2</sub>]<sup>-</sup>, and the transformation of a *P*-platina-*P*-chloroylid complex into a *C*-platina phosphalkene by intramolecular chlorosilane elimination. Properties of the heavier congeners [(RMe<sub>2</sub>Si)<sub>2</sub>C=P]<sub>2</sub>E (E = S, Se, Te, PR, P<sup>-</sup>, As<sup>-</sup>) and (RMe<sub>2</sub>Si)<sub>2</sub>C=P–E–PR''<sub>2</sub> (E = S, Se, Te) are also described.

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## 1. Introduction

The strong π-accepting capacity of phosphalkene ligands has made them an innovative tool in coordination chemistry and catalysis [1,2]. Most relevant applications in catalysis have involved the use of bidentate phosphalkene ligands such as Yoshifuji's 1,2,-diaryl-3,4-diphosphinidene cyclobutene ligands DPCB-Y (**A**, Scheme 1) [3] and Brookhart's phosphalkene-sulfide and phosphalkene-imine ligands (**B**) [4,5]. The exceptional efficiency of the DPCB-Y system is explained by inherent enhanced π-acceptor properties of the P=C bond, [6] which is reinforced through π-conjugation with remote aromatic substituents [1–3].

In type **A** and **B** ligands, π-conjugation is made possible by sp<sup>2</sup> hybridised organic scaffolds. Alternatively, single heteroatoms with p-type lone pairs could play the role of a

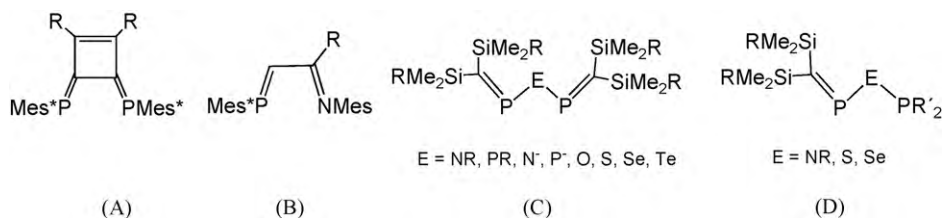
connector between the two P=C systems, creating heteropentadienide-like 5c-6π electron systems in a new class of small bite angle ligands, which are the “P=C-unsaturated” relatives (**C**) of classic imino- and imidobisphosphanes, related phosphinous anhydrides, and their heavier congeners with bridging elements from the third and fourth period (R<sub>2</sub>P)<sub>2</sub>E (E = NR, N<sup>-</sup>, PR, O, S, Se, etc.).

An alternative case would be the insertion of the potentially π-interacting heteroatom between a phosphalkene moiety and another coordinating phosphorus atom leading to “hybrid” ligands (**D**).

Examples of type **C** and **D** ligands (R<sub>2</sub>C=P)<sub>2</sub>E and R<sub>2</sub>C=P–E–PR''<sub>2</sub> are extremely rare in the literature. In the group of R. Appel the triphosphane-related compound [(Me<sub>3</sub>Si)<sub>2</sub>C=P]<sub>2</sub>PtBu [7] was characterised and used as a chelate ligand toward M(CO)<sub>4</sub> acceptors (M = Cr, Mo, W), and E. Niecke et al. reported the lithium salt Li(THF)<sub>x</sub> {[(Me<sub>3</sub>Si)<sub>2</sub>C=P]<sub>2</sub>P} [8] containing a 2,3,4-triphosphapentadienide anion, which represents the first case of a π-donor heteroatom-bridged bis-phosphalkene anion allowing electronic communication between the π-systems (P=C

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Scheme 1. Types of bidentate phosphalkene ligands allowing  $\pi$ -conjugation.

bonds) of two neighbouring phosphalkene moieties. Thermal and protolytic decomposition reactions of the anion were studied and anionic complexes with  $M(\text{CO})_4$  acceptors were compared with R. Appel's uncharged compounds [7–9]. In a study on the reactivity of *P*-phosphanylphosphalkenes  $(\text{Me}_3\text{Si})_2\text{C}=\text{P}-\text{PR}_2$  towards chalcogens, type **D** molecules  $(\text{Me}_3\text{Si})_2\text{C}=\text{PEPR}_2$  ( $\text{E} = \text{S}, \text{Se}$ ;  $\text{R} = i\text{Pr}, t\text{Bu}$ ) were recognized to be products of the monoinsertion of sulfur and selenium into the P–P bonds [10]. With help of a tiny  $^{31}\text{P}$ -NMR singlet signal exhibiting  $^{77}\text{Se}$  satellites in solutions containing the crude selenium compound  $(\text{Me}_3\text{Si})_2\text{C}=\text{PSePiPr}_2$ , the selenium-bridged bisphosphalkene  $[(\text{Me}_3\text{Si})_2\text{C}=\text{P}]_2\text{Se}$  was fortuitously recognized [10,11]. Subsequently this compound and the related sulfide  $[(\text{Me}_3\text{Si})_2\text{C}=\text{P}]_2\text{S}$  were synthesised and cycloaddition, chalcogen addition, and coordination reactions were studied [11]. In the context of possible application in catalysis, however, the *O*- and *N*-bridged “P=C-unsaturated” compounds (type **C**) related to classic “saturated PNP” ligands  $(\text{Ph}_2\text{P})_2\text{NR}$  appear to be particularly attractive goals. This expectation gave the incentive to focus on novel type **C** *N*- and *O*-bridged bisphosphalkenes [12,13] and on type **D** phosphanylaminophosphalkenes  $(\text{Me}_3\text{Si})_2\text{C}=\text{PN}(\text{R})\text{PR}'_2$  [14].

In this overview, recent results on type **C** structures  $[(\text{RMe}_2\text{Si})_2\text{C}=\text{P}]_2\text{E}$  ( $\text{E} = \text{O}, \text{NR}, \text{N}^-$ ) will be presented in Section 2 and properties of type **D** ligands  $(\text{RMe}_2\text{Si})_2\text{C}=\text{P}-\text{N}(\text{R})-\text{PR}_2$  and related compounds will be discussed subsequently (Section 3). A discussion of the heavier *P*-, *As*-, *S*-, *Se*-, and *Te*-bridged analogs is added to each section.

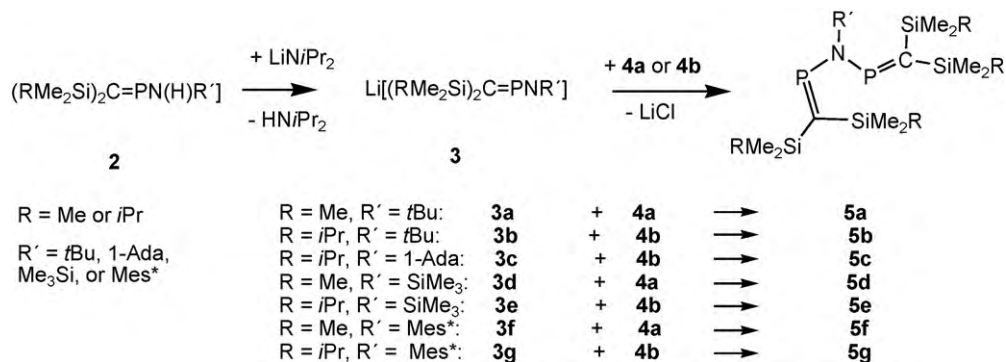
## 2. Heteroatom-bridged bisphosphalkenes $[(\text{RMe}_2\text{Si})_2\text{C}=\text{P}]_2\text{E}$ (type **C** structures)

### 2.1. Imino- and imido-bridged bisphosphalkenes, $\text{E} = \text{NR}$

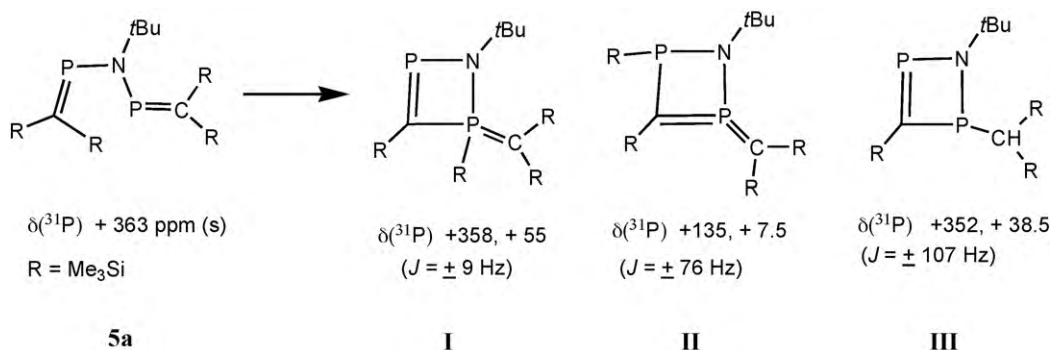
#### 2.1.1. *N*-alkylimino-bridged bisphosphalkenes $[\text{Ph}(\text{Me}_3\text{Si})\text{C}=\text{P}]_2\text{N}(\text{nC}_3\text{H}_7)$

(1), the first *N*-alkyl-2,4-diphospha-3-azapentadiene reported in the literature, is thermally unstable [15]. For related compounds  $[(\text{Me}_3\text{Si})_2\text{C}=\text{P}]_2\text{NR}$  it was necessary to turn to alkali metal chloride elimination procedures based on the deprotonation of aminophosphalkenes **2** such as  $(\text{Me}_3\text{Si})_2\text{C}=\text{PN}(\text{H})t\text{Bu}$ , [6] followed by coupling of the in situ-prepared anion  $[(\text{Me}_3\text{Si})_2\text{C}=\text{PN}t\text{Bu}]^-$  **3a** [16,17] with *P*-chlorophosphalkene  $(\text{Me}_3\text{Si})_2\text{C}=\text{P}\text{Cl}$  (**4a**; Scheme 2). Since it turned out that the outcome of these reactions, i.e. the insufficient stability of the products, precluded the isolation of single-crystalline solids, precursors with bulkier silyl groups at carbon were developed. These reactions are based on the new starting material  $(i\text{PrMe}_2\text{Si})_2\text{C}=\text{P}\text{Cl}$  **4b** [18,19]. To improve crystallisation properties of thermolabile *N*-alkyl products, *N*-1-adamantyl derivatives were also used [13].

Metalated aminophosphalkenes  $\text{Li}[(\text{RMe}_2\text{Si})_2\text{C}=\text{PN}t\text{Bu}]$  (**3a**:  $\text{R} = \text{Me}$ ; **3b**:  $\text{R} = i\text{Pr}$ ) react with the corresponding *P*-chlorophosphalkenes at low temperatures, furnishing solutions of the desired *tbuty*limino-bridged bisphosphalkenes **5a**, **5b** (Scheme 2), which exhibit singlet signals in  $^{31}\text{P}$ -NMR [13]. Raising the temperature to  $0^\circ\text{C}$  and above leads to formation of products from rearrangement reactions indicated by the occurrence of one or more



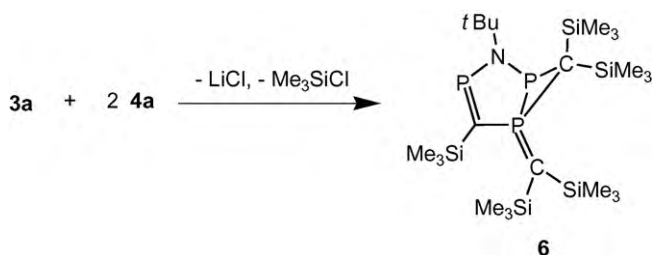
Scheme 2. Formation of alkyl-, silyl- and arylimino-bridged bisphosphalkenes.

Scheme 3. Proposed structures of products from decomposition of **5a**.

“growing”  $^{31}\text{P}$ -NMR signals that appear as AX-type patterns.

In the case of  $[(\text{Me}_3\text{Si})_2\text{C}=\text{P}]\text{NtBu}$  **5a**, one of the new AX patterns ( $\delta^{31}\text{P} = 358.4$  and  $55.1$ ,  $J = 9 \text{ Hz}$ ; species **I** in Scheme 3) indicates the presence of a phosphalkene-type  $^{31}\text{P}$  nucleus coupling with a tri- or tetra-coordinated phosphorus atom. The second AX pattern ( $\delta^{31}\text{P} = 135$  and  $7.7$ ,  $J = 76 \text{ Hz}$ ; species **II**) involves two nuclei that are both *not* parts of phosphalkene functions, and a third AX pattern ( $\delta^{31}\text{P} = 351.9$  and  $38.5$ ,  $J = 107 \text{ Hz}$ ; species **III**) has to be assigned to another  $^{31}\text{P}(\text{C})$  nucleus coupling with another tri- or tetra-coordinated phosphorus atom that is part of a  $^{31}\text{P}\text{-C-H}$  function ( $^2J_{\text{PH}} = 13 \text{ Hz}$ ) [13].

Addition of **4a** to a reaction mixture containing decomposing **5a** leads to consumption of **5a** and of rearranged species **I** with formation of a new compound **6** exhibiting an AMX pattern in  $^{31}\text{P}$ -NMR ( $\delta^{31}\text{P} = 330.8$ ,  $-17.1$  and  $-24.3$ ), involving one  $^{31}\text{P}(\text{C})$  phosphorus atom coupling with two inequivalent “*non-P=C*”  $^{31}\text{P}$  nuclei in a diphosphirane unit. Compound **6** is also formed from the straightforward 1:2 reaction of **3a** with **4a**. Single crystals of **6** were isolated from the latter reaction Eq. (1).



An X-ray crystal structure determination revealed that **6** is a bicyclic  $\text{C}_2\text{N}_2\text{P}_3$  species containing an endocyclic  $\text{P}=\text{C}$  bond [ $1.679(3) \text{ \AA}$ ] “in conjugation” with an exocyclic ylidic  $\text{P}^{(+)}\text{-C}^{(-)}(\text{SiMe}_3)_2$  function [ $1.688(3) \text{ \AA}$ ] involving one of the two bridgehead phosphorus atoms that form a diphosphirane unit [13]. We assume that the motif of a  $(\text{p-p})\pi$   $\text{P}=\text{C}$  double bond “in conjugation” with an exocyclic ylidic  $\text{P}^{(+)}\text{-C}^{(-)}$  bond from compound **6** is also present in species **I** (Scheme 3), which is a precursor to **6**.

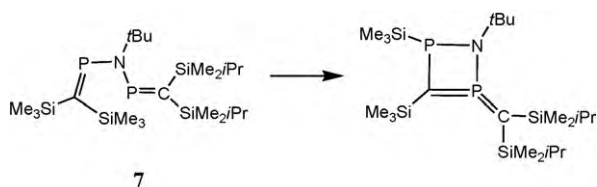
**6** is derived from **4a** by the reaction with **5a**, or by the reaction with species **I** (Scheme 3) by elimination of one equivalent of  $\text{Me}_3\text{SiCl}$ . Formation of rearranged

products **I–II** from **5a** involves trimethylsilyl group migration, and **III** is apparently a product from protolytic  $\text{P-Si}$  bond cleavage, followed by proton migration to the basic ylid carbon atom.

When in a “cross” experiment anion **3a** reacted in an NMR tube with the bulkier chlorophosphane **4b**, or anion **3b** reacted with **4a**, the mixed-substituted bisphosphaalkene  $(\text{Me}_3\text{Si})_2\text{C}=\text{P}(\text{NtBu})\text{-P}=\text{C}(\text{SiMe}_2\text{iPr})_2$  **7** (AB pattern,  $\delta^{31}\text{P} = 365.3$  and  $361.8 \text{ ppm}$ ,  $^2J_{\text{PP}} = \pm 18 \text{ Hz}$ ) was accompanied by only *one* rearranged species (AX pattern,  $\delta^{31}\text{P} = 136.7$  and  $7.3 \text{ ppm}$ ,  $J = 78 \text{ Hz}$ ) that relates to the proposed species **II** from the “symmetric” experiment. This result indicates that the silyl group migration pathway leading to the exocyclic ylid function is closed when two bulkier  $\text{iPrMe}_2\text{Si}$  groups are introduced at the carbon atom of one of the participating  $\text{P}=\text{C}$  bonds (Schemes 3 and 4) [13].

In the case of *tert*-butylimino-bisphosphaalkene **5b** (with only  $\text{iPrMe}_2\text{Si}$  groups at carbon) decomposition is significantly slower than in the case of **5a**, but isolation of pure **5b** was still precluded by decomposition. Low-temperature single crystal growing was enabled by switching to the corresponding *N*-1-adamantyliminophosphaalkene anion

**3c**, thus furnishing *N*-1-adamantyliminobis-phosphaalkene **5c**, which was X-rayed as solid tetrahydrofuran solvate at low temperature. In solution, **5c** exhibits a  $^{31}\text{P}$ -NMR singlet resonance signal, but in the solid, the two  $\text{P}=\text{C}$  moieties of each independent molecule are inequivalent. Different adamantyl group orientations relative to the common “helically distorted” CPNPC skeleton in solid **5c** of the three independent molecules coincide with different contacts to the solvating THF molecules (Fig. 1). The conformations of the non-planar  $\text{C-P-N(R)-P}'\text{C}'$  backbones (in molecule #1: torsion angles  $\text{C11-P1-N-P2}$  and  $\text{C22-P2-N-P1}$ ) of the three independent molecules are similar

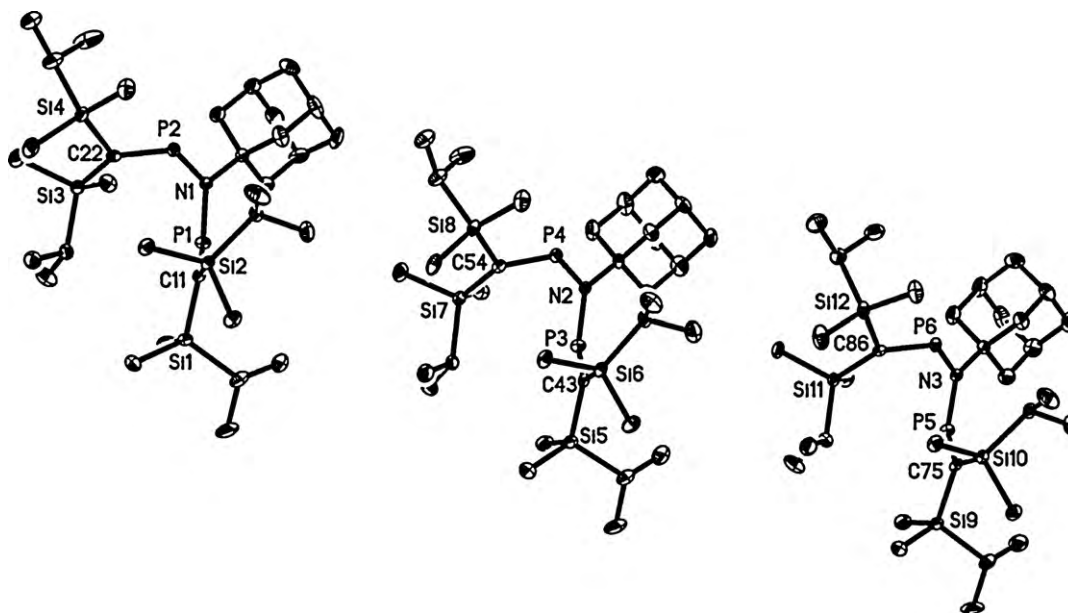


**Scheme 4.** Proposed structure of a major product from the cyclisation of the unsymmetric bisphosphaalkene  $(\text{Me}_3\text{Si})_2\text{C}=\text{P}(\text{N}t\text{Bu})-\text{P}=\text{C}(\text{SiMe}_2i\text{Pr})_2$  (**7**).

[molecule #1:  $-40.9(2)$  and  $-55.6(2)^\circ$ , molecule #2:  $-41.1(2)$  and  $-54.2(2)^\circ$ , molecule #3:  $-48.4(2)$  and  $-48.5(2)^\circ$ ], the  $\text{P}=\text{C}$  moieties being directed out of the  $\text{NP}_2$  planes about half-way between orthogonal [20] and planar. Within the non-planar  $\text{CPNPC}$  moieties,  $\text{P}=\text{C}$  ( $1.664\text{--}1.670 \text{ \AA}$ ) and  $\text{P}-\text{N}$  bonds ( $1.712\text{--}1.737 \text{ \AA}$ ) appear essentially undisturbed by conjugative effects. In this respect, **5c** is comparable to the 2-[6-bis(trimethylsilyl)amino]pyridylimino-bridged bisphosphaalkene (Scheme 5, see also Section 2.1.3) [20].

### 2.1.2. *N*-silyl-bridged bisphosphaalkenes

$[(\text{Me}_3\text{Si})_2\text{C}=\text{P}]_2\text{NSiMe}_3$  (**5d**), made from  $\text{Li}[(\text{Me}_3\text{Si})_2\text{C}=\text{PNSiMe}_3]$  (**3d**) with **4a**, is a thermally unstable oil, [9b,17,21] but bulkier ( $i\text{PrMe}_2\text{Si}$ ) $_2\text{C}=\text{P}$  groups [19] stabilise type **C** compounds. The reactions of the bulkier aminophosphaalkene **2e** with lithiumdiisopropylamide (LDA) in THF solution (Scheme 2), followed by reactions of the lithium salt **3e** with *P*-chlorophosphaalkenes  $(\text{RMe}_2\text{Si})_2\text{C}=\text{P}\text{Cl}$  ( $\text{R} = i\text{Pr}$ : **4a**;  $\text{Me}$ : **4b**;  $\text{Ph}$ : **4c**) at temperatures below  $-40^\circ\text{C}$  furnish solutions of *N*-trimethylsilylimino-bridged bisphosphaalkenes **5e** and the unsymmetric compounds **8a**, **8b** (Scheme 6).

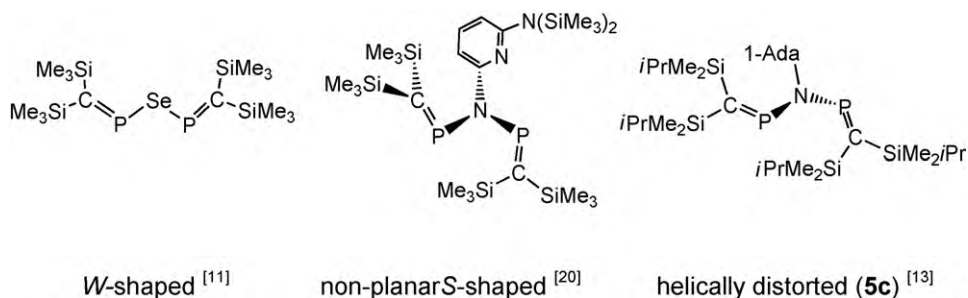


**Fig. 1.** Arrangement of the three independent molecules of THF-solvated **5c**. Selected bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] of molecule #1:  $\text{P1}-\text{C11}$   $1.6670(3)$ ,  $\text{P2}-\text{C22}$   $1.6606(3)$ ,  $\text{P1}-\text{N1}$   $1.712(2)$ ,  $\text{P2}-\text{N1}$   $1.737(2)$ ,  $\text{C23}-\text{N1}$   $1.524(13)$ ,  $\text{P1}-\text{N1}-\text{P2}$   $126.77(13)$ ,  $\text{P1}-\text{N1}-\text{C23}$   $119.36(18)$ ,  $\text{P2}-\text{N1}-\text{C23}$   $113.72(17)$ ,  $\text{C11}-\text{P1}-\text{N1}$   $-40.9(2)$ ,  $\text{C22}-\text{P2}-\text{N1}$   $55.6(2)$ . Hydrogen atoms are omitted for clarity. Atoms are drawn as 50% thermal ellipsoids.

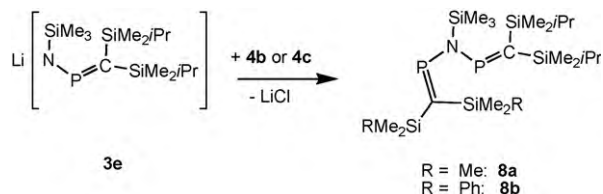
The  $^{31}\text{P}$  NMR spectrum of **5e** exhibits a single resonance whereas the mixed substituted compounds **8a**, **8b** show AM patterns [**8a**:  $\delta^{31}\text{P} = 365.4$  and  $361.7$  ppm,  $^2J_{\text{PP}} = 19.6$  Hz; **8b**:  $\delta^{31}\text{P} = 370.6$  and  $365.6$  ppm,  $^2J_{\text{PP}} = 19.7$  Hz]. The NMR equivalence of the two  $^{31}\text{P}$  nuclei of **5e** in solution would be consistent with either a symmetric structure or with a less symmetric ground state conformation (Scheme 5), which still allows free rotation of the  $\text{P}-\text{N}$  bonds on the NMR time scale at room temperature in solution [19]. All the B3LYP/6-31+ $G^*$  optimized structures of the  $[(\text{R}_3\text{Si})_2\text{C}=\text{P}]_2\text{N}(\text{SiR}_3)$  molecules ( $\text{R} = \text{H}, \text{Me}$ ) were non-planar. For  $\text{R} = \text{H}$  the minima were located within an  $0.9 \text{ kcal mol}^{-1}$  energy range, including the *S*- and *W*-shaped forms (Scheme 5). The fact that several conformers exist with similar energies on the rotational potential energy surface is an indicative of their low energy interconversion. For  $\text{R} = \text{Me}$  only the non-symmetrical *S*-shaped structure could be optimized, in agreement with the X-ray structure (see below). Similar behaviour was observed in case of the di(phosphavinyl)ether analogues, [12] indicating the effect of steric encumbrance in determining the final structure. The X-ray crystal structure determinations of solid **5e** and **8a** at low temperature reveal (as for **5c**, see above) the presence of helically distorted structures with two inequivalent  $\text{P}=\text{C}$  groups (**5e**: torsion angles  $\text{C11}-\text{P1}-\text{N}-\text{P2}$  and  $\text{C22}-\text{P2}-\text{N}-\text{P1}$   $-52^\circ$  and  $-45^\circ$ ), but within the solid unsymmetric compound **8a** all  $(i\text{PrMe}_2\text{Si})_2\text{C}=\text{P}$  groups and all  $(\text{Me}_3\text{Si})_2\text{C}=\text{P}$  groups are equivalent. The  $\text{P}=\text{C}$  and  $\text{P}-\text{N}$  bonds distances in **5e** and **8a** do not indicate significant conjugation within the  $\text{C}=\text{P}-\text{N}-\text{P}=\text{C}$  moieties [13,19,20].

### 2.1.3. *N*-aryl-bridged bisphosphaalkenes

A  $^{31}\text{P}$ -NMR-study on *N*- $\text{Me}_3^+$ -bridged bisphosphaalkenes reveals that the reaction mixtures from metalation of



Scheme 5. Conformations of uncharged heteroatom-bridged bisphosphaalkenes.



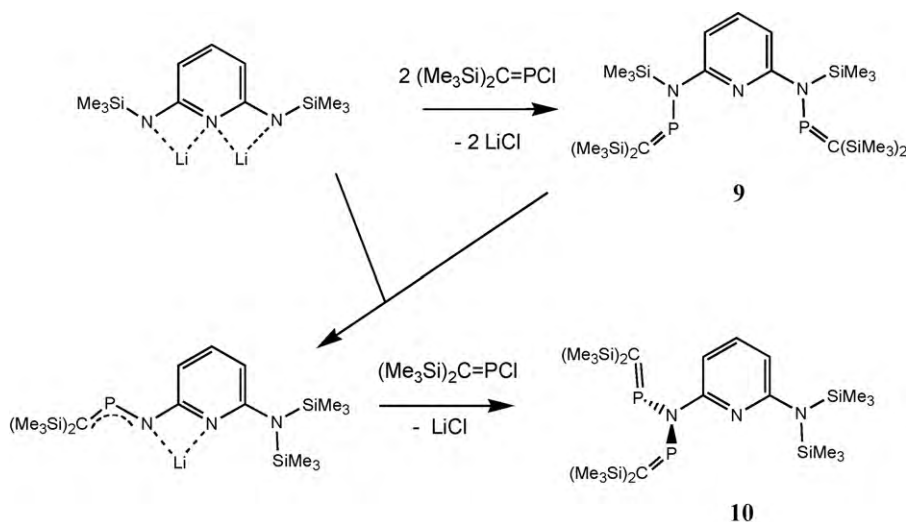
Scheme 6. Formation of mixed substituted silyliminobis (phosphaalkenes).

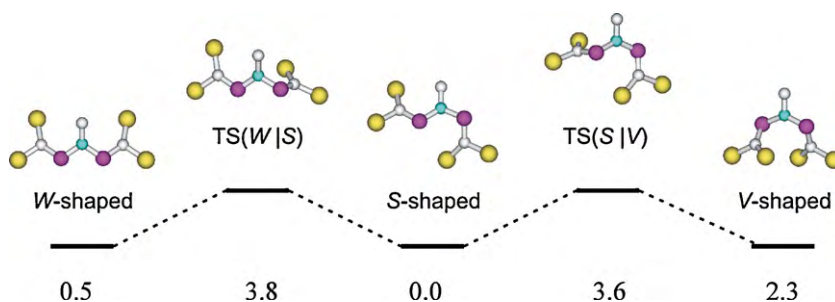
( $\text{RMe}_2\text{Si}$ )<sub>2</sub>C=PN(H)Mes\* (R = Me or R = *i*Pr) with LDA, followed by reactions of the lithium salts with chlorophosphaalkenes (**3f** with **4a** and **3g** with **4b**), each exhibit in <sup>31</sup>P-NMR a singlet signal accompanied by an AM-pattern of [( $\text{Me}_3\text{Si}$ )<sub>2</sub>C=P]<sub>2</sub>NMes\*, **5f**:  $\delta = 352$  (s), 329 (d) and 323 (d) ppm, <sup>2</sup>*J*<sub>PP</sub> = 7.4 Hz and of [(*i*PrMe<sub>2</sub>Si)<sub>2</sub>C=P]<sub>2</sub>NMes\*, **5g**:  $\delta = 352$  (s), 332 (d) and 326 (d), <sup>2</sup>*J*<sub>PP</sub> = 13.5 Hz [13] together with another small singlet assignable to [( $\text{Me}_3\text{Si}$ )<sub>2</sub>C=P]<sub>2</sub>O (353 ppm) and [(*i*PrMe<sub>2</sub>Si)<sub>2</sub>C=P]<sub>2</sub>O (354 ppm) [12]. Apparently the bulky NMes\* groups enhance the rotational barrier(s) of rotameric interconversion of symmetric **5f-sym** or **5g-sym** and unsymmetric  $S$ -shaped **5f-asym** or **5g-asym**. Initially, the <sup>31</sup>P-NMR peak height of symmetric **5g-sym** is larger than the added intensities of the AM-pattern

from **5g-asym** (ratio about 5:2), but after a slight relative increase of the amount of asymmetric species within 2 days, an approximately 5:3 ratio of the two species in solution stays constant for an extended period.

In the context of syntheses of pyridine-bridged bidentate phosphoalkene and iminophosphane ligands such as compound **9**, the *N*-pyridylimido-bridged bisphosphaalkene **10** (an isomer of **9**) was detected and structurally characterised [20]. Compound **10** adopts a non-planar  $S$ -shaped structure of the heteropentadiene moiety (Schemes 5 and 7). In contrast to **5c**, **5e** and **8a**, P=C functions of pyridylimino derivative **10** are directed approximately orthogonal to the CNP<sub>2</sub> plane. According to its AM-pattern ( $\delta^{31}\text{P} = 340.4$  and 328.9 ppm) in solution <sup>31</sup>P-NMR at  $-60^\circ\text{C}$ , **10** also adopts an unsymmetric structure in solution. Equilibration of the two phosphorus nuclei on the <sup>31</sup>P-NMR timescale takes place at room temperature ( $\delta^{31}\text{P} = 336.1$  ppm) [20].

The reaction of **10** with nickel tetracarbonyl leads to a product that shows: (i) two <sup>31</sup>P-NMR resonances at 96.1 and 66.9 ppm (*J*<sub>PP</sub> = ± 8.9 Hz), i.e. far upfield from ligand **10**; (ii) two <sup>13</sup>C resonances of the coordinated PC functions (75.7 ppm [*J*<sub>PC</sub> = ± 108.3 Hz] and 45.6 ppm [*J*<sub>PC</sub> = ± 103.4 Hz]); and (iii) four <sup>13</sup>C-NMR signals in the “CO” range (192.2, 192.3, 202.0, 202.9 ppm) suggesting η<sup>2</sup>-coordination of both PC functions, one of them with an Ni(CO)<sub>2</sub> acceptor (that will

Scheme 7. Formation of the *N*-pyridylimido-bridged bis(phosphaalkene) **10**.



Scheme 8.  $[(\text{H}_3\text{Si})_2\text{C}=\text{P}]_2\text{NCH}_3$  rotamers and their connecting transition structures; relative energies (in  $\text{kcal mol}^{-1}$ ) at the B3LYP/6-31+G\* level [13].

also be in contact with the pyridine N atom) and the other one with an  $\text{Ni}(\text{CO})_3$  acceptor [20].

#### 2.1.4. DFT calculations on 2,4-diphospha-3-azapentadienes (iminobisphosphaalkenes)

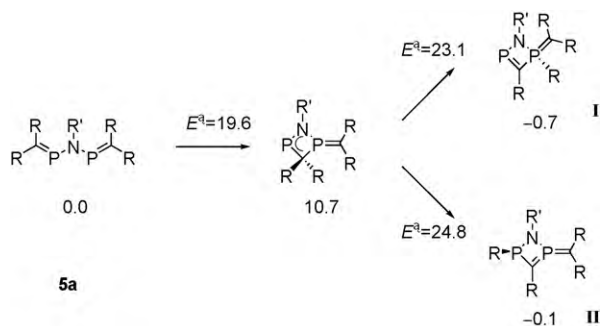
At the B3LYP/6-31+G\* level have been found three minima of very similar energy on the potential energy surface of the parent  $[(\text{H}_3\text{Si})_2\text{C}=\text{P}]_2\text{NCH}_3$  system. They are representing S-shaped, W-shaped, and V-shaped  $\text{C}=\text{P}-\text{N}-\text{P}=\text{C}$  moieties (Scheme 8). The particular non-planar distortion of compound **8** will have steric grounds [13].

Concerning silyl group migration (Schemes 3 and 4), the reaction was calculated (Scheme 9; energies in  $\text{kcal mol}^{-1}$ ) for **5a** [13].

### 2.2. Imido-bridged bisphosphaalkenes

#### 2.2.1. Formation of imido-bridged bisphosphaalkene complexes

2,4-Diphospha-3-azapentadienyl anions were unknown until recently, when reactions of the *N*-silylimino-bridged bisphosphaalkene **5e** became synthetically accessible. Experiments on the reactivity of **5e** with  $\text{AuCl}(\text{THT})$  and with  $[\text{RhCl}(\text{COD})]_2$  allowed the observation of Si–N bond cleavage under very mild conditions by chlorotrimethylsilane elimination furnishing the dinuclear complexes  $\{\text{Au}[(i\text{PrMe}_2\text{Si})_2\text{C}=\text{P}]_2\text{N}\}_2$  (**11**) and  $\text{Rh}_2\text{Cl}\{[(i\text{PrMe}_2\text{Si})_2\text{C}=\text{P}]_2\text{N}\}(\text{COD})_2$  (**12**), which, according to X-ray crystal structure determinations, contain 2,4-diphospha-3-azapentadienyl anions as *P,P*-coordinated bidentate ligands (Scheme 10) [19].



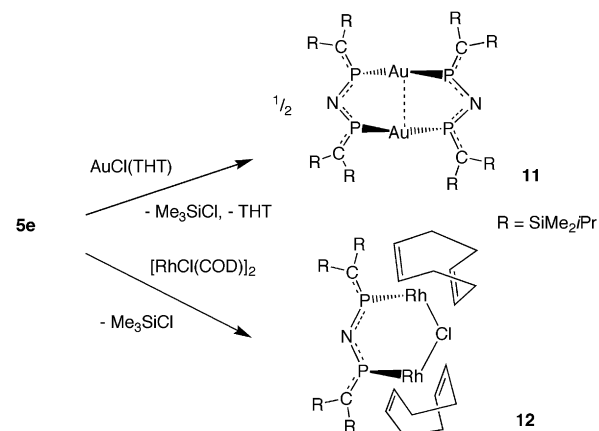
Scheme 9. Cyclisation pathway of alkyliminobisphosphaalkenes at the MPW1K/6-311+G\*\*/B3LYP/6-31+G\* level of theory ( $\text{R} = \text{SiMe}_3$ ,  $\text{R}' = t\text{Bu}$ ) [13].

Yellow **11** [ $d(\text{Au}-\text{Au})$  3.02 Å] is related to the insoluble white bis(diphenylphosphanyl)amide gold complex  $[\text{Au}(\text{Ph}_2\text{P})_2\text{N}]_2$  made first by Schmidbaur et al. and Laguna et al. [22,23] and also regarded as a dimer.

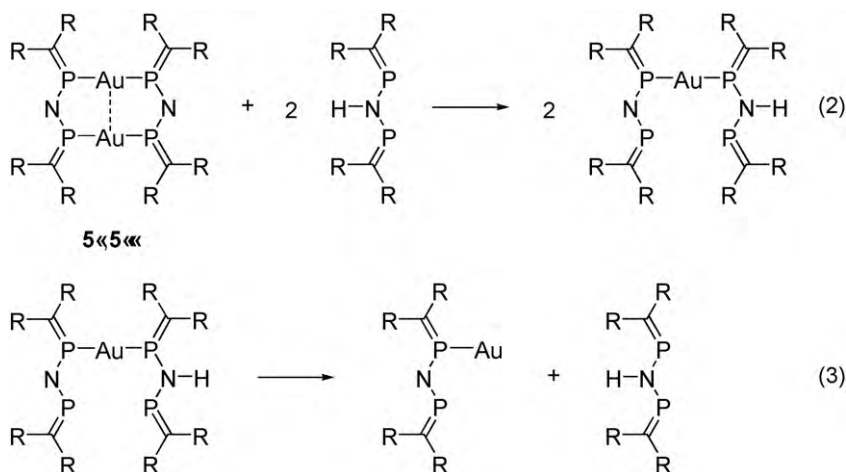
The dinuclear Rh(I) complex **12** contains as bridging ligands one chloride anion and one sterically crowded  $[(i\text{PrMe}_2\text{Si})_2\text{C}=\text{P}]_2\text{N}^-$  anion, which clearly prevents reactions of **12** with another equivalent of ligand **5e**. Each of the COD ligands chelates an Rh atom as in the starting material  $[\text{RhCl}(\text{COD})]_2$  [24]. The PN distances in **11** and **12** are about 10 pm shorter than those in the uncharged ligand **5e**. Since the P=C distances are unaffected or even slightly shorter in the complexes, compared with **5e**, [19] the large increase of PN bond strength suggests the presence of a highly delocalized heteropentadienide  $6\pi$  system.

#### 2.2.2. DFT calculations on imido-bridged bisphosphaalkenes

DFT calculations on 2,4-diphospha-3-azapentadienes (type C structures,  $\text{E} = \text{N}$ ) [19,25] reveal that, while the  $(\text{C}=\text{P})_2\text{NSi}$  moieties in compounds  $[(\text{R}_3\text{Si})_2\text{C}=\text{P}]_2\text{N}(\text{SiR}_3)$  are non-planar even with the small  $\text{R} = \text{H}$  substituent, the  $(\text{C}=\text{P})_2\text{NSi}$  moiety in the corresponding imide anion  $[(\text{R}_3\text{Si})_2\text{C}=\text{P}]_2\text{N}^-$  is planar in the case of  $\text{R} = \text{H}$ . This planarity, together with the short PN distances, indicates that the stabilization of the anion by delocalisation exceeds that of the amine. Indeed, the second order perturbational analysis of the Fock matrix in the NBO basis provides



Scheme 10. Reactions of **5e** with  $\text{Au}^{\text{I}}$  and  $\text{Rh}^{\text{I}}$  chloro complexes leading by N–Si cleavage to metal complexes of an imidobis(phosphaalkene) anion.



Scheme 11. Isodesmic reactions (see text).

37.0 kcal mol<sup>-1</sup> stabilization energy between the nitrogen lone pair and each  $\pi(\text{P}=\text{C})^*$  orbital, exceeding the stabilization energy for [(H<sub>3</sub>Si)<sub>2</sub>C=P]<sub>2</sub>NH (19.7 kcal mol<sup>-1</sup>) significantly. [(Me<sub>3</sub>Si)<sub>2</sub>C=P]<sub>2</sub>N<sup>-</sup> has an S-shaped and an energetically nearly identical, slightly non-planar W-shaped [still with 33.0 kcal mol<sup>-1</sup>  $n \geq \pi(\text{P}=\text{C})^*$  interaction energy] structure.

The energetic consequences of the aurophilic interaction were estimated using the isodesmic reactions (2) and (3) in Scheme 11. The energy of the reaction (2) is remarkably large (27–30 kcal mol<sup>-1</sup> at different levels of theory), comparable with the Au–P binding energy (30–34 kcal mol<sup>-1</sup>) [19], which was determined as the reaction energy of reaction (3). It is important to note that this unusually large interaction energy [26] is only partly attributable to the aurophilicity because the extended  $\pi$ -conjugation in the dimeric complex (see the MO representing  $\pi$ -delocalisation in Fig. 2) also contributes to the overall stabilization of this reaction.

### 2.3. Oxygen-bridged bisphosphaalkenes

#### 2.3.1. Synthetic aspects

The P–O–P unit is undoubtedly the most common structural motif in phosphorus chemistry. In naturally occurring and anthropogenic phosphorus compounds,

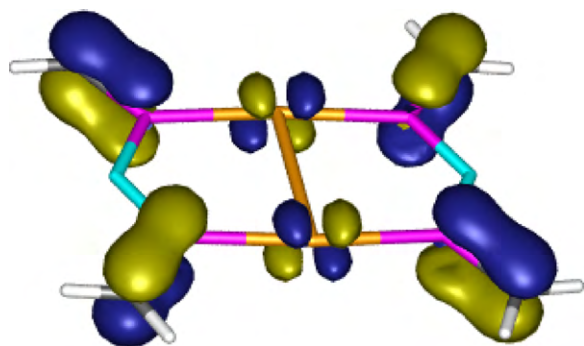
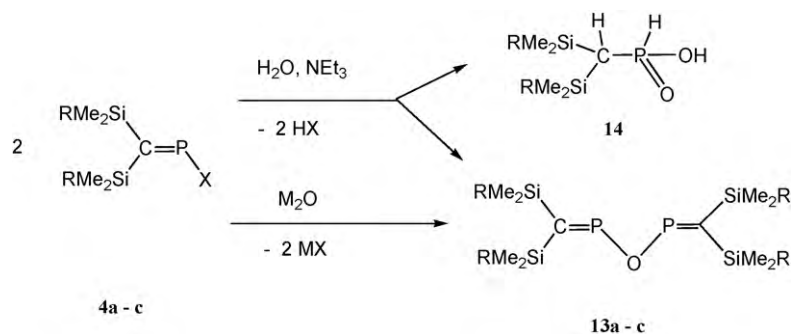


Fig. 2. The HOMO-3 of the gold complex 11 [19].

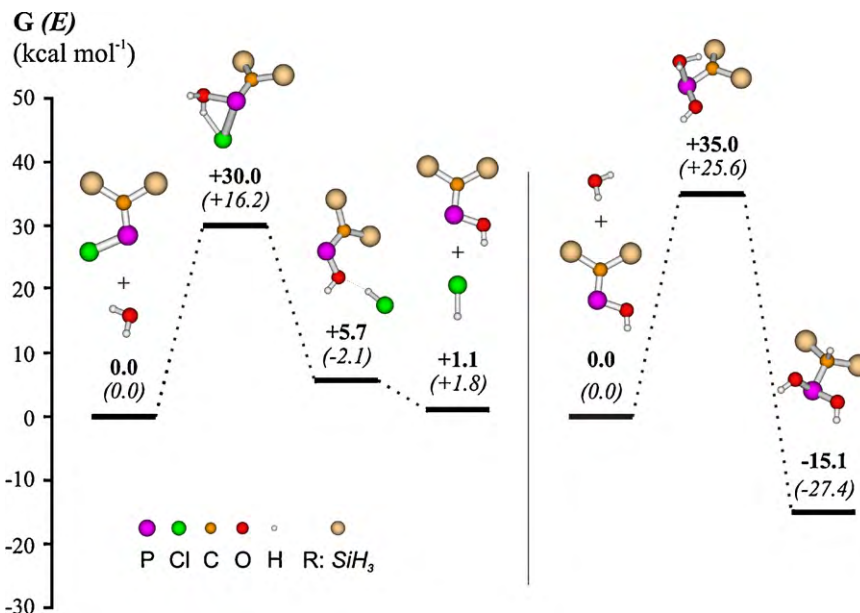
P<sup>V</sup>OP<sup>V</sup> systems with tetracoordinated phosphorus (such as P<sub>4</sub>O<sub>10</sub> and oligo- or polyphosphates) are the most abundant. Higher coordination numbers (e.g. P<sup>V</sup>OP<sup>V</sup> with pentacoordinated phosphorus, e.g. P<sub>4</sub>O<sub>18</sub>) [27] and lower coordination numbers (P<sup>III</sup>OP<sup>III</sup>, e.g. P<sub>4</sub>O<sub>6</sub> and phosphinous anhydrides) [28] have been investigated to a much lesser extent. POP-systems involving two-coordinated phosphorus, however, are new. When studying reactions with *P*-halogenophosphaalkenes (Me<sub>3</sub>Si)<sub>2</sub>C=PX (X = F, Cl, I) for a number of synthetic purposes, we tentatively assigned a minor <sup>31</sup>P NMR signal at about +352 (±1) ppm in the reaction mixtures to [(Me<sub>3</sub>Si)<sub>2</sub>C=P]<sub>2</sub>O (“POP”) (13a) [12] as a possible hydrolysis product. In the context of current work on related PNP-ligands [(RMe<sub>2</sub>Si)<sub>2</sub>C=P]<sub>2</sub>NR’ (R = Me, *i*Pr, Ph; R’ = *t*Bu, Me<sub>3</sub>Si) [13,19] that exhibit, as does “POP”, <sup>31</sup>P NMR resonances in the range of +350 to +360 ppm, it became necessary to undertake a synthetic study of the as yet unexplored unsaturated POP-system (2,4-diphospha-3-oxapentadienes = oxobisphosphaalkenes), in order to enable the unambiguous <sup>31</sup>P NMR spectroscopic discrimination of transient PNP compounds from POP hydrolysis products.

Controlled hydrolysis of *P*-chlorophosphaalkenes is accompanied by formation of alkylphosphinic acids 14 (about 10–15%), but with the help of metal oxides and using more reactive iodophosphaalkenes, pure samples of oxobisphosphaalkenes are available [12] (Scheme 12).

The hydrolysis reaction of *P*-chlorophosphaalkenes 4 was also investigated by density functional calculations. All the calculations were performed on the model compound (H<sub>3</sub>Si)<sub>2</sub>C=PCl (4’). As the hydrolysis usually starts with the substitution of the halogen by the OH group, we assumed the formation of (H<sub>3</sub>Si)<sub>2</sub>C=POH (disilylmethylene phosphinous acid) in the first step. The activation barrier of this substitution reaction involving a single water molecule (Scheme 13) is quite large. It is clearly seen in the transition structure that the direct transfer of the proton from the O to the Cl atom is energetically demanding because of the formation of the strained four-membered ring. It is known, however, that the barrier of hydrolysis reactions is lowered in the presence of three or four water molecules, which enable



Scheme 12. Formation of oxabis(phosphaalkenes) (M = Li, Ag; R = Me, *i*Pr, Ph) [12].



Scheme 13. Energy (E, kcal mol<sup>-1</sup>, in italics) and Gibbs free energy (G, kcal mol<sup>-1</sup>, in bold) of the hydrolysis products of (H<sub>3</sub>Si)<sub>2</sub>C=P-Cl along the reaction coordinate. Left: formation of (H<sub>3</sub>Si)<sub>2</sub>C=POH; right: formation of (H<sub>3</sub>Si)<sub>2</sub>CH-P(OH)<sub>2</sub> [12].

the proton transfer via a hydrogen bonded network in the transition structure [12]. Whereas this reaction step is somewhat endothermic, the presence of the base (which then reacts with HCl) drives the formation of the product.

The addition of the second molecule of water at the double bond of (H<sub>3</sub>Si)<sub>2</sub>C=POH produces the disilylmethylphosphonous acid (H<sub>3</sub>Si)<sub>2</sub>CH-P(OH)<sub>2</sub>, which is a tautomer of the disilylmethylphosphonic acid **14**. The reaction is exothermic and the activation energy of this step (26 kcal mol<sup>-1</sup>) is larger than that of the first step (16 kcal mol<sup>-1</sup>). The experimental finding that **14** is formed only in small amounts besides **13**, is in good accordance with the substantial activation barrier of this reaction step. The formation of the bis(phosphaalkene) ether **13'** in a condensation reaction is a well-known reaction that needs no further evaluation.

### 2.3.2. Structure and bonding

Among the B3LYP/6-31+G\* optimized **13a** and **13a'** structures (Fig. 3) the **13a** isomer is more stable by 1.2 kcal mol<sup>-1</sup>. In both structures the C=P-O-P=C linkage

forms a W-shape with C<sub>2</sub> symmetry. While the corresponding structure with SiH<sub>3</sub> groups is planar, the trimethylsilyl substituted **13a** is nearly planar, and in **13a'** the deviation from planarity is substantial, presumably for a better steric accommodation of the bulky trimethylsilyl groups. The bond lengths and bond angles are in the usual ranges.

The stabilising effect of the conjugation for the SiH<sub>3</sub> substituted model compounds was estimated by the isodesmic reactions below (see ref. [11a] for the S analogue) (Schemes 14).

The computed stabilisation energies are collected in Table 1. Reaction (4) is nearly thermoneutral for each chalcogen, showing that the stabilisation energy in the two C=P-OH fragments is nearly equal to that in the C=P-O-P=C moiety. Data for reaction (5) estimate the interaction between the C=P and chalcogen fragments, which is 30.2 kcal mol<sup>-1</sup> for oxygen, i.e. a remarkably high value of 15.1 kcal mol<sup>-1</sup> for each of the C=P-O units. In the case of **13a**, the isodesmic reaction energy is somewhat reduced to 27.0 kcal mol<sup>-1</sup> (13.5 kcal mol<sup>-1</sup> for each C=P-O unit). The slight decrease can be attributed to the non-planarity of



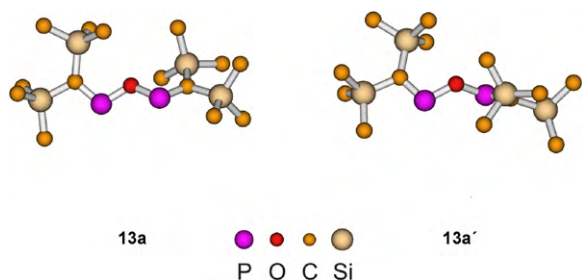


Fig. 3. Calculated structures of conformers of  $[(\text{Me}_3\text{Si})_2\text{C}=\text{P}]_2\text{O}$  (**13a**). Bond lengths and bond angles: **13a**: PO 1.697, PC 1.665; POP 120.5, CPO 107.5; **13a'**: PO 1.691, PC 1.666; POP 127.9, CPO 107.4.

the molecule, resulting in a weaker interaction between the lone pair of the oxygen and the  $\pi^*(\text{C}=\text{P})$  orbitals. According to the second order perturbational analysis of the Fock matrix in the NBO basis (which estimates the energy of donor–acceptor interactions between natural orbitals) a value of  $9.4 \text{ kcal mol}^{-1}$  was obtained for the interaction between the oxygen lone pair and each antibonding  $\pi^*(\text{C}=\text{P})$  orbital, which is comparable to that obtained using reaction (3) for **13a** – see above.

The conjugation effect can also be illustrated by the molecular orbitals of  $[(\text{H}_3\text{Si})_2\text{C}=\text{P}]_2\text{O}$  (Fig. 4), which clearly show the characteristic nodal properties of five-membered conjugated systems. The energies of the isodesmic reactions (3) and (4) give similar results for the sulfur and selenium analogues, but the stabilization for the oxygen analogue is higher than for the heavier chalcogens.

### 2.3.3. Cycloaddition reactions

**13a** reacts with two equivalents of cyclopentadiene in dichloromethane at room temperature within 24 h to form the bis-[2 + 4] cycloadduct **15**, accompanied by the phosphinous acid **14a** because of impurities in the starting material (Schemes 12 and 15). **15** is identified by two singlet signals in the  $\{^1\text{H}\}$ - $^{31}\text{P}$ -NMR-spectrum indicating the presence of new oxygen-bridged bis(2-phosphanorbornene) derivatives as pairs, either: (i) *endo,endo* and *exo,exo* isomers of diastereochemically pure *RS/SR* or *RR/SS*; or (ii) as *RS/SR* and *RR/SS* configured products, existing either as *endo,endo* or as *exo,exo*-isomers [10]. Since in the case of [2 + 4] cycloadditions of related thio- and selenophosphaalkenes  $(\text{Me}_3\text{Si})_2\text{C}=\text{P}-\text{E}-\text{PR}_2$  ( $\text{R} = t\text{Bu}$ ,  $i\text{Pr}$ ) with cyclopentadiene, rearrangements of the *endo*-isomers, as initially formed, into more stable *exo*-isomers occurred within 24 h [10,12], we assume that both diastereomers of the phosphinous anhydride **15** exist as the *exo,exo*-isomers [10], as depicted in Scheme 15.

The formation of the 1:2 adduct **16** from the reaction of **13a** with two equivalents of tetrachloro-*o*-benzoquinone

Table 1  
Stabilisation energies of the reactions (4) and (5): E = O, S, Se ( $\text{kcal mol}^{-1}$ ) [11,12].

	O	S	Se
(4)	-1.8	0.1	-1.5
(5)	30.2	17.6	20.7

(TOB) [12] proceeds diastereoselectively (Scheme 16). In the recrystallisation of **16** the phosphinic acid **14a** (from the impure starting material) is removed.

The proposed identity and stereochemistry of the oxo-bridged bis(2-phospha-2,5-dioxo-3,4-benzophospholene) derivative **16** were confirmed by X-ray crystallography. Compound **16** crystallizes as a racemic mixture of (*RR*) and (*SS*) enantiomers with approximate  $C_2$ -symmetry.

The C1–P1–O1–P2–C2 moiety of **16** exhibits a distorted *W*-shaped arrangement, whereby the five atoms are approximately coplanar. From this central unit the heterocycles extend in opposite directions, allowing the phosphorus atoms to minimise their lone pair interactions in a “*gauche*”-type fashion. The angle P–O–P is  $118.81(6)^\circ$ , significantly larger than in the analogous selenium-bridged compound **17** [ $87.86(3)^\circ$ ] [11]. The two molecules are otherwise very similar, but the structures are not isotopic; the selenium derivative crystallizes as a chloroform solvate [11].

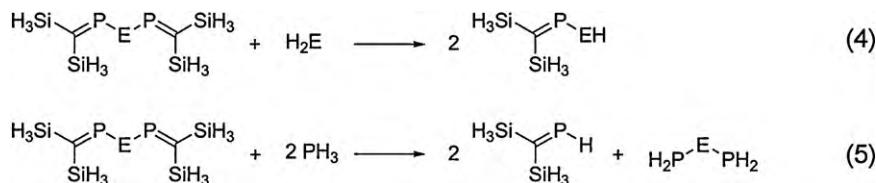
### 2.4. The heavier congeners $[(\text{RMe}_2\text{Si})_2\text{C}=\text{P}]_2\text{E}$ (E = PR, P<sup>-</sup>, As<sup>-</sup>, S, Se, Te,)

#### 2.4.1. Phosphanediyl-, phosphido-, and arsenido-bridged bisphosphaalkenes

The reaction of *t*butylbis(trimethylsilyl)phosphane with two equivalents of the *P*-chlorophosphaalkene **4a** provides the 1,3-bisalkylidene triphosphane **18** [7], which can act as a bidentate ligand towards the  $\text{Mo}(\text{CO})_4$  acceptor moiety [1,7] leading to the chelate complex **19**.

A charged equivalent of **18** is present in the lithium salt  $\text{Li}(\text{THF})_x\{[(\text{Me}_3\text{Si})_2\text{C}=\text{P}]_2\text{P}\}$  **20** [8]. This 2,3,4-triphosphapentadienide anion represented in 1996 the first case of a  $\pi$ -donor heteroatom-bridged bis-phosphaalkene anion allowing electronic communication between the  $\pi$ -systems (P=C bonds) of two neighbouring phosphaalkene moieties. Like the uncharged ligand **18**, **20** can act as small bite angle chelate ligand towards metal carbonyl acceptors (Scheme 17).

The structure determination of the ion pair-like compound **20** reveals some P=C/P=P  $\pi$ -delocalisation and a remarkably small central bond angle PPP. In the related arsenidobis(phosphaalkene) lithium salt  $\text{Li}(\text{THF})_x\{[(\text{Me}_3\text{Si})_2\text{C}=\text{P}]_2\text{As}\}$  **22** [9,29], the bond angle PAsP



Scheme 14. Isodesmic reactions of chalcogen-bridged bisphosphaalkenes [11,12].

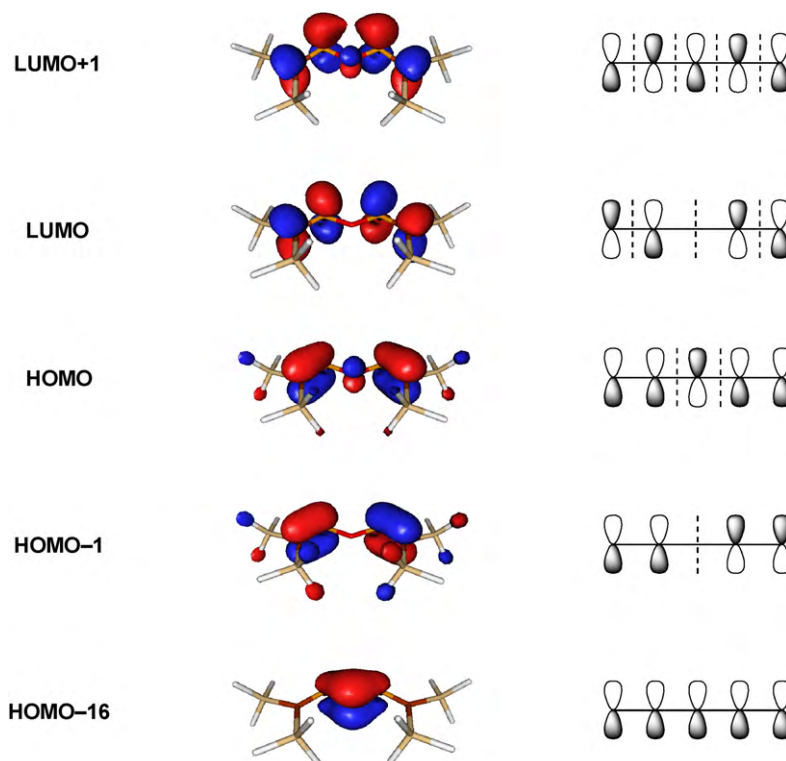
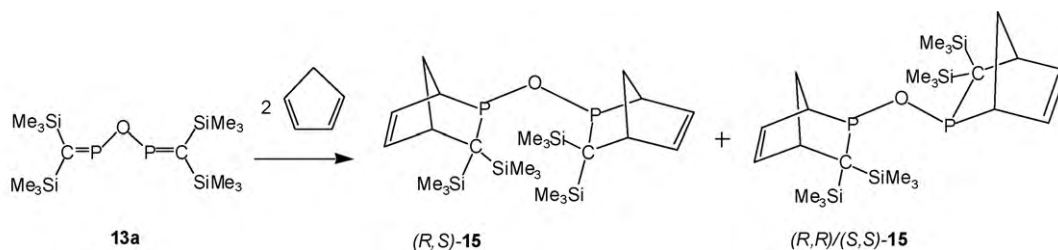
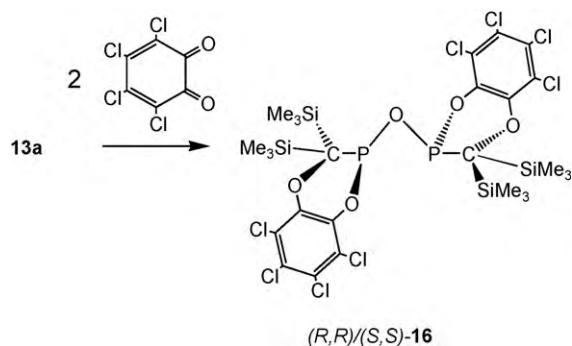


Fig. 4. Canonic molecular orbitals of an oxabisphosphaalkene (HF/6-31G\*\*//B3LYP/6-31+G\*) [12].



Scheme 15. Proposed structures of products from **13a** with cyclopentadiene.

is even smaller, suggesting attractive 1,3-P··P interactions in both anions. Comparison of the spectroscopic data of chelate complexes **19** and **21** reveals that – as expected – the anionic ligand **20** donates more electron density to the transition metal than the uncharged ligand **18**.

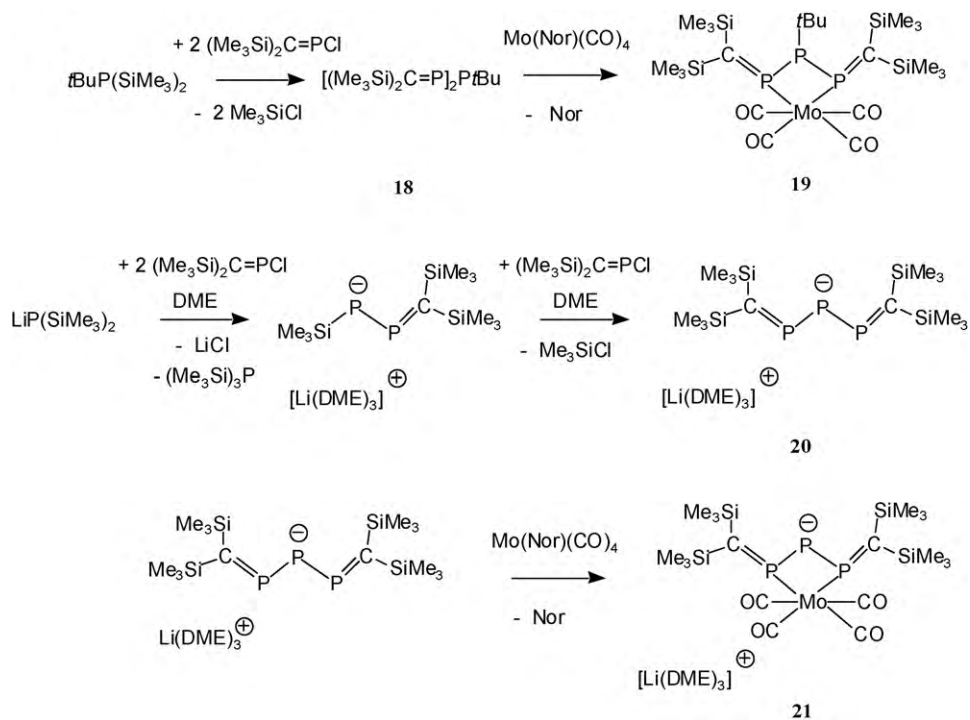


Scheme 16. Reaction of **13a** with tetrachloro-*o*-benzoquinone (TOB).

#### 2.4.2. Sulfur-, selenium- and tellurium-bridged bisphosphaalkenes

Sulfur-, selenium- and tellurium-bridged bisphosphaalkenes are synthetically available from  $(\text{RMe}_2\text{Si})_2\text{C}=\text{P}(\text{Cl})$  (**4a–c**) with bis(trialkylsilyl)chalcogenides (by chlorosilane elimination, similar as the synthesis of compound **18**) or with *in situ* prepared lithium chalcogenides (by lithium chloride precipitation [11]). Single crystalline samples were obtained from  $[(\text{PhMe}_2\text{Si})_2\text{C}=\text{P}]_2\text{S}$  (**23c**) and from  $[(\text{RMe}_2\text{Si})_2\text{C}=\text{P}]_2\text{Se}$  (R = Me: **24a** [11], *i*Pr: **24b**). In the solid, these molecules exist in slightly distorted W-shaped conformations (see Scheme 5). The angles PSP and PSeP in **23** and **24** are larger than angles PPP and PASP in the isoelectronic anions **20** and **22**.

In case of the telluride  $[(\text{Me}_3\text{Si})_2\text{C}=\text{P}]_2\text{Te}$  (**25a**), the synthesis is – even at  $-40\text{ }^\circ\text{C}$  – accompanied by immediate precipitation of tellurium allowing only the  $^{31}\text{P}$ -NMR-spectroscopic observation of the desired product in the black suspension, and within 30 minutes 90% of **25a** has lost tellurium to furnish the known bicyclobutane



Scheme 17. Phosphorus-bridged bis(phosphaalkenes) and their chelate complexes.

isomer of the elusive diphosphabutadiene derivative  $[(\text{Me}_3\text{Si})_2\text{C}=\text{P}]_2$  (Scheme 18) [30].

Reaction of the bulkier *P*-chlorophosphaalkene **4b**, however, with  $(i\text{PrMe}_2\text{Si})_2\text{Te}$  provides solutions containing  $[(i\text{PrMe}_2\text{Si})_2\text{C}=\text{P}]_2\text{Te}$  (**25b**) in fair yields. Telluride **25b** can be kept in solution in the cold for an extended time, but removal of the solvent leads to impure samples through loss of tellurium.

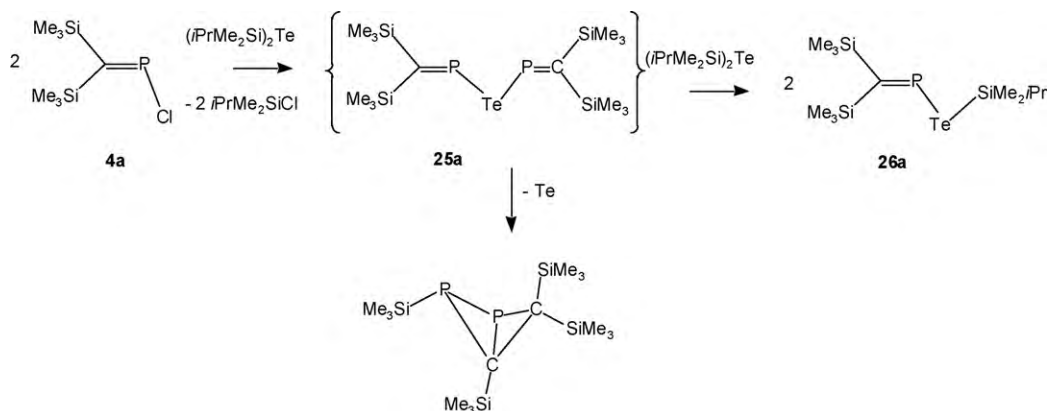
With two equivalents of 1,3-dienes or -heterodienes (such as tetrachloro-*o*-benzoquinone [TOB]) the sulfide  $[(\text{Me}_3\text{Si})_2\text{C}=\text{P}]_2\text{S}$  (**23a**) and the homologous selenide **24a** furnish S- and Se-bridged bisphosphanes through straightforward [2 + 4] cycloaddition reactions [13], as for **13a**. With three equivalents of TOB,  $\text{P}^{\text{III}}\text{-E-P}^{\text{V}}$ -units are formed (compounds **27**, **28**; Schemes 19 and 20).

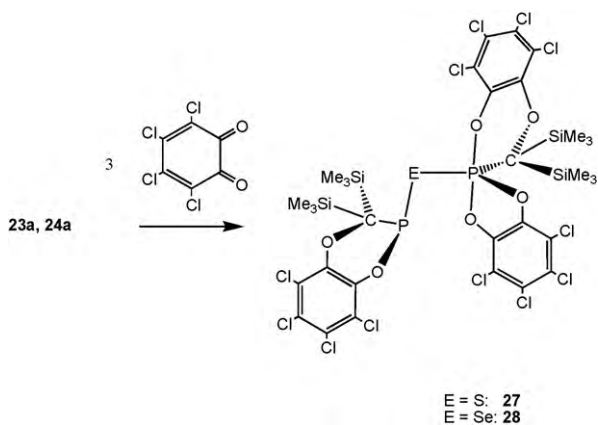
From norbornadiene complexes of group 6 metal tetracarbonyls and ligands **23a** and **24a**, *P,P'*-coordinated chelate complexes such as **29** and **30** (closely related to complex **19**) are formed as expected.

With elemental sulfur and selenium, however, the heteropentadienes  $[(\text{Me}_3\text{Si})_2\text{C}=\text{P}]_2\text{E}$  **23a**, **24a** react in a surprising way that is dissimilar from that of comparable monofunctional phosphoalkenes, delivering bicyclic compounds with norbornane-type  $\text{P}_2\text{Se}_5$ -related  $[(\text{Me}_3\text{Si})_2\text{CP}]_2\text{E}_3$  backbones (E = S, Se).

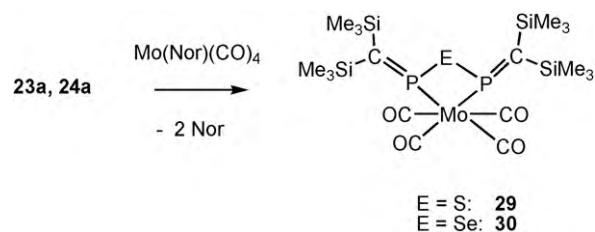
$[(\text{Me}_3\text{Si})_2\text{C}]_2\text{P}_2\text{S}_5$  (**33**,  $\text{P}^{\text{V}}, \text{P}^{\text{V}}$ ) (Scheme 21) was obtained crystalline as the final product of the addition of sulfur to **23a** (Scheme 22).

In a similar way the reaction of **24a** with two equivalents of Se provides in high yield  $[(\text{Me}_3\text{Si})_2\text{C}]_2\text{P}_2\text{Se}_3$

Scheme 18. Reaction of **4a** with  $(i\text{PrMe}_2\text{Si})_2\text{Te}$ .



Scheme 19. Products from cycloaddition of  $[(\text{Me}_3\text{Si})_2\text{C}=\text{P}]_2\text{E}$  (E = S, Se) with three equivalents of TOB.



Scheme 20. Coordination reactions of **23a** and **24a**.

(**34**,  $\text{P}^{\text{III}}$ ,  $\text{P}^{\text{III}}$ ) as a stable yellow solid that is not further oxidised by selenium. Crude **34** is accompanied by minute amounts of *P,P'*-di[bis(trimethylsilyl)methyl]selenadiphosphirane (**35**) [11].

The formation of the heteronorborene-like  $\text{C}_2\text{P}_2\text{E}_3$  cages **31–34** is unexpected because related thia- and

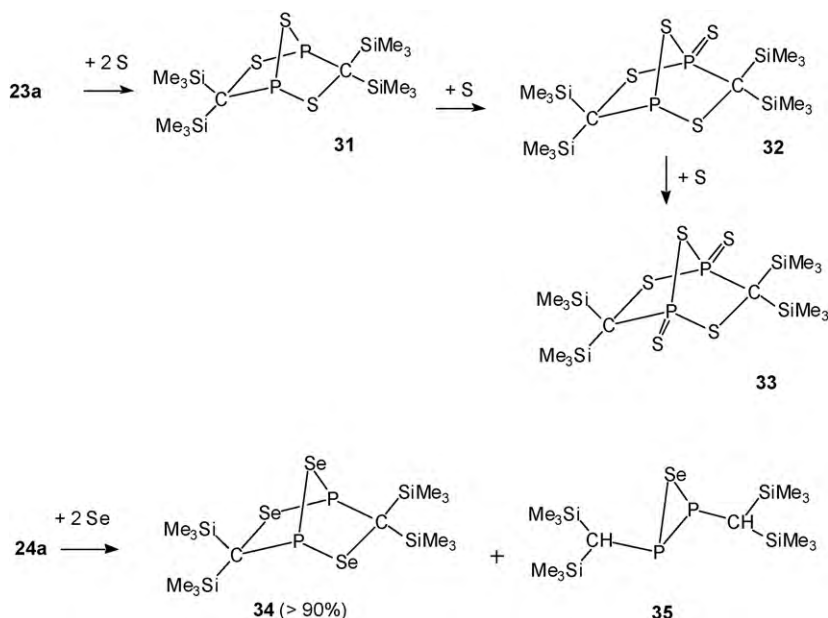
selenaphosphiranes do not dimerise under comparable conditions. Quantum chemical calculations on the rearrangements of a bis-phosphirane type model compound **A** into the norbornane-type isomer **E** reveal that the most favourable pathway involves a type phosphirane/phosphorane intermediate **B** [11].

#### 2.4.3. Discussion of the heavier congeners $[(\text{RMe}_2\text{Si})_2\text{C}=\text{P}]_2\text{E}$

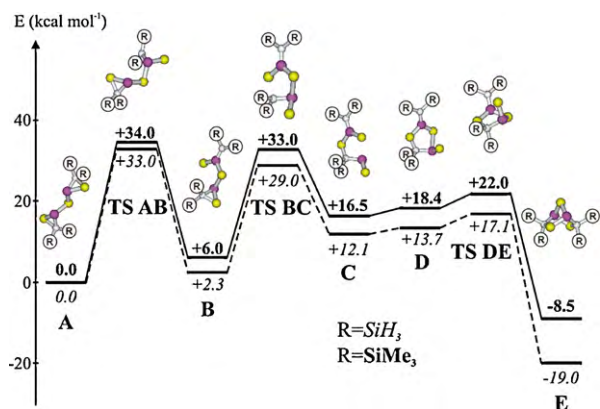
Containing a *W*-shaped central SePEPSe moiety that is close to planarity, the selenium-bridged bis-phosphaalkene  $[(\text{Me}_3\text{Si})_2\text{C}=\text{P}]_2\text{Se}$  (**24a**) [11] is structurally related to Nieckes' 2,3,4-triphosphapentadienide anion **20**  $\{[(\text{Me}_3\text{Si})_2\text{C}=\text{P}]_2\text{P}\}^-$  [8], which represents a  $\pi$ -donor heteroatom-bridged bis-phosphaalkene anion that allows electronic communication between the  $\pi$ -systems ( $\text{P}=\text{C}$  bonds) of two neighbouring phosphaalkene moieties. Recently, it was reported that in the related arsenide anion  $\{[(\text{Me}_3\text{Si})_2\text{C}=\text{P}]_2\text{As}\}^-$  (isoelectronic with **20**) the angle  $\text{PAsP}$  shrinks to  $85.8^\circ$ ; quantum chemical calculations implied  $\text{C}-\text{P}-\text{As}$   $\pi$ -delocalisation of the negative charge, including *island homoaromaticity* for the  $\text{AsP}_2$  moiety [8,9]. Crystallographic data of **23c** and **24a**, however, do not provide evidence of a significant ground state  $\pi$ -conjugation in the  $\text{C}=\text{P}-\text{E}-\text{P}=\text{C}$  (E = S, Se) system. The reactivity of **23a** and **24a** is towards sulfur and selenium is markedly different from that of monofunctional phosphaalkenes [11].

### 3. Phosphanilaminophosphaalkenes $(\text{RMe}_2\text{Si})_2\text{C}=\text{P}-\text{N}(\text{R})-\text{PR}'_2$

In this section, initial results of the characterisation of the novel complexes  $\text{M}[(\text{Me}_3\text{Si})_2\text{C}=\text{P}(\text{Cl})\text{N}(1\text{-Ada})\text{PPh}_2]_2$  (1-Ada = 1-adamantyl; M = Pd, Pt) are presented, which are unprecedented in phosphaalkene coordination chemistry [14].



Scheme 21. Sulfur addition to **23a** and selenium addition to **24a**.



**Scheme 22.** Calculated pathway of isomerisation of a bis(thiophosphiranyl)sulfide **A** (energies of R=SiH<sub>3</sub> in italics and R=SiMe<sub>3</sub> in bold, in kcal mol<sup>-1</sup>) to the related heteronorbormane **E**.

### 3.1. Ligand synthesis

Synthetic experiments on the type **D** (Scheme 1) ligands showed that (Me<sub>3</sub>Si)<sub>2</sub>C=P(OR)Cl fortuitously reacted with lithium iminophosphanides Li[Ph<sub>2</sub>PNR], [31] prepared in situ from the aminophosphanes Ph<sub>2</sub>PN(H)1-Ada [32] and Ph<sub>2</sub>PN(H)*t*Bu with LDA, [33] to give the *P*-(phosphanyl-amino)phosphaalkenes (Me<sub>3</sub>Si)<sub>2</sub>C=PN(1-Ada)PPh<sub>2</sub> (**36**) and (Me<sub>3</sub>Si)<sub>2</sub>C=PN(*t*Bu)PPh<sub>2</sub> (**37**), [14,17] whereas the reaction of the 1-aza-2-phosphaallyl anion [(Me<sub>3</sub>Si)<sub>2</sub>C=PN*t*Bu]<sup>-</sup> [16,17] with R<sub>2</sub>PCl led preferentially by P–P bond formation to the undesired phosphanylphosphorane isomers (Me<sub>3</sub>Si)<sub>2</sub>C=P(=N*t*Bu)PR<sub>2</sub> [17]. The molecular structure of solid **36** was determined by X-ray crystallography [14].

### 3.2. Platinum and palladium dichloride complexes

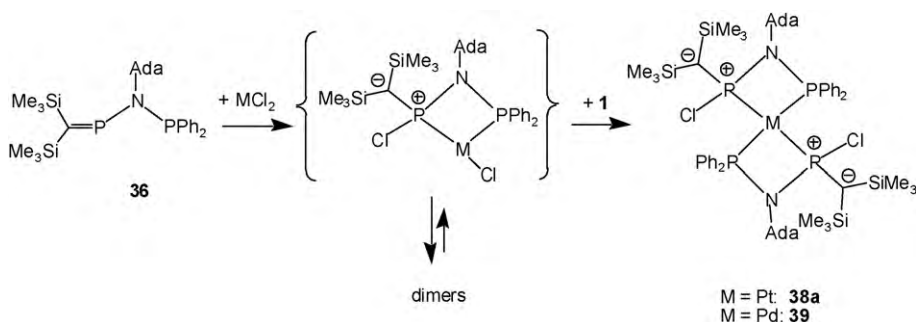
After adding a solution of the ligand **36** in an aprotic solvent to an equimolar amount of the PtCl<sub>2</sub> cyclooctadiene (COD) complex suspended in dichloromethane, <sup>31</sup>P-NMR spectra of the orange solution indicate the complete consumption of **36** [AX-pattern, δ = +373.5, +37.7 ppm, <sup>2</sup>J<sub>PP</sub> = ±12 Hz] and the formation, depending on the reaction conditions, of up to three new species exhibiting AX-patterns

that all appear in the chemical shift range of +60 to +15 ppm, showing couplings <sup>2</sup>J<sub>PP</sub> and <sup>1</sup>J<sub>PtP</sub>. Sets of further weak <sup>31</sup>P-NMR signals are assigned to an A<sub>2</sub>M<sub>2</sub> pattern [δ = +71, +42; <sup>2</sup>J<sub>PP</sub> = ±21 Hz], and tentatively to higher order multiplets, partially hidden by platinum satellites of the stronger signals. An X-ray structure determination revealed that the compound with the A<sub>2</sub>M<sub>2</sub>-like pattern is a very unusual 1:2 chelate complex of PtCl<sub>2</sub> with ligand **36** [14]. When two equivalents of ligand **36** were used to favour the formation of the 1:2 complex, ligand **36** and the coordinated species giving rise to AX-patterns were consumed within several days according to <sup>31</sup>P-NMR, that showed, *inter alia*, overlapping signals of multiplets including the A<sub>2</sub>M<sub>2</sub> pattern of **38a** as a major product.

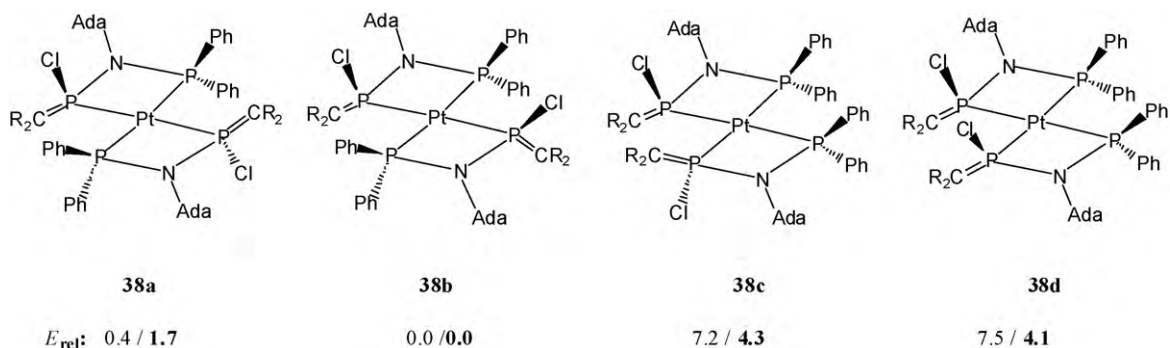
The X-ray crystallographic structure determination confirmed that the solid **38a** is a complex of the composition [PtCl<sub>2</sub>(**36**)<sub>2</sub>] (as a 1:1 pentane solvate) with tetra-coordinated platinum surrounded by two *trans*-oriented *P,P'*-chelating ligands in a square-planar fashion, but is uniquely different from usual cationic platinum bis-chelates of the type {[PtL<sub>4</sub>]<sup>2+</sup>(X<sup>-</sup>)<sub>2</sub>}; there are covalent bonds between the phosphorus atoms of the hypothetical cationic moiety [Pt(**1**)<sub>2</sub>]<sup>2+</sup> and the two chlorine atoms. The related 1:1 reaction of ligand **1** with PdCl<sub>2</sub>(COD) provided a few crystals of the solid pentane-solvated palladium complex **39**, which is isotopic to **38a** (Scheme 23) [14].

The addition of two chloride ions to the phosphoalkene phosphorus atoms of the hypothetical cationic moiety *trans*-[M(**36**)<sub>2</sub>]<sup>2+</sup> (M = Pd, Pt) leads formally to two four-coordinated stereogenic phosphorus atoms P(C)(N)(Cl)(M) in the resulting molecular complexes. Complexes **38a** and **39** consist of centrosymmetric molecules with *trans*-orientation of the two types of phosphorus atoms around palladium and platinum; the chlorine atoms are *anti*-oriented, one above and below the square plane (*R,S*). The alternative (*R*)- or (*S*)-configurations at phosphorus, together with the intrinsic possibility of *cis*- or *trans*-*P,P'*-chelate ligand orientations around square planar platinum or palladium, mean that up to four stereoisomers **38a–38d** (or **39a–39d**) are possible (Scheme 24).

Variation of the reaction conditions and of the solvent mixtures for crystallisation allowed the isolation of a few single crystals of two further isomers **38b** and **38c** (Scheme 24) of the platinum complex **38**. Solid **38b** and **38c** exist as racemic mixtures of (*R,R*) and (*S,S*) enantiomers.



**Scheme 23.** Reaction of **36** with Pt and Pd dichlorides.



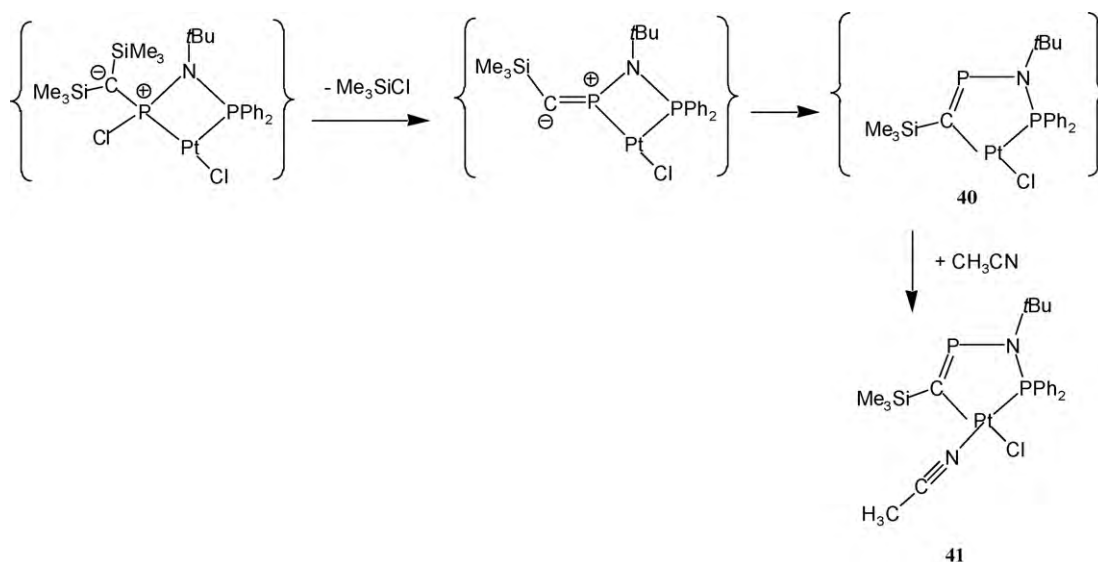
**Scheme 24.** Relative energies of complexes related to isomers **38a–38d** ( $R = \text{Me}_3\text{Si}$ ) for ligand **36'**, for **36''** in boldface [ $(\text{H}_3\text{Si})_2\text{C}=\text{PN}(\text{Me})\text{PR}'_2$ ,  $R'$ : Me (**36'**), Ph (**36''**)], in kcal mol<sup>-1</sup> [14].

Bond distances and angles of **38b** and **38c** show no significant differences to those of **38a**. In all three isomers, each bidentate ligand **36** unit has acquired one chlorine atom bonded to a (formerly) phosphalkene phosphorus atom. This phosphorus atom acts as a  $\sigma$ -donor towards platinum and as a  $\sigma$ -acceptor towards the chlorine atom, *i.e.* the phosphalkene phosphorus atom has inserted in a carbene-like fashion into the Pt–Cl bond. In order to understand the remarkable electrophilicity of the *P*-(phosphanyl-amino)phosphalkene ligands, model calculations based on density functional theory have been performed [14]. On the basis of these results, the known strong electron acceptor behaviour of the  $\pi^*(\text{C}=\text{P})$  unit [6] is remarkably increased by the silyl groups (the LUMO energy drops). The effect is corroborated by considering phenyl groups at the  $\sigma^3$ ,  $\lambda^3$ -P atom instead of methyl groups. Further enhancement of the electrophilicity is achieved for the entire ligand by the metal complexation [14].

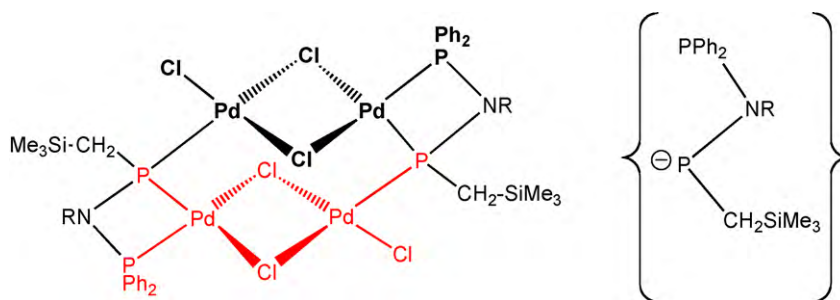
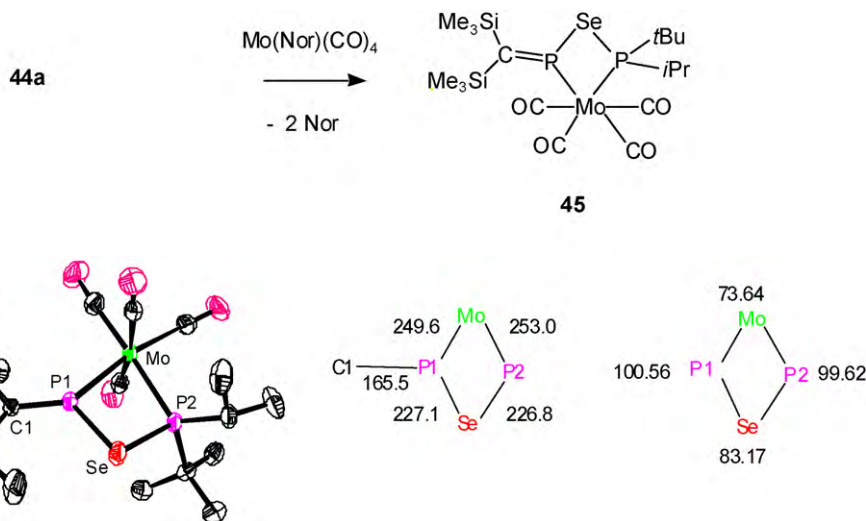
The coordination of ligand **37** to platinum dichloride in dichloromethane solution competes with a reaction that involves elimination of chlorotrimethylsilane, furnishing

as a yellow solid the cyclic C-metallophosphalkene **40**, which exists according to NMR as an isomeric mixture of Cl-bridged dimers. Crystallisation of this material from acetonitrile led to a monomeric acetonitrile complex **41** (Scheme 25). Complex **41** is expected to be formed from a *P*-chloroylide complex that may undergo  $\beta$ -elimination of  $\text{Me}_3\text{SiCl}$ , leading to a kind of silyl(phosphanyl)carbene intermediate. From this species,  $\text{P}\rightarrow\text{C}$  migration of platinum can lead to the unusual C-metalated cyclic phosphalkene that crystallises as acetonitrile complex **41** [21b,32].

In the course of the attempts to isolate the palladium complex **39** and related species based on ligands **36** and **37**, we fortuitously isolated a unique tetranuclear hexachloropalladium complex **42** consisting of two planar  $\text{Pd}_2\text{Cl}_3$  moieties connected by two of the bidentate anionic hydrogenated phosphane/phosphido ligands [ $\text{Ph}_2\text{P}-\text{N}(\text{tBu})\text{P}(\ominus)\text{CH}_2\text{SiMe}_3$ ]<sup>-</sup> [21b,32]. Each phosphido function bridges two Pd atoms from the two different planar  $\text{Pd}_2\text{Cl}_3$  moieties, and the  $\text{PPh}_2$  groups play their usual role as terminal ligands. The anion (Scheme 26, below/right) is related to the C-coordinated anionic ligand in the platinum



**Scheme 25.** Chlorosilane elimination following the reaction of ligand **37** with  $\text{PtCl}_2$ .

Scheme 26. Left: topology of complex **42**; right: an anionic ligand in **42**; R = *t*Bu [21b,32].Scheme 27. Formation (above) and structural features (below) of complex **45**: molecular structure (left), distances (central) and angles (right) [10b].

complex **41** by addition of two hydrogen atoms to the “carbene” carbon atom (of the “carbene” intermediate, see Scheme 25).

### 3.3. Heavier congeners: sulfur- and selenium-bridged “hybrid ligands” ( $(\text{Me}_3\text{Si})_2\text{C}=\text{P}-\text{E}-\text{PR}_2$ ( $\text{E} = \text{S}, \text{Se}$ ))

In a study on the reactivity of *P*-phosphanylphosphaalkenes ( $(\text{Me}_3\text{Si})_2\text{C}=\text{P}-\text{PR}_2$  towards chalcogens, type **D** molecules ( $(\text{Me}_3\text{Si})_2\text{C}=\text{PEPR}_2$  ( $\text{R} = i\text{Pr}, t\text{Bu}$ ;  $\text{E} = \text{S}$ : **43**;  $\text{Se}$ : **44**) were recognized to be products of the monoinsertion of sulfur and selenium into the P–P bonds [10]. Subsequent chalcogen addition leads by  $\text{P}^{\text{III}} \rightarrow \text{P}^{\text{V}}$  oxidation of **43** and **44** to dithio- and diselenophosphinato-phosphaalkenes ( $(\text{Me}_3\text{Si})_2\text{C}=\text{PEP}(\text{=E})\text{R}_2$ ). This oxidation is followed by S or Se addition to the P=C double bond, providing *P*-dithio- and diselenophosphinato-thia- or -selenophosphiranes as final products. Since pure **43** and **44** could not be isolated, the coordination with  $\text{M}(\text{CO})_4$  moieties was used as a trapping reaction. This led also to the crystallographic characterisation of a molybdenum complex **45** of the “hybrid” ligand ( $(\text{Me}_3\text{Si})_2\text{C}=\text{PSeP}(i\text{Pr})(t\text{Bu})$  (**44a**) [10] (Scheme 27).

## 4. Conclusion

Following previous work on heavier heteroatom-bridged bifunctional phosphaalkenes  $[(\text{RMe}_2\text{Si})_2\text{C}=\text{P}]_2\text{E}$

( $\text{E} = \text{S}, \text{Se}, \text{Te}, \text{PR}, \text{P}^-, \text{As}^-$ ) and  $(\text{RMe}_2\text{Si})_2\text{C}=\text{P}-\text{E}-\text{PR}'_2$  ( $\text{E} = \text{S}, \text{Se}, \text{Te}$ ), nitrogen- and oxygen-bridged bidentate phosphaalkene ligands  $[(\text{RMe}_2\text{Si})_2\text{C}=\text{P}]_2\text{E}$  ( $\text{E} = \text{O}, \text{NR}', \text{N}^-$ ;  $\text{R} = \text{Me}, i\text{Pr}, \text{Ph}$ ) and  $(\text{RMe}_2\text{Si})_2\text{C}=\text{P}-\text{N}(\text{R}')-\text{PPh}_2$  are now accessible by salt elimination methods from the corresponding *P*-halogenophosphaalkenes  $(\text{RMe}_2\text{Si})_2\text{C}=\text{PX}$  with lithium imidophosphaalkenes and imidophosphanes. Alkyliminobisphosphaalkenes without bulky *C*-*i*Pr $\text{Me}_2\text{Si}$  substituents undergo intramolecular rearrangements leading to mixtures of four-membered heterocycles. The stable *N*-trimethylsilylimino derivative  $[(i\text{PrMe}_2\text{Si})_2\text{C}=\text{P}]_2\text{NSiMe}_3$  reacts with  $\text{Au}^{\text{I}}$  and  $\text{Rh}^{\text{I}}$  chloro complexes with N–Si bond cleavage furnishing binuclear complexes of the  $6\pi$ -delocalised imidobisphosphaalkene anion  $[(i\text{PrMe}_2\text{Si})_2\text{C}=\text{P}]_2\text{N}^-$ . The most exceptional property of *P*-phosphanylaminophosphaalkene ligands  $(\text{RMe}_2\text{Si})_2\text{C}=\text{P}-\text{N}(\text{R}')-\text{PPh}_2$  is the chlorotropic formation of molecular  $\text{Pd}^{\text{II}}$  and  $\text{Pt}^{\text{II}}$  metallochloroylid complexes. Several stereoisomers of the 2:1 complex **38** were characterised by X-ray crystallography. Chlorosilane elimination from an intermediate *P*-platina-*P*-chloroylid 1:1 complex (Scheme 25) can explain the formation of the unusual C-platina phosphaalkene complex **41** and of the tetranuclear palladium complex **42**, suggesting a considerable synthetic potential of the chloroylid complexes derived from *P*-phosphanylaminophosphaalkene ligands.

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