

# Phosphinomethanides and Group 15 element halides: redox reactions, rearrangements and novel heterocycles

H.H. Karsch<sup>\*</sup>, E. Witt

Anorganisch-chemisches Institut, Technische Universität München, Lichtenbergstraße 4, D-85747 Garching, Germany

Received 4 April 1996; revised 5 June 1996

## Abstract

The reactions of  $\text{ECl}_3$  (E = P, As, Sb, Bi),  $\text{RPhCl}_2$  (R = Me, Ph, <sup>t</sup>Bu,  $\text{Cy}_2\text{N}$ ) and  $\text{Ph}_2\text{PCl}$ , respectively, with ambident lithium phosphinomethanides are described. The reaction with  $\text{LiCH}_2\text{PMe}_2$ , **1**, by E–C bond formation, leads to the substitution products  $\text{E}(\text{CH}_2\text{PMe}_2)_3$ , **2a–d**, (E = P, As, Sb, Bi) and  $\text{R–P}(\text{CH}_2\text{PMe}_2)_2$  (R = Me, Ph, <sup>t</sup>Bu,  $\text{Cy}_2\text{N}$ ) **5a–d**. In contrast,  $\text{LiC}(\text{PMe}_2)(\text{SiMe}_3)_2 \cdot 0.5\text{TMEDA}$ , **6**, gives substitution products with  $\text{ECl}_3$  (E = P, As, Sb), by E–P bond formation. Thus, the first element–tris(P–ylide) derivatives  $\text{E}(\text{PMe}_2=\text{C}(\text{SiMe}_3)_2)_3$ , **7a–c**, are obtained. **7b** is characterized by X-ray structure determination. In these reactions, oxidative P–P coupling to give  $[(\text{Me}_3\text{Si})_2\text{C}=\text{PMe}_2]_2$ , **8**, is also observed, and exclusively in the reaction of  $\text{BiCl}_3$  with **6**. The reaction of  $\text{RPhCl}_2$  (R = Me, Ph, <sup>t</sup>Bu,  $\text{Cy}_2\text{N}$ ) with **6** strongly is dependent on the nature of R. For R = Me, only substitution is observed, yielding  $\text{Me–P}(\text{PMe}_2=\text{C}(\text{SiMe}_3)_2)_2$ , **10**, while for R = Ph, both substitution and Li/Cl exchange with subsequent formation of **8** and the diphosphane  $[(\text{Me}_3\text{Si})_2\text{C}=\text{PMe}_2\text{–PPh}]_2$ , **12**, are found. The latter has been characterized structurally. In contrast, for R = <sup>t</sup>Bu, only  $(^t\text{BuP})_3$ , **13**, and  $(^t\text{BuP})_4$ , **14**, are obtained. An analogous result is observed in the reaction of <sup>t</sup>Bu $\text{PCl}_2$  with  $\text{LiC}(\text{PMe}_2)_2(\text{SiMe}_3)$ , **17**. The reaction of  $\text{Cy}_2\text{NPCl}_2$  with two equivalents of  $\text{LiC}(\text{PMe}_2)(\text{SiMe}_3)_2 \cdot 0.5\text{TMEDA}$ , **6**, gives a phospho-alkene  $\text{Cy}_2\text{N–P}=\text{C}(\text{SiMe}_3)_2$ , **16**, and the substitution product  $\text{Cy}_2\text{N–P}(\text{PMe}_2=\text{C}(\text{SiMe}_3)_2)_2$ , **15**. Likewise,  $\text{LiC}(\text{PMe}_2)_2(\text{SiMe}_3)$ , **17**, reacts with  $\text{PhPCl}_2$  to give the substitution product  $\text{Ph–P}(\text{PMe}_2=\text{C}(\text{SiMe}_3)_2)_2$ , **18**, which is characterized by X-ray structure determination, whereas with  $\text{MePCl}_2$  only the P–ylide  $\text{Me}_2\text{P–PMe}_2=\text{C}(\text{PMe}_2)(\text{SiMe}_3)$ , **20**, and the coupling product  $[(\text{Me}_2\text{P}(\text{Me}_3\text{Si})\text{C}=\text{PMe}_2)]_2$ , **19**, are formed. The latter is also obtained in the reactions of  $\text{BiCl}_3$  or  $\text{SbCl}_3$  with  $\text{LiC}(\text{PMe}_2)_2(\text{SiMe}_3)$ , **17**. Analogous redox reactions with  $\text{AsCl}_3$  and  $\text{PCl}_3$ , respectively, lead to the bis-pentacyclic  $\{\mu\text{–}[\text{C}(\text{PMe}_2)_2(\text{SiMe}_3)]\text{As}_2\}_2$ , **21**, and the hexacyclic  $\text{P–PMe}_2\text{–C}(\text{SiMe}_3)\text{–PMe}_2\text{–C}(\text{SiMe}_3)\text{–PMe}_2$ , **22**, which were structurally characterized by X-ray analyses. Depending on the reaction conditions, the reaction of  $\text{PCl}_3$  with  $\text{LiC}(\text{PMe}_2)_2(\text{SiMe}_3)$ , **17**, alternatively may lead to the triphosphite  $\text{P–PMe}_2\text{–C}(\text{SiMe}_3)\text{–PMe}_2$ , **24**. By using P–phenyl-substituents instead of P–methyl-substituents, i.e. in the reaction of  $\text{LiC}(\text{PPh}_2)_2(\text{SiMe}_3)$ , **25**, with  $\text{PCl}_3$  or  $\text{AsCl}_3$ , the triphosphite  $\text{P–PPh}_2\text{–C}(\text{SiMe}_3)\text{–PPh}_2$ , **26a**, or its arsenic analogue  $\text{As–PPh}_2\text{–C}(\text{SiMe}_3)\text{–PPh}_2$ , **26b**, are respectively formed, along with the chlorine substituted ylide  $(\text{Cl})(\text{Ph})_2\text{P}=\text{C}(\text{PPh}_2)(\text{SiMe}_3)$ , **27**. **26a,b** are characterized by X-ray structure determinations. The synthesis of the first ten-electron phosphorus cation  $[\text{C}(\text{PPh}_2)_2(\text{SiMe}_3)]_2^+$ , **30**, with a homonuclear, spirocyclic  $\text{PP}_4$ -framework was achieved by reacting the triphosphite **26a** with the ylide **27** in the presence of  $\text{NaBPh}_4$ . The crystal structure of the cation of **30**, which adopts a  $\Psi$ -tbp geometry, was determined.

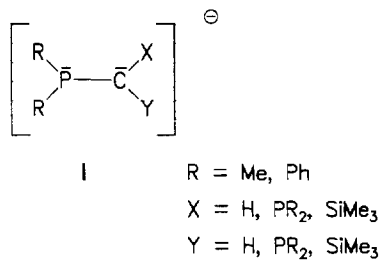
**Keywords:** Group 15; Redox reactions; Phosphinomethanides; Heterocycles; Phosphorus ylides; P–P bond formation

## 1. Introduction

Owing to the ambident nature of phosphinomethanides **I** (Scheme 1), where both carbon and phosphorus are linked together directly and both exhibit the same count of valence electrons and number of bonds, these electron-rich, anionic nucleophiles are ex-

cellent ligands both to hard and soft metal centers [1]. Simple phosphinomethanides (X = Y = H) prefer to bind to an electrophile via carbon or, in certain cases, via carbon and phosphorus. In contrast, with heteroelement substituents at the carbanionic carbon atom (X, Y =  $\text{PR}_2$ ,  $\text{SiMe}_3$ ), phosphorus coordination is often preferred, leading to an ylide-type of bonding. In the case of diphosphinomethanide (Y =  $\text{PMe}_2$ ), a chelating P, P-coordination leads to high phosphine coordination numbers [2–6]. Furthermore, heteroelement substitution at the carbanionic C atom may lead to rearrangement

<sup>\*</sup> Corresponding author.



Scheme 1.

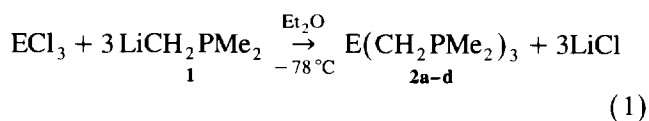
reactions of the resulting coordination compounds, involving the whole skeleton of the complex. This is particularly true for silicon derivatives of phosphinomethanides [7]. A particularly useful feature of phosphinomethanides is their stability toward reduction: thus, low valent species, including examples from main group elements, are stabilized by phosphinomethanide ligands [8]. In contrast, oxidative coupling is easily feasible and, again depending on the substitution pattern, may give C–C, P–C, or P–P coupling products, for instance at titanocene metal centers [9].

This kind of chemistry could also be extended to main group element coordination centers, i.e. BiCl<sub>3</sub>, but stable reduced bismuth species with ligands derived from the phosphinomethanides used could not be obtained [9,10]. A further extension to other Group 15 element halides is described in this paper. Some preliminary accounts have been given previously [11–13].

## 2. Results and discussion

### 2.1. Reaction of ECl<sub>3</sub> (E = P, As, Sb, Bi) and RPCl<sub>2</sub> (R = Me, Ph, <sup>t</sup>Bu, Cy<sub>2</sub>N) with LiCH<sub>2</sub>PMe<sub>2</sub>, 1

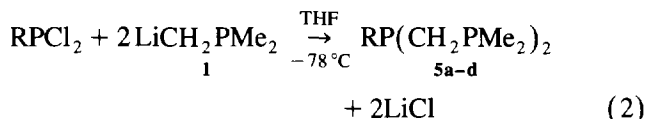
Reaction of ECl<sub>3</sub> (E = P, As, Sb, Bi) with three equivalents of the lithium phosphinomethanide LiCH<sub>2</sub>PMe<sub>2</sub>, **1**, leads to phosphinomethyl-substituted compounds **2a–d** via element–carbon bond formation in high yield (Eq. (1)).



E = P, As, Sb, Bi

Compounds **2a–c** are stable liquids at room temperature and represent a new type of tripod ligand which has been characterized spectroscopically (see Section 3). **2a** has been described previously [14]. Their behavior towards transition metals is currently under investigation. **2d** decomposes slowly at room temperature. After a few weeks, formation of a black precipitate (Bi) is observed. A controlled thermolysis at 60 °C gives a mixture of products due to oxidative coupling reactions (P–C, C–C)

and eventually some hydrolysis: Me<sub>3</sub>P=CH–PMe<sub>2</sub>, **3a** [15], Me<sub>3</sub>P=CH<sub>2</sub>, **3b** [16], PMe<sub>3</sub>, **3c** [17], and Me<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PMe<sub>2</sub>, **4** [10]. The reaction of dichloroorganophosphanes RPCl<sub>2</sub> (R = Me, Ph, <sup>t</sup>Bu, Cy<sub>2</sub>N) with two equivalents of LiCH<sub>2</sub>PMe<sub>2</sub>, **1**, likewise leads to phosphinomethyl derivatives (Eq. (2)):

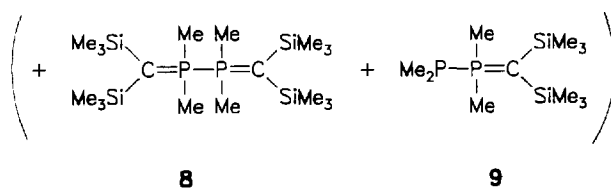
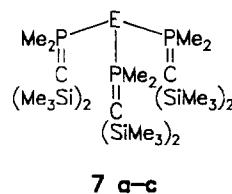
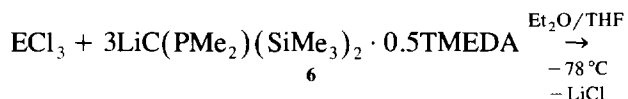


R = **a**: Me, **b**: Ph, **c**: <sup>t</sup>Bu, **d**: Cy<sub>2</sub>N

**5a** has been described previously [18]. **5a–d** are obtained as yellow oils in good yields. They are fully characterized spectroscopically (see Section 3).

### 2.2. Reaction of ECl<sub>3</sub> (E = P, As, Sb, Bi) and RPCl<sub>2</sub> (R = Me, Ph, <sup>t</sup>Bu, Cy<sub>2</sub>N) with LiC(PMe<sub>2</sub>)(SiMe<sub>3</sub>)<sub>2</sub> · 0.5TMEDA, 6

Reaction of ECl<sub>3</sub> (E = P, As, Sb) with three equivalents of LiC(PMe<sub>2</sub>)(SiMe<sub>3</sub>)<sub>2</sub> · 0.5TMEDA, **6**, in all three cases leads to element–phosphorus bond formation and the ylides **7a–c** are obtained, along with some by-products (Eq. (3)):



(3)

E = **a**: P, **b**: As, **c**: Sb

Compounds **7a–c** are the first element–tris(P–ylide)derivatives (tris(alkylidenphosphoranyl)-phosphane and its homologues). For E = P, the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum shows an A<sub>3</sub>B spin-system for **7a** (15%) along with the signals for the by-products **8** [10] (see below) and **9** [7]. **8** obviously is formed by an oxidative coupling reaction of the phosphinomethanide **6**, whereby the correspond-

ing reduced species could not be detected. The way of formation of **9** is not yet clear but obviously due to a skeleton rearrangement involving a  $\text{PMe}_2$  transfer reaction.

**7b** was isolated in pure form (yellow crystals,  $P\bar{1}$ ) and characterized by  $^{31}\text{P}\{^1\text{H}\}$  NMR and by a single crystal X-ray study. The molecular structure of **7b** (Fig. 1, Table 1) is characterized by an arsenic atom with a trigonal pyramidal geometry, surrounded by three ylidic phosphorus atoms (sum of  $\text{P}-\text{As}-\text{P}$  angles:  $316.8^\circ$ ). The  $\text{As}-\text{P}$  distances ( $\text{As1}-\text{P1}$ :  $2.3830(7)$  Å,  $\text{As1}-\text{P2}$ :  $2.3858(7)$  Å,  $\text{As1}-\text{P3}$ :  $2.3874(7)$  Å) are in the range expected for single bonds. The  $\text{P1}-\text{C1}$ ,  $\text{P2}-\text{C2}$  and  $\text{P3}-\text{C3}$  bonds are typical for ylidic phosphorus-carbon bonds. Compound **7c** shows a singlet resonance in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum, but, again, **8** is also formed as a by-product. **7b,c** are unstable in solution; repeated NMR measurements of their sealed NMR samples indicate a decrease of the respective signals for **7b,c** and an increase of the signals for **8** and for  $\text{HC}(\text{PMe}_2)(\text{SiMe}_3)_2$ . In addition, a new AB spin system appears ( $\delta P_A = 12.84$ ,  $\delta P_B = -29.56$ ,  $^2J(P_A P_B) = 84.4$  Hz), which tentatively is assigned to  $\text{Me}_3\text{Si}-\text{PMe}_2=\text{C}(\text{SiMe}_3)-(\text{PMe}_2=\text{C}(\text{SiMe}_3)_2)$ , **7'**. The formation of the ylide **7'** may be understood by an initial  $\text{P}-\text{C}$  coupling reaction and a subsequent silyl rearrangement. For  $\text{E} = \text{Bi}$ , only the bisylide  $[(\text{Me}_3\text{Si})_2\text{C}=\text{PMe}_2]_2$ , **8**, besides elemental

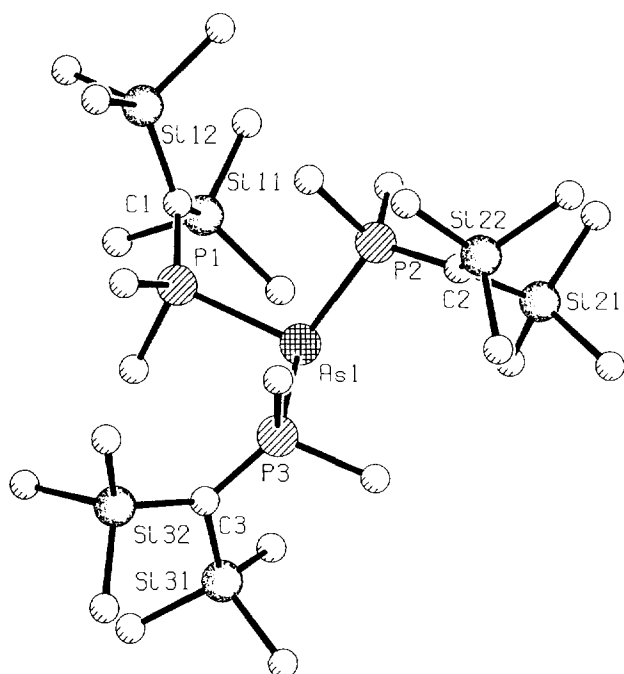
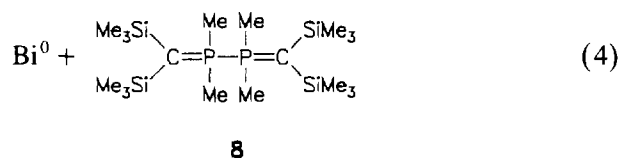
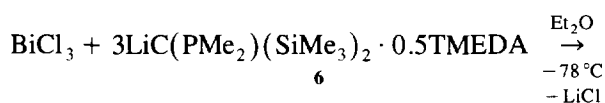


Fig. 1. Molecular structure of **7b** (H atoms omitted).

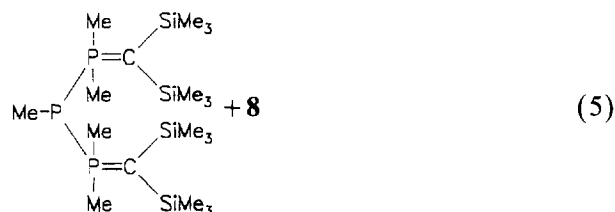
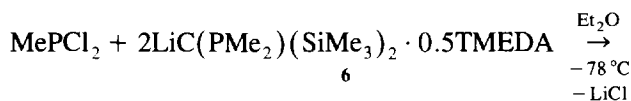
Table 1  
Bond lengths (Å) and angles (deg) for **7b**

As1-P1	2.3830(7)	As1-P2	2.3858(7)
As1-P3	2.3874(7)	P1-C1	1.680(3)
P2-C2	1.684(2)	P3-C3	1.686(2)
Si11-C1	1.858(3)	Si12-C1	1.847(3)
Si21-C2	1.849(2)	Si22-C2	1.839(2)
Si31-C3	1.860(3)	Si32-C3	1.843(3)
P1-As1-P2	104.82(2)	P1-As1-P3	106.06(2)
P2-As1-P3	105.88(2)	C1-P1-As1	116.9(1)
C2-P2-As1	116.96(9)	C3-P3-As1	117.71(9)
P2-C2-Si21	116.4(1)	P2-C2-Si22	126.8(1)
Si22-C2-Si21	116.2(1)	P1-C1-Si12	126.0(2)
P1-C1-Si11	116.3(2)	Si12-C1-Si11	117.1(1)
P3-C3-Si32	126.3(2)	P3-C3-Si31	116.4(1)
Si32-C3-Si31	116.9(1)		

bismuth, is obtained [10]. No Bi-containing compound could be identified (Eq. (4)):



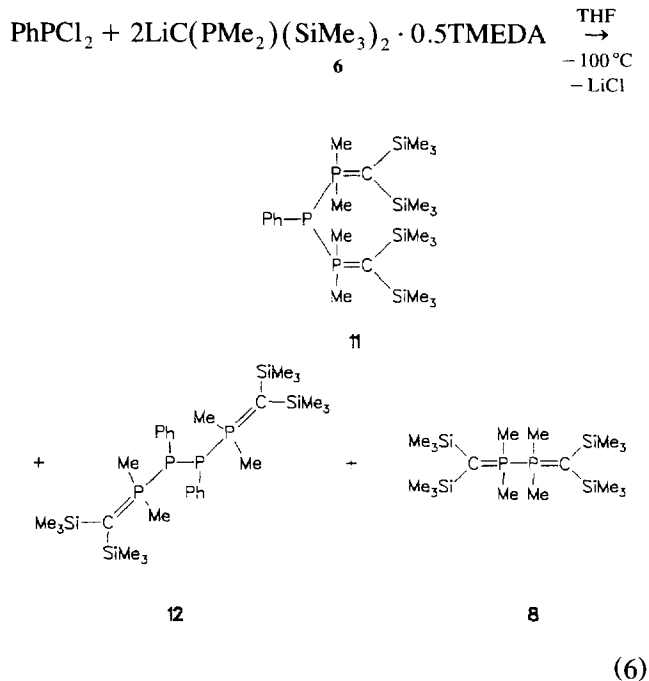
The reaction of dichlororganophosphanes  $\text{RPCl}_2$  ( $\text{R} = \text{Me}$ ,  $\text{Ph}$ ,  $t\text{Bu}$ ,  $\text{Cy}_2\text{N}$ ) with  $\text{LiC}(\text{PMe}_2)(\text{SiMe}_3)_2 \cdot 0.5\text{TMEDA}$ , **6**, leads, at least in part, to some unexpected results. As in the reaction of  $\text{ECl}_3$  (Eq. (3)) with  $\text{LiC}(\text{PMe}_2)(\text{SiMe}_3)_2 \cdot 0.5\text{TMEDA}$ , **6**,  $\text{P}-\text{P}$  bond formation is also observed in the reaction of  $\text{MePCl}_2$  with two equivalents of **6**. The bisylide **10** is obtained in good yield, but traces of **8** are also formed (Eq. (5)):



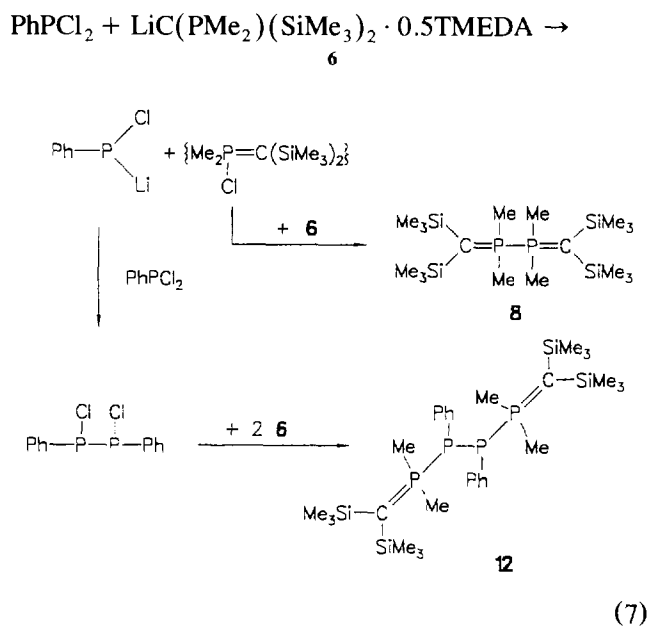
**10**

If the steric demand of  $\text{R}$  in  $\text{RPCl}_2$  is increased, i.e. by reacting  $\text{PhPCl}_2$  with **6**, in addition to **8** and **11** (main product), a new coupling product, the diphosphane-

bridged bisylide **12**, possessing a backbone of four phosphorus atoms, is formed (Eq. (6)):



The formation of **8** and **12** may be easily understood by an initial Li/Cl exchange and subsequent coupling reaction under LiCl elimination (Eq. (7)):



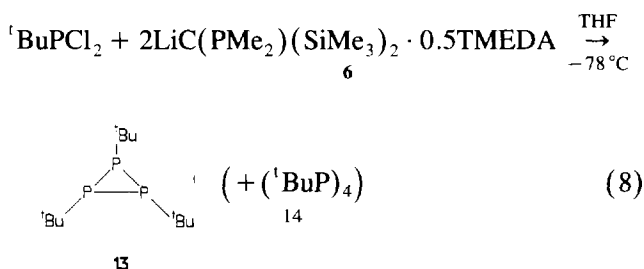
In contrast to other cases, where diphosphanes with different substituents are formed (e.g. Ref. [19]), only one isomer of **12** is observed in solution by  $^{31}\text{P}\{^1\text{H}\}$  NMR. The molecular structure of compound **12** (yellow crystals,  $P2_1/n$ ) in the solid state has been established by a single crystal X-ray study (Fig. 2(a), Table 2). Only the meso isomer is present in the crystal. The

Table 2  
Bond lengths (Å) and angles (deg) for **12**

P1–C11	1.839(1)	P1–P1'	2.2243(7)
P1–P2	2.2516(5)	P2–C9	1.684(1)
P2–C2	1.810(2)	P2–C1	1.813(2)
Si1–C9	1.851(1)	Si2–C9	1.844(1)
C11–P1–P1'	100.81(5)	C11–P1–P2	95.84(4)
P1'–P1–P2	105.15(2)	P2–C9–Si2	123.59(8)
P2–C9–Si1	119.34(8)	Si2–C9–Si1	116.49(7)

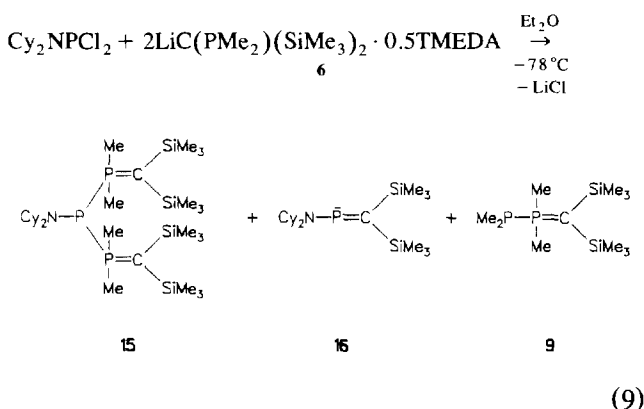
distances P1–P1' (2.2243(7) Å) and P1–P2 (2.2516(5) Å) are in the typical range for P–P single bonds. The geometry at the P1 atom is trigonal pyramidal (sum of the angles 301.8°) whereas the carbanionic C-atoms are planar. The P2–C9 distance with 1.684(1) Å is typical for ylidic phosphorus–carbon bonds. A Newman-projection (Fig. 2(b)) shows the molecule to adopt the sterically most favorable trans-conformation.

With further increase in the steric demand of R in  $\text{RPCl}_2$ , i.e. with  $^t\text{BuPCl}_2$ , **13** and **14** [20] are obtained, but no substitution product (Eq. (8)):



Obviously, reduction of  $^t\text{BuPCl}_2$  occurs, but the nature of the oxidation product(s) is not clear, since several unidentified species are observed by  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy.

In the reaction of  $\text{Cy}_2\text{NPCl}_2$  with two equivalents of  $\text{LiC}(\text{PMe}_2)(\text{SiMe}_3)_2 \cdot 0.5\text{TMEDA}$ , **6**, besides the disubstitution product **15**, the phosphalkene **16** and the ylide **9** are formed (Eq. (9)):



Obviously, besides a P–P bond formation, a P–C bond formation is also possible, leading to the highly crowded

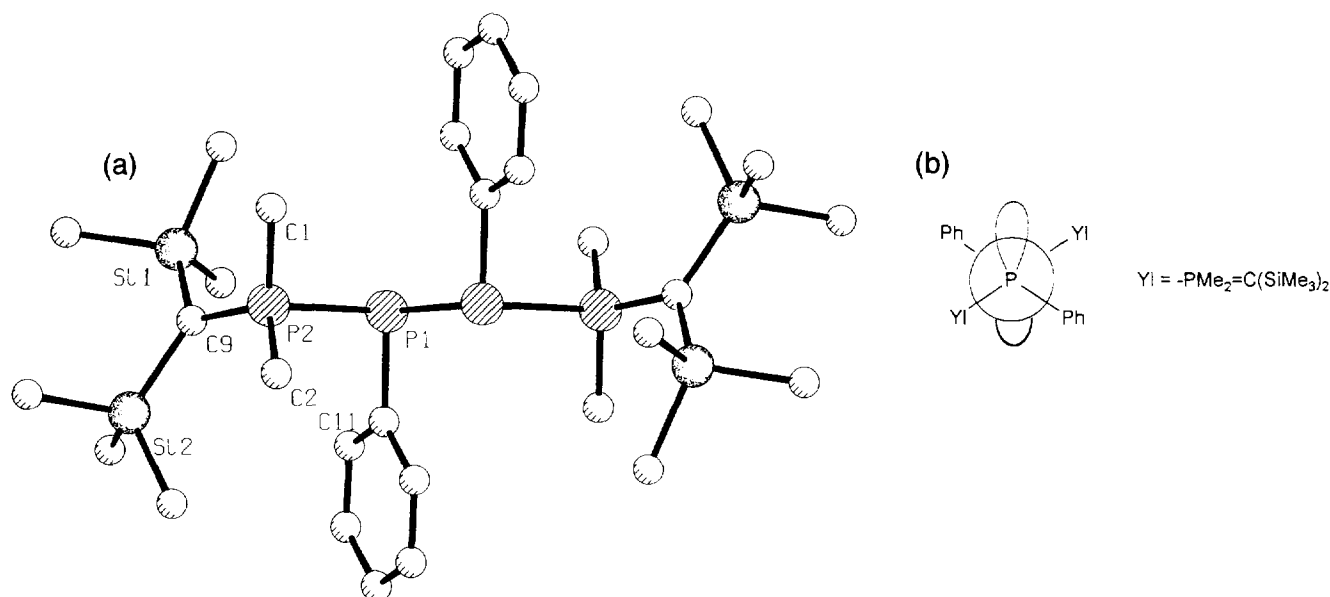
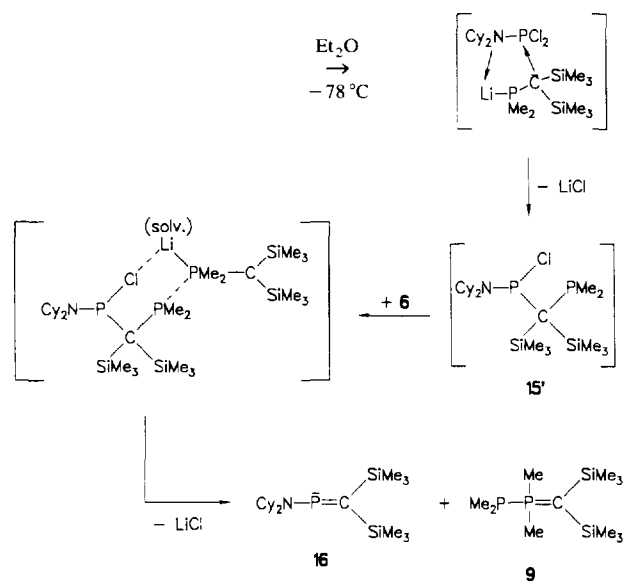
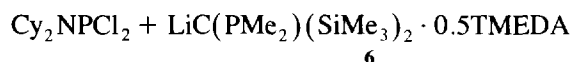


Fig. 2. (a) Molecular structure of **12** (H atoms omitted); (b) Newman projection of **12**.

derivative **15'**. In a 1:1 reaction, this intermediate **15'** can be characterized spectroscopically in solution ( $^{31}\text{P}\{^1\text{H}\}$  NMR:  $\delta\text{P}_A = 167.0$ ,  $\delta\text{P}_B = -59.32$ ,  $J(\text{P}_A\text{P}_B) = 178.9$  Hz). Obviously under the concomitant attack of further **6**, formally  $\text{Me}_2\text{PCLi}$  is eliminated from **15'** and the  $\text{PMe}_2$  group transferred to the phosphinomethanide to give **9** under elimination of  $\text{LiCl}$  (Eq. (10)):

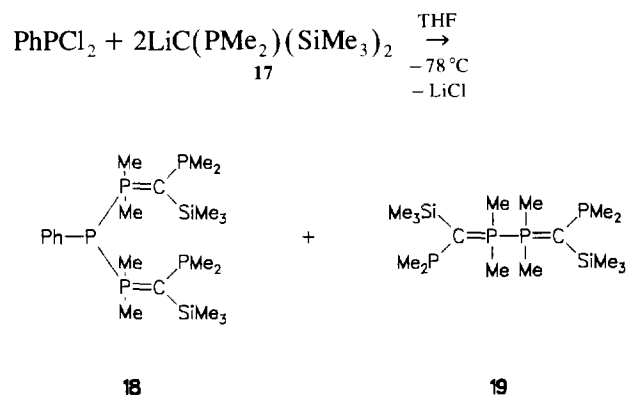


(10)

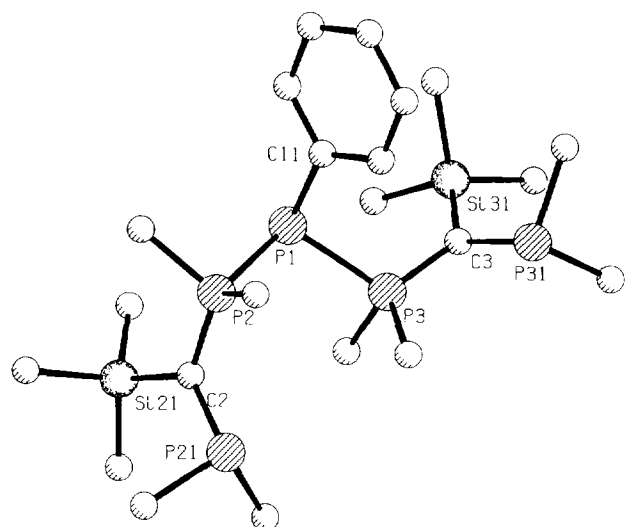
The remaining phosphalkene **16** is characterized by  $^{31}\text{P}\{^1\text{H}\}$  NMR and by mass spectroscopy. The reason for the initial P–C bond formation in this specific case, which is at variance to all other reactions with the phosphinomethanide **6**, probably lies in the specific role of the P–amino substituent: by coordination of this functionality to the lithium atom of the phosphinomethanide, this type of reaction may be facilitated.

### 2.3. Reaction of $\text{RPhCl}_2$ ( $\text{R} = \text{Ph}, \text{'Bu}, \text{Me}$ ) with $\text{LiC}(\text{PMe}_2)_2(\text{SiMe}_3)$ , **17**

The reaction of  $\text{PhPCl}_2$  with two equivalents of  $\text{LiC}(\text{PMe}_2)_2(\text{SiMe}_3)$ , **17**, leads to the phenylphosphane **18** and the bisylide **19** [10]. A reduced species derived from  $\text{PhPCl}_2$ , i.e.  $(\text{PhP})_n$ , could not be detected, however (Eq. (11)):

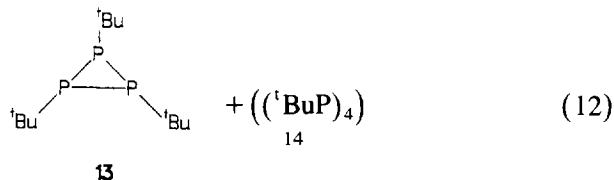
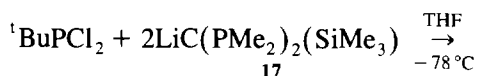


(11)

Fig. 3. Molecular structure of **18** (H atoms omitted).

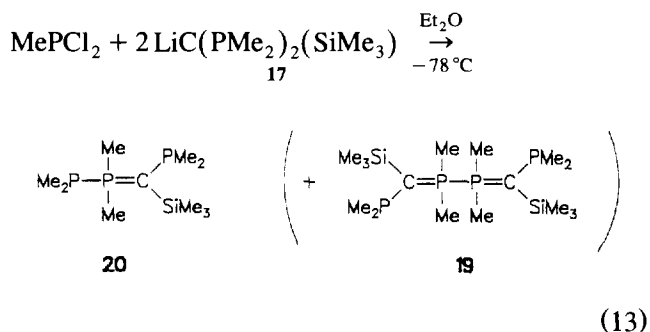
**18** represents a new type of phosphane/phosphorane combination. The two  $\lambda^5$ -phosphorus atoms are connected via a  $\lambda^3$ -phosphorus bridge and their ylidic functionality is completed by terminal phosphane functionalities, thus establishing a new type of chelating ligand. The molecular structure of **18** (yellow crystals, *P1*) has been confirmed by a single crystal X-ray study. Very air-sensitive, yellow crystals are obtained from pentane solution. The structure of **18** is shown in Fig. 3. The central P1-atom is pyramidal, the sum of angles ( $316.5^\circ$ ) reflects the steric demand in the molecule. The P1–P2 (2.2456(6) Å) and P1–P3 (2.2348(6) Å) bonds are in the usual range for P–P single bonds (Table 3). The P2–C2 (1.697(2) Å) and P3–C3 (1.693(2) Å) distances reflect the ylidic character of these bonds. Again, as expected, the carbanionic C-atoms are planar.

The reaction of  $t\text{BuPCl}_2$  with two equivalents of **17** yields the compounds **13** and **14** (Eq. (12)), in analogy to (Eq. (8)):



Again, the fate of the oxidation product(s) could not be established.

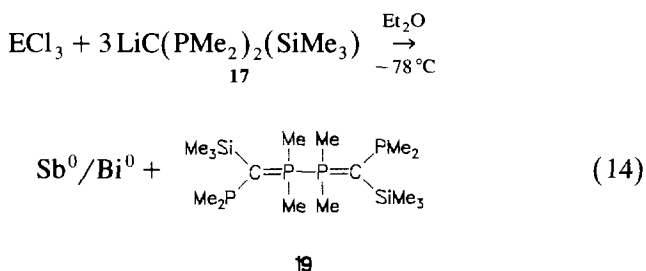
The reaction of  $\text{MePCl}_2$  with two equivalents of  $\text{LiC}(\text{PMe}_2)_2(\text{SiMe}_3)$ , **17**, gives **19** and **20** [7] (Eq. (13)):



No substitution product and no reduced phosphorus compound were detected.

#### 2.4. Reaction of $\text{ECl}_3$ ( $\text{E} = \text{P}, \text{As}, \text{Sb}, \text{Bi}$ ) with $\text{LiC}(\text{PMe}_2)_2(\text{SiMe}_3)$ , **17**

As mentioned earlier, phosphinomethanides undergo oxidative coupling reactions at transition metals, and C–C, C–P and P–P bond formation is feasible. In some cases, reduced metal complexes with the oxidatively coupled phosphinomethanides as ligands are isolable. No such low valent antimony or bismuth species are obtained in the redox reaction of  $\text{LiC}(\text{PMe}_2)_2(\text{SiMe}_3)$ , **17**, with  $\text{ECl}_3$  ( $\text{E} = \text{Sb}, \text{Bi}$ ) (Eq. (14)):

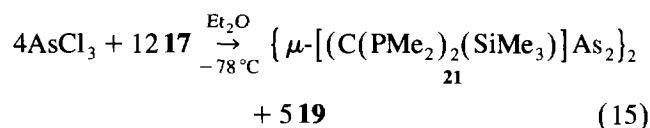


Besides either elemental Sb or Bi, the only product isolated as a yellow oil is the bisylide **19**. In the analogous reaction with the less reducible  $\text{AsCl}_3$ , besides **19**, a partially reduced, mixed valent intermediate

Table 3  
Bond lengths (Å) and angles (deg) for **18**

P1–C11	1.832(2)	P1–P3	2.2348(6)
P1–P2	2.2456(6)	P2–C2	1.697(2)
P3–C3	1.693(2)	P21–C2	1.793(2)
P31–C3	1.797(2)	Si21–C2	1.855(2)
Si31–C3	1.846(2)		
C11–P1–P3	104.41(5)	C11–P1–P2	104.18(5)
P3–P1–P2	107.93(2)	P2–C2–P21	114.37(8)
P21–C2–Si21	118.84(8)	P21–C2–Si21	125.88(8)
P3–C3–P31	112.7(1)	P3–C3–Si31	121.7(1)
P31–C3–Si31	124.57(9)		

**21** is obtained with arsenic in an average oxidation state of 0.5 (Eq. (15)) [12]:



The idealized stoichiometry of Eq. (15) is not fully obeyed, however. Elemental arsenic and some unidentified products are formed as well. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **21** shows an AA'BB' spin system; the presence of two diphosphinomethanide ligands, connected via arsenic coordination centers, may be deduced. The red crystals of **21** ( $P2_1/c$ ) can be easily separated from **19**.

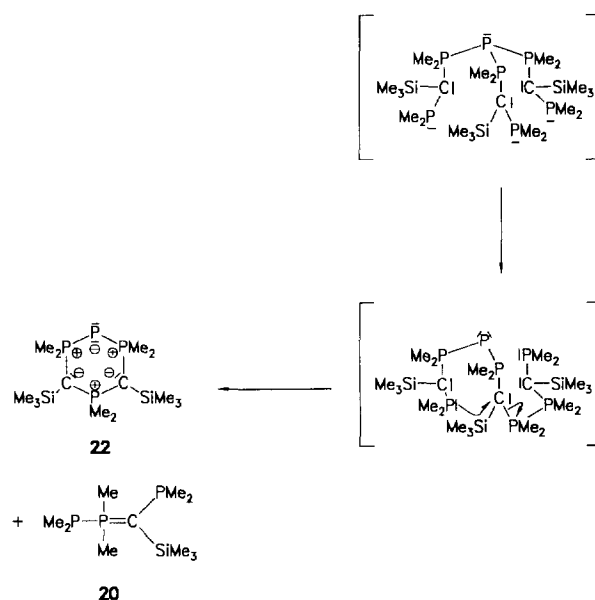
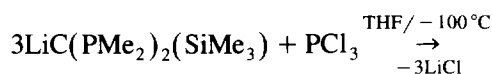
The molecular structure of **21** was determined by a single crystal X-ray study and is shown in Fig. 4. Two diphosphinomethanide ligands each form a bridge between two arsenic atoms of a puckered  $\text{As}_4$  chain. Thus, two five-membered, envelope-shaped  $\text{As}_2\text{P}_2\text{C}$  rings are linked via the arsenic atoms in such a way, that a centrosymmetric, transoid arrangement along the  $\text{As}(1)\text{--As}(1a)$  bond results. The  $\text{As}(1)$  atom deviates by 1.03 Å from a nearly planar  $\text{As}(2)\text{--P}(2)\text{--C}(01)\text{--P}(1)$  chain. Within these rings,  $\text{As}(2)$  is di-coordinate, whereas  $\text{As}(1)$  is tri-coordinate. The  $\text{As}(2)\text{--P}(2)$  bond (2.256(1) Å) involving the di-coordinate arsenic atom, is significantly shorter than the  $\text{As}(1)\text{--P}(1)$  bond (2.301(1) Å), though the latter is the shortest  $\text{As}\text{--P}$  single bond involving tri-coordinate arsenic [21,22]. The different  $\text{As}\text{--As}$  bond lengths ( $\text{As}(2)\text{--As}(1)$ : 2.391(1),  $\text{As}(1)\text{--As}(1a)$ : 2.492(1) Å) reflect the different coordination numbers of  $\text{As}(1)$  and  $\text{As}(2)$ . Both  $\text{P}\text{--C}$  distances ( $\text{P}(1)\text{--C}(01)$ : 1.718(4),  $\text{P}(2)\text{--C}(01)$ : 1.733(4) Å) are relatively short and indicate the partial ylidic character of these bonds, in line with current observations on phosphinomethanide structures. In line with this view, the carbanionic C-atoms are planar. The angle at  $\text{As}(2)$  is only 94.5(1)°, whereas the sum of angles at  $\text{As}(1)$  amounts to 288.4° (Table 4). Particularly interesting is a comparison with other  $\text{As}\text{--As}$  structures, e.g. with  $^1\text{Bu}_6\text{As}_2\text{P}_6$  [21]: in the latter case, the  $\text{As}\text{--As}$  distance (2.441(2) Å) roughly amounts to the average of the

Table 4  
Bond lengths (Å) and angles (deg) for **21**

As1–As2	2.391(1)	As1–As1a	2.492(1)
As1–P1	2.301(1)	As2–P2	2.256(1)
P1–C01	1.718(4)	P2–C01	1.733(4)
P1–As1–As2	90.2(1)	As1a–As1–As2	104.9(1)
As1a–As1–P1	93.3(1)	P2–As2–As1	94.5(1)
C01–P1–As1	112.0(2)	C01–P2–As2	113.6(1)
P2–C01–P1	112.4(2)		

respective bond lengths in **21**. The  $\text{As}\text{--P}$  distances (2.350(3) Å, 2.361(2) Å) are significantly longer, however, in the latter case.

$\text{PCl}_3$ , which is even less reducible than  $\text{AsCl}_3$ , reacts with  $\text{LiC}(\text{PMe}_2)_2(\text{SiMe}_3)$ , **17**, giving an access to reduced phosphorus species in the oxidation state +1. The reaction in THF at  $-78^\circ\text{C}$  and slowly warming up the mixture to room temperature, leads to **20** and **22** according to Eq. (16) [11]:



(16)

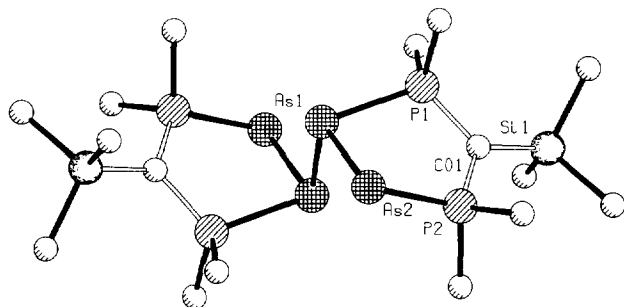
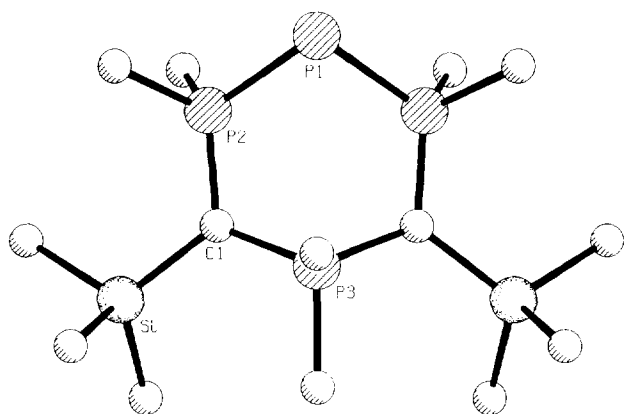


Fig. 4. Molecular structure of **21** (H atoms omitted).

No intermediate is detected, but the reaction sequence seems understandable in the light of Eq. (3). A trisilydic intermediate might be formed and  $\text{P}\text{--P}$  and  $\text{P}\text{--C}$  bond formation and cleavage might occur in a concerted manner, thus generating the ylide **20** and the novel six-membered heterocycle **22**, the latter being obtained as colourless crystals ( $P2_1/m$ ).

This tetraphosphinine derivative ('tetraphosphabenzene'), formally may be regarded as a 'superposition' of

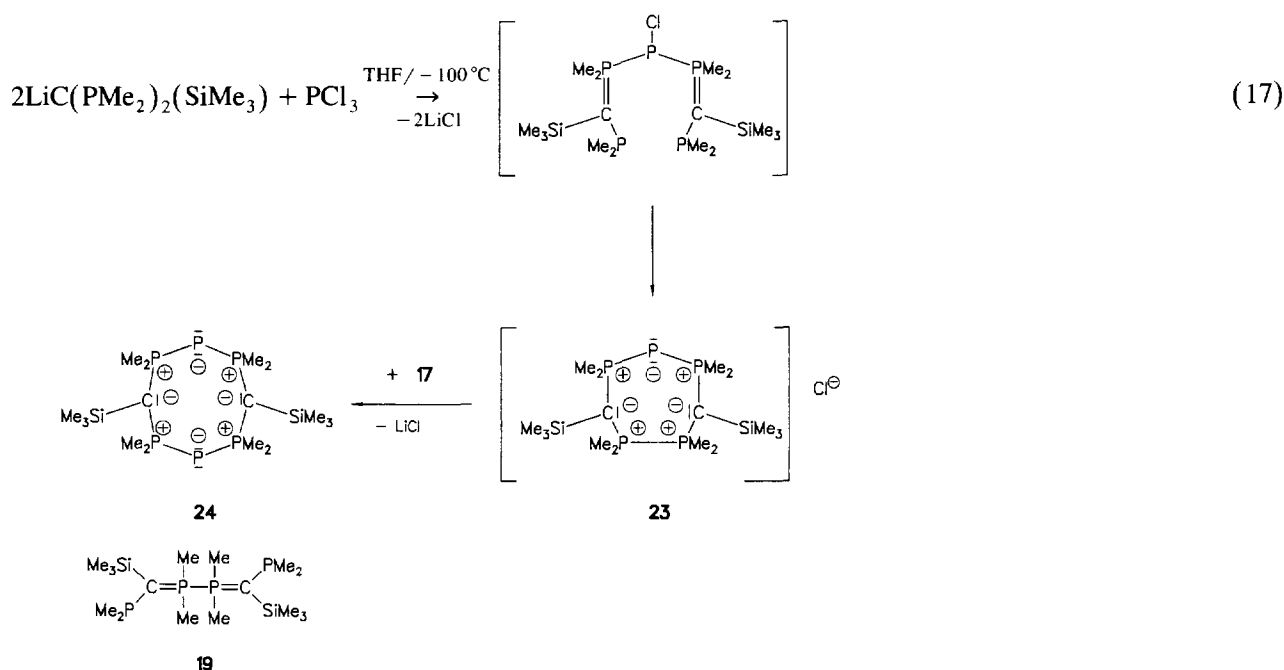
Fig. 5. Molecular structure of **22** (H atoms omitted).

a  $1\lambda^5,3\lambda^5,5\lambda^5$ -triphosphinine [23] and a  $1\lambda^3$  phosphinine [24]. In contrast to this expectation, the heterocycle is not planar, as shown by the molecular structure as determined by a single crystal X-ray study (Fig. 5, Table 5): the molecule is folded along the P1–P3 axis, with the interplanar angle amounting to  $127^\circ$ . This P1–P3 axis encloses a molecular mirror plane. A cyclic change of formal charges ('amphipolar') [11] donates an ylidic character to the endocyclic P–C bonds (P2–C1: 1.725(1) Å, P3–C1: 1.742(2) Å) as well as to the P1–P2 bond (2.134(1) Å) and is responsible for this bond shortening. As expected, the endocyclic carbon atoms are planar. The angle P2–P1–P2a amounts to  $98.1(3)^\circ$ , which compares with  $102.9^\circ$  in 2,6-dimethyl-4-phenyl- $\lambda^3$ -phosphinine [25], and  $102.2(2)^\circ$  in  $\text{Ph}_3\text{P}-\bar{\text{P}}-\text{PPh}_3$  [26]. The coupling product **19** is formed in the reaction of  $\text{PCl}_3$  with three equivalents of **17** in THF at  $-100^\circ\text{C}$  and quickly warming up the mixture to room temperature. As the corresponding reduced species, the P(I)

Table 5  
Bond lengths (Å) and angles (deg) for **22**

P1–P2	2.134(1)	P2–C1	1.725(1)
P3–C1	1.742(2)	Si–C1	1.842(2)
P2–P1–P2a	98.1(3)	P1–P2–C1	116.4(1)
P2–C1–P3	114.7(1)	C1–P3–C1a	117.0(1)
P2–C1–Si	122.0(4)	P3–C1–Si	122.0(1)

derivative **24**, a neutral four-membered ring molecule, was identified. This 'triphosphete' **24** is difficult to separate from **19** and some minor impurities, in particular  $\text{HC}(\text{PMe}_2)_2(\text{SiMe}_3)$ , as a consequence of some hydrolysis. From the yellow oil obtained, **24** crystallizes slowly as faint yellow plates, which were, however, not suitable for a single crystal X-ray study; this impurity of **24** originally led to some uncertainty about the nuclearity of **24**. Since in a related system, an eight-membered analogue of **24** was formulated [27], a dimeric nature of **24**, i.e. an eight-membered ring structure could not be ruled out. An  $\text{AB}_2$  spin system in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum with a characteristic high field shift for the central, dicoordinate P(I) atom with formal charge  $-1$  is indicative for the first triphosphete; 1,3-diphosphetes have been described previously, see Ref. [28]. A possible explanation for the formation of **24** is derived from the observation, that in the respective 1:2 reaction, an ionic intermediate **23** can be isolated. According to the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum, this intermediate contains a seven-membered ring, where the P–P coupling of the two phosphinomethanides, necessary for the redox process and the formation of **19**, already is preformed. Thus, a reaction pathway according to Eq. (17) seems reasonable:

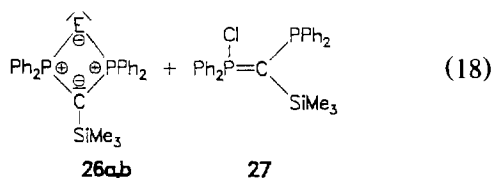
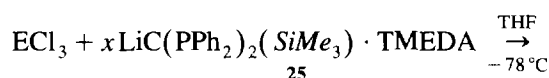




The same results are achieved using a non-polar solvent, i.e. toluene. If a solvent of medium polarity, i.e. diethyl ether, is used, a mixture of **19**, **20**, **22** and **24** is obtained.

### 2.5. Reaction of $ECl_3$ ( $E = P, As, Sb, Bi$ ) and of $Ph_2PCl$ with $LiC(PPh_2)_2(SiMe_3) \cdot TMEDA$ , **25**

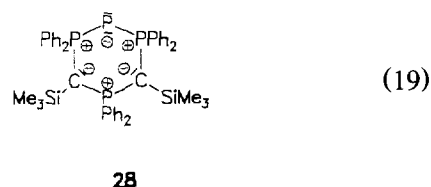
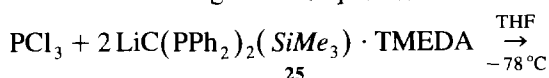
The key for the above-mentioned reactions obviously is the ease of oxidative P–P coupling of the phosphinomethanide ligands. This type of reaction is facilitated by the low steric demand of the  $PMe_2$ -moiety. It is well known, that the coupling of more demanding  $PPh_2$  groups in diphosphinomethanides is much less favorable [29]. Therefore, it seems challenging to replace the lithium diphosphinomethanide  $LiC(PMe_2)_2(SiMe_3)$ , **17**, by its phenyl analogue, i.e.  $LiC(PPh_2)_2(SiMe_3) \cdot TMEDA$ , **25**.



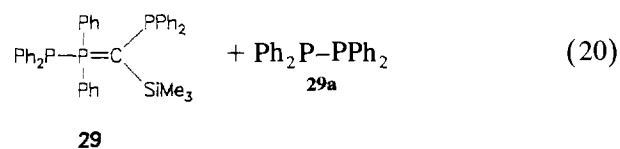
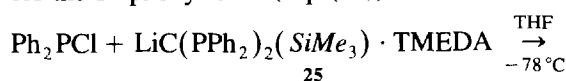
$E = \mathbf{a}: P, \mathbf{b}: As; x = 2, 3$

Reaction of  $ECl_3$  ( $E = P, As$ ) with two or three equivalents of **25** leads to the triphosphete **26a** and its arsenic analogue **26b**, respectively, in good yields along with the chlorophosphorane **27** in both cases (Eq. (18)). Quite remarkably, **27** does not react with an excess of the lithium diphosphinomethanide **25**: coupling in this way does not occur. Therefore, the formation of **26a,b** has to be explained by a Li/Cl exchange reaction, either initially or after the first substitution step in the reaction course. This is the decisive difference for the reactions described above: P–P coupling and formation of a bisylide is not feasible. Therefore, the reactions obviously proceed in a very different manner, though the reaction products, i.e. the formation of the triphosphetes, are comparable. Also comparable is the fact, that as a by-product in the 1:2 reaction (inverse reaction, see Section 3) the P–phenyl analogue to **22** may be identified ( $AB_2C$  spin system,  $\delta(P_A) = -122.81$ ,  $\delta(P_B) = 29.3$ ,  $\delta(P_C) = -3.32$ ,  $^1J(P_A P_B) =$

$282.4 \text{ Hz}$ ,  $^2J(P_B P_C) = 64.0$ ,  $^3J(P_A P_C) = 28.5 \text{ Hz}$ ). i.e. the six-membered ring of **28** (Eq. (19)):

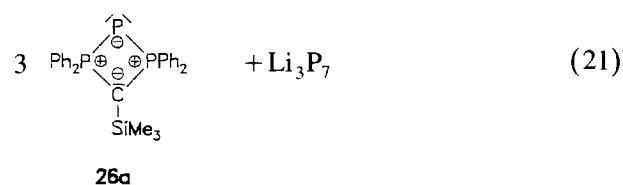
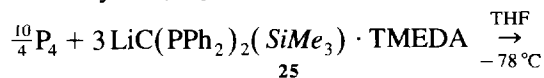


It is not clear, whether the formation of **28** follows the same scheme as in the case of **22**, but **28** is only a minor species in the reaction: the main products are **26a** and **27**. Nevertheless, the possibility of a P–P bond formation in a substitution reaction, which seems a prerequisite for the reaction pathway outlined in Eq. (16) for the formation of **22**, can be demonstrated also for the P–phenyl case (Eq. (20)).



The ylide **29** is obtained along with the diphosphane **29a** as a yellow solid. Quite interestingly, a Li/Cl exchange pathway obviously competes with the substitution reaction and is responsible for the formation of  $Ph_2P-PPh_2$ .

Similar to **24**, the triphosphete **26a** shows an  $AB_2$  spin system in the  $^{31}P\{^1H\}$  NMR spectrum with again a high field shift for the di-coordinate P atom as a consequence of the formal negative charge on it. The coordination shift of the diphosphinomethanide ligand bonded to the formal  $P^+$  and  $As^+$  coordination center amounts to  $\delta = 20.18$  for **26a** and  $\delta = -0.51$  for **26b**. An alternative approach to **26a**, which gives the triphosphete essentially free of the chlorophosphorane **27**, though in modest yield (30%), is the reaction according to (Eq. (21)); similarly, the P–methyl-substituted triphosphete **24** can be obtained by reaction of  $P_4$  and  $Li[C(PMe_2)_2(SiMe_3)]$  in THF, though again only in modest yield [30]:



A similar strategy for the isolation of P(I) derivatives has been described previously by Schmidpeter and Burget [31] (the formation of  $\text{Li}_3\text{P}$  has not been confirmed; however, its formulation in Eq. (21) simply reflects the choice of stoichiometric ratio and the analogy to the work of Schmidpeter and Burget). It is difficult and tedious to separate the chlorophosphorane **27** from the four-membered rings **26a,b**. Nevertheless, crystals of **26a,b** which unexpectedly are not highly air-sensitive, can be grown from the oily mixture and separated mechanically for a single crystal X-ray study.

Both compounds crystallize isotypic in space group  $P\bar{1}$  and possess two crystallographically independent molecules in the asymmetrical unit. These two molecules, a and b, show very similar geometry; therefore, in the following description only molecule a is considered in either case (Figs. 6 and 7, Tables 6 and 7). As usual in phosphinomethanide structures, the carbanionic C1 atom is strictly planar, but the four-membered rings deviate significantly from planarity: P3a and As1a deviate from the plane C1a, P1a, P2a by 0.148(1) Å and 0.177(1) Å respectively (interplanar angle: 4.9° and 5.5° respectively). The P1a/P2a–P3a (2.1489(5) Å/2.1530(6) Å) and the P1a/P2a–As1a (2.2710(7) Å/2.2692(7) Å) distances are within the expected range, as are the P1a/P2a–C1a distances (**26a**: 1.729(1) Å/1.738(1) Å; **26b**: 1.741(2) Å/1.731(2) Å). Very unusual, however, are the small angles at P3a (72.65(2)°) and As1a (69.90(2)°): they are by far the smallest angles for di-coordinate phosphorus and arsenic respectively. For instance, in  $(\text{Pr}_2\text{N})_2\text{P}^\ominus$  the

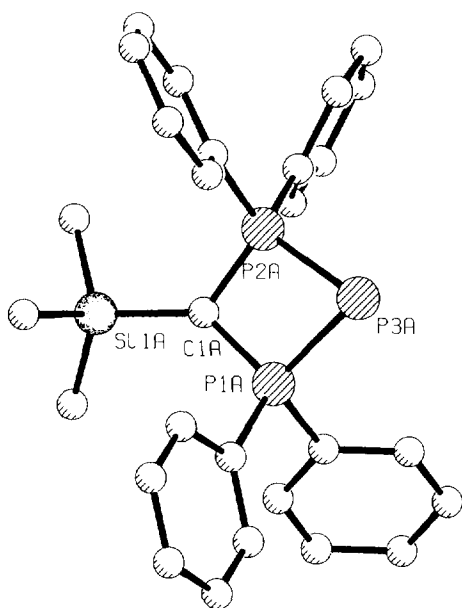


Fig. 6. Molecular structure of **26a** (H atoms omitted). The asymmetrical unit contains two molecules a and b; only one molecule is shown.

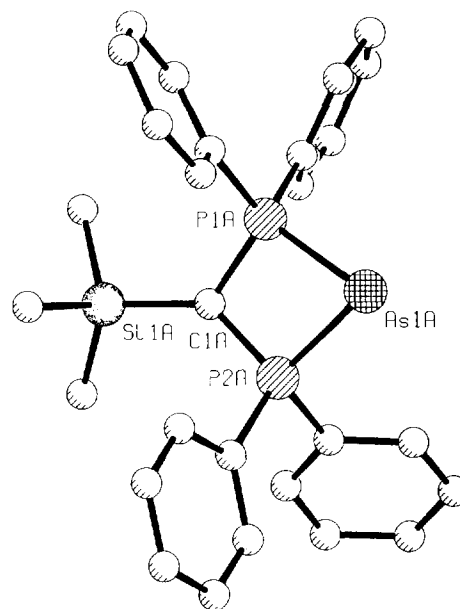


Fig. 7. Molecular structure of **26b** (H atoms omitted). The asymmetrical unit contains two molecules a and b; only one molecule is shown.

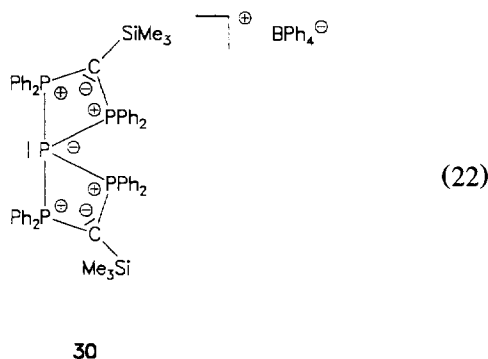
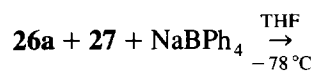
Table 6  
Bond lengths (Å) and angles (deg) for **26a** (the asymmetrical unit contains two molecules a and b)

	Molecule a	Molecule b
P1–P3	2.1489(5)	2.1526(5)
P1–C1	1.729(1)	1.738(1)
P2–P3	2.1530(6)	2.1488(5)
P2–C1	1.738(1)	1.733(1)
P1...P2	2.5483(5)	2.5347(5)
P1–C1–P2	94.64(7)	93.83(7)
C1–P2–P3	96.03(5)	97.07(5)
C1–P1–P3	96.44(5)	96.77(5)
P1–P3–P2	72.65(2)	72.21(2)

Table 7  
Bond lengths (Å) and angles (deg) for **26b** (the asymmetrical unit contains two molecules a and b)

	Molecule a	Molecule b
P1–As1	2.2710(7)	2.2729(7)
P1–C1	1.741(2)	1.740(2)
P2–As1	2.2692(7)	2.2681(7)
P2–C1	1.731(2)	1.730(2)
P1...P2	2.6008(9)	2.5868(9)
P1–C1–P2	97.0(1)	96.4(1)
C1–P2–As1	96.59(8)	97.27(8)
C1–P1–As1	96.21(8)	96.78(8)
P1–As1–P2	69.90(2)	69.45(2)

angle N–P–N is 114.8(2)° [32]; in  $\text{Ph}_3\text{P}-\bar{\text{P}}-\text{PPh}_3^{\oplus}$  the P–P–P angle amounts to 102.2(2)° [26], the C–P–C angle in 2,6-dimethyl-4-phenyl- $\lambda^3$ -phosphinine has been determined as 102.9° [25], and in R–P=C=P–R (R = 2,4,6-*t*-Bu<sub>3</sub>C<sub>6</sub>H<sub>2</sub>) to 100.3(4)° and 99.9(4)° respectively [33]. In **21**, the angle P2–As2–As1 is 94.5° (this work); in As–PPh<sub>2</sub>–CH<sub>2</sub>–C(=CH<sub>2</sub>)–CH<sub>2</sub>–PPh<sub>2</sub><sup>⊕</sup>, the P–As–P angle amounts to 93.0(1)° [34].



One might expect an enhanced nucleophilicity as a consequence of these small angles within a rigid four-membered ring, but respective studies were hampered by the fact, that **26a,b** could not be obtained free of **27** in amounts large enough for reactivity studies. Therefore, the 1:1 mixture of **26a** and **27** obtained according to Eq. (18) was used to generate a suitable electrophile ‘in situ’: by addition of NaBPh<sub>4</sub> to the mixture, the chlorophosphorane obviously is transformed to the respective cation, which adds to the triphosphete to give a salt **30** containing a novel cationic spirocycle (Eq. (22)).

Particularly indicative for the nature of the cation of **30** is the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum: a doublet at  $\delta = 37.73$  and a quintet at  $\delta = -76.26$  ( $J(\text{P}_A\text{P}_B) = 137.3$  Hz), not only demonstrate the presence of four magnetically equivalent phosphorus nuclei around a phosphorus atom (the first PP<sub>4</sub> arrangement) but also the hypervalent nature (comparable with phosphoranides [35]) with a free electron pair at the central P atom due to its high field shift. Obviously, the cation suffers dynamic non-rigidity in solution (pseudorotation): on cooling (–107°C), a  $\Psi$ -tbp ground state structure is revealed by the appearance of an AB<sub>2</sub>C<sub>2</sub> spin system.

From these observations, a classification of this unusual system as the first ten-electron phosphorus cation (P<sup>III</sup>) with a PP<sub>4</sub> framework is derived and confirmed by a single crystal X-ray study. Yellow crystals of **30** (*P*2<sub>1</sub>/*c*) are grown from THF. The distorted  $\Psi$ -tbp geometry of the cation (Fig. 8(a) and Fig. 8(b), Table 8) is reminiscent of similar structures of the neutral

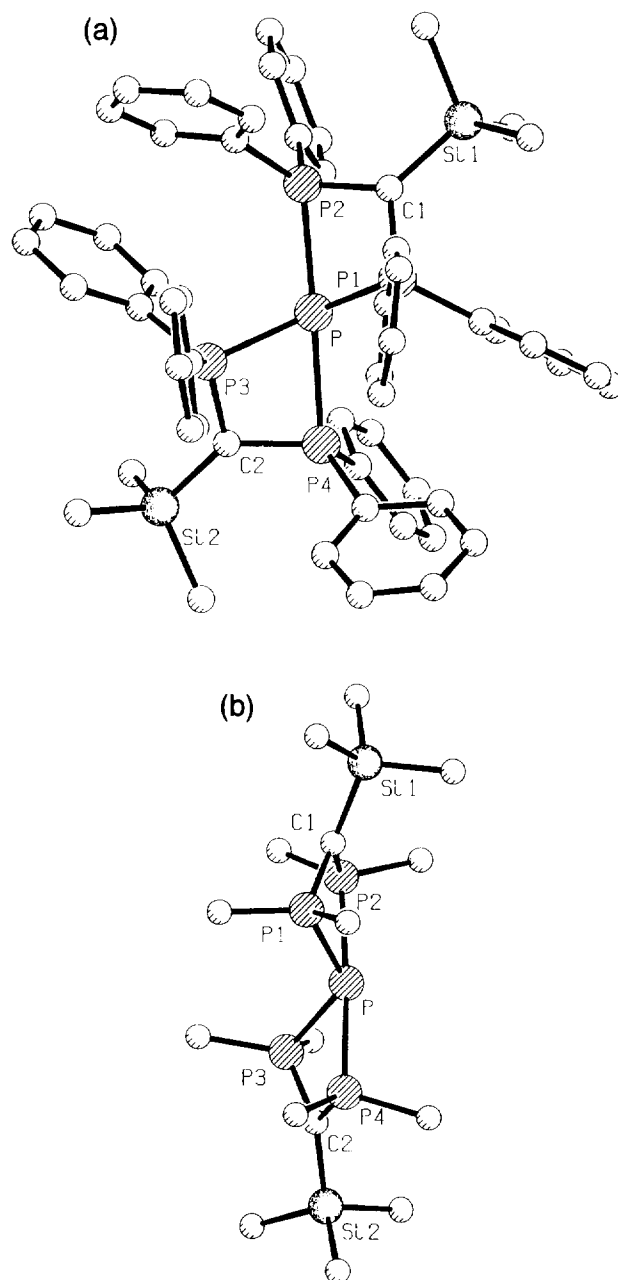


Fig. 8. (a,b) Crystal structure of the cation of **30** (H atoms omitted).

Table 8  
Bond lengths (Å) and angles (deg) for the cation of **30**

P–P1	2.2012(9)	P–P2	2.4077(8)
P–P4	2.4616(9)	P–P3	2.2009(9)
P1–C1	1.712(2)	P2–C1	1.737(2)
P3–C2	1.718(2)	P4–C2	1.733(2)
P1–P–P2	71.15(3)	P1–P–P3	125.12(4)
P1–P–P4	107.81(3)	P2–P–P3	107.22(3)
P2–P–P4	176.41(3)	P3–P–P4	70.41(3)
P–P1–C1	93.97(8)	P–P2–C1	86.46(8)
P–P3–C2	95.06(8)	P–P4–C2	85.98(9)
P1–C1–P2	102.3(1)	P3–C2–P4	102.8(1)

Table 9  
Comparison of the cation of **30** with the Group 14 element homologues

	$E[C(X)(PMe_2)_2]_2$				
	X = SiMe <sub>3</sub>	X = SiMe <sub>3</sub>	X = PMe <sub>2</sub>	X = PMe <sub>2</sub>	X = SiMe <sub>3</sub>
E–P <sub>ax</sub> (Å)	2.41/2.46	2.51/2.61	2.55/2.93	2.79/2.84	2.80/2.85
E–P <sub>eq</sub> (Å)	2.20/2.20	2.27/2.27	2.36/2.36	2.60/2.60	2.59/2.62
P <sub>ax</sub> EP <sub>ax</sub> (°)	176	154	147	143	142
P <sub>eq</sub> EP <sub>eq</sub> (°)	125	112	108	106	97
ΔEN	?	0.4	0.1	0.4	0.4

molecules  $E[C(PMe_2)_2X]_2$  (E = Si [8], Ge [36], Sn [37], Pb<sup>1</sup> [39]; X = PMe<sub>2</sub>, SiMe<sub>3</sub>) — which might be expected (isoelectronic exchange of Si for P<sup>+</sup>). However, there are also some unexpected differences: a compilation of relevant data is given in Table 9.

In all cases, the axial element–phosphorus distances are longer than the equatorial ones; but, in the cation of **30** both axial distances are not very different from each other. In the case of E = Ge, this difference is particularly drastic and has been explained by the non-polarity of the Ge–P bonds [36]. In the sense of this argument, the P–P bonds in **30**<sup>+</sup> should be quite polar; indeed, this most likely is the case, as it is also evidenced by a representation of **30**<sup>+</sup> with formal charges. There are some other differences between **30**<sup>+</sup> and its isoelectronic counterparts: the four-membered chelate rings are not planar, but to a much larger extent than in the case of **26a,b**: C1/C2 deviates from the plane P1, P, P2 and P3, P, P4 by 0.480(2) Å and 0.467(3) Å (interplane angle: 26.3° and 25.7°) respectively. Furthermore, the angles P2–P–P4 and P1–P–P3 are much closer to those expected for an ideal tbp-structure at the expense of the orthogonality of the equatorial plane to the axial bonds (the P1–P–P2 and P3–P–P4 bond angles within the four-membered rings amount only to 71.2(1)° and 70.4(1)° respectively, which is close to the respective value in **26a**). Quite remarkably, this folding of the two four-membered rings occurs in the opposite direction towards the ‘empty’ side of the central phosphorus, thus increasing the distance between the two C–silyl groups. Both the two carbanionic C atoms (C1 and C2) are again planar, however. These observations, at least in part, may be ascribed to the steric demand of the

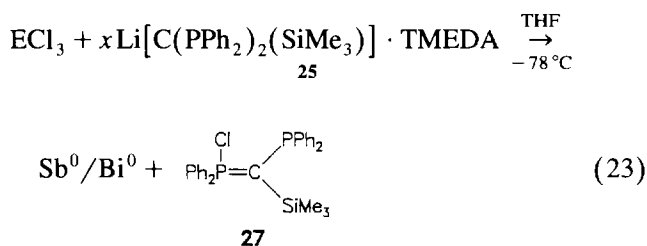
P–phenyl and C–SiMe<sub>3</sub> groups. The classification of a novel compound in terms of known structures is highly desirable for the sake of understanding and clarity.

Unfortunately, **30** cannot be classified in this way unambiguously. On the one hand, the cation of **30** may be regarded as a ten-electron double phosphane adduct to a phosphonium cation [32,40–42] (in short: ten-electron phosphonium cation), which readily relates to the cationic charge and the similarity to the Group 14 element analogues. Simple (eight-electron) base [40] and, in particular, phosphane adducts of phosphonium cations are known [43]. Less convincing would be a notation as a phosphane adduct to a trionium phosphane [41] — this would divide the P<sub>4</sub> phosphonium set of substituents into a 3:1 ratio. Nevertheless, this formulation clarifies that the cation of **30** may be regarded as the first representative of a phosphane–phosphane adduct — admittedly involving very special phosphanes. On the other hand, the cation of **30** electronically (neglecting of charge) resembles phosphoranide anions. Therefore, it alternatively may be classified as tetraphosphonium phosphoranide, the charge in part being balanced by two internal carbanion moieties. Neither description really is satisfying, thus underlining the novelty and unprecedented nature of this species.

Finally, it should be noted that the tendency for the formation of the cation **30**<sup>+</sup> is very high: also GeCl<sub>2</sub> is an efficient Cl<sup>−</sup> acceptor in the system **26a/27**, and **30**<sup>+</sup> is formed. In contrast, without the presence of the triphosphete **26a**, **27** does not react with NaBPh<sub>4</sub> to give the respective cation. Therefore, the chlorine abstraction of **27** has to be understood as an equilibrium reaction, which is shifted to the right by the action of **26a** to give **30**<sup>+</sup>; with AlCl<sub>3</sub> as a chloride acceptor, however, a new species is observed by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy (δP = +67.26), which tentatively is assigned to the ‘diphosphino carbocation’ (Ph<sub>2</sub>P)<sub>2</sub>(Me<sub>3</sub>Si)C<sup>⊕</sup>. The pure chlorophosphorane, free

<sup>1</sup> For Pb[C(PPh<sub>2</sub>)<sub>2</sub>(SiMe<sub>3</sub>)<sub>2</sub>] see Ref. [38].

of **26a** or **26b**, is available by the reaction according to Eq. (23), though the yield is modest.



E = Sb, Bi; x = 2, 3

### 3. Experimental part

All compounds were prepared and handled in dry nitrogen atmosphere. A two-armed glass frit, as described previously [44], was used together with conventional vacuum line techniques. Sodium–potassium alloys were employed for drying and storage of the solvents, which were redistilled immediately prior to use.  $\text{PCl}_3$ ,  $\text{AsCl}_3$ ,  $\text{PhPCl}_2$ ,  $\text{MePCl}_2$ ,  $\text{Ph}_2\text{PCl}$  were dried over  $\text{K}_2\text{CO}_3$  and distilled prior to use.  $\text{LiCH}_2\text{PMe}_2$ , **1**,  $\text{LiC}(\text{PMe}_2)(\text{SiMe}_3)_2 \cdot 0.5\text{TMEDA}$ , **6**,  $\text{LiC}(\text{PMe}_2)_2(\text{SiMe}_3)$ , **17**,  $\text{LiC}(\text{PPh}_2)_2(\text{SiMe}_3) \cdot \text{TMEDA}$ , **25**, were synthesized according to the literature [45,46]. Instrumentation, spectroscopy and elemental analysis were as described previously [47]. Not in every case was satisfactory elemental analysis data obtained. In many cases,  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR data reflect the presence of complex spin systems, e.g.  $\text{X}_n\text{AA}'\text{X}'_n$ ,  $\text{X}_n\text{A}(\text{A}'\text{X}'_n)_n$ ,  $\text{AA}'\text{X}$ ,  $\text{A}(\text{A}')_2\text{X}$  etc., where non-binomial multiplets and virtual coupling phenomena predominate. These multiplets are denoted as 'd', 't', 'm', etc. and  $N$  the distance of the two outermost lines (hertz) is given instead of  $J$  values.

#### 3.1. Preparation of compounds

##### 3.1.1. General procedure

Very similar procedures were used throughout; three methods (a)–(c) were selected to describe the individual syntheses of compounds.

**3.1.1.1. Method (a).**  $\text{ECl}_3/\text{RPCl}_2/\text{Ph}_2\text{PCl}$  (E = P, As, Sb, Bi; R = Ph,  $\text{Cy}_2\text{N}$ ,  $^t\text{Bu}$ , Me) was added to a solution of  $\text{LiC}(\text{PR}_2)(\text{X})(\text{Y})$  (R = Me, Ph; X =  $\text{PMe}_2$ ,  $\text{PPh}_2$ ,  $\text{SiMe}_3$ ; Y = H,  $\text{SiMe}_3$ ) in 30–40 ml of  $\text{Et}_2\text{O}$  (THF) at  $-78^\circ\text{C}$  ( $-100^\circ\text{C}$ ). After warming up to room temperature, the suspension was stirred for 12 h. The solvent was replaced by pentane and, after filtration and evaporation of the pentane, the residue was characterized by spectroscopy. In cases of low solubility of the product(s) in pentane, further extraction of the remaining solid was

performed with toluene and, subsequently, with THF (in rare cases).

**3.1.1.2. Method (b).** A solution of  $\text{ECl}_3/\text{RPCl}_2$  (E = P, As, Sb, Bi; R = Me, Ph,  $^t\text{Bu}$ ,  $\text{Cy}_2\text{N}$ ) in 10–15 ml of THF was added slowly to a solution of  $\text{LiC}(\text{PR}_2)(\text{X})(\text{Y})$  (R = Me, Ph; X =  $\text{PMe}_2$ ,  $\text{PPh}_2$ ,  $\text{SiMe}_3$ ; Y = H,  $\text{SiMe}_3$ ) in 30–40 ml of THF at  $-78^\circ\text{C}$  ( $-100^\circ\text{C}$ ). The further procedure follows method (a).

**3.1.1.3. Method (c).** Solid  $\text{ECl}_3/\text{RPCl}_2$  (E = Sb, Bi; R =  $\text{Cy}_2\text{N}$ ) and  $\text{LiC}(\text{PR}_2)(\text{X})(\text{Y})$  (R = Me, Ph; X =  $\text{PMe}_2$ ,  $\text{PPh}_2$ ,  $\text{SiMe}_3$ ; Y = H,  $\text{SiMe}_3$ ) were combined at  $-78^\circ\text{C}$  and 40 ml  $\text{Et}_2\text{O}$  (THF) was slowly condensed onto the solids in the reaction vessel through the vacuum line. The further procedure follows method (a).

##### 3.1.2. Preparation of $\text{E}(\text{CH}_2\text{PMe}_2)_3$ , E = P, As, Sb, Bi, **2a–d**

**3.1.2.1.  $\text{P}(\text{CH}_2\text{PMe}_2)_3$ , **2a.**** The preparation of **2a** followed that described previously [14].

**3.1.2.2.  $\text{As}(\text{CH}_2\text{PMe}_2)_3$ , **2b.**** Method (a), solvent:  $\text{Et}_2\text{O}$ ,  $-78^\circ\text{C}$ . 0.45 ml (5.35 mmol)  $\text{AsCl}_3$ ; 1.40 g (17.07 mmol)  $\text{LiCH}_2\text{PMe}_2$ , **1**. Yield: 1.36 g (84.5%), orange oil.

NMR ( $\text{C}_6\text{D}_6$ ,  $+25^\circ\text{C}$ ):  $^{31}\text{P}\{^1\text{H}\}$ :  $\delta(\text{P}) = -54.18$  (s).  $^{13}\text{C}\{^1\text{H}\}$ :  $\delta(\text{C}) = 29.50$  (dt,  $^1J(\text{PC}) = 33.3$ ,  $^3J(\text{PC}) = 7.7$  Hz,  $\text{CH}_2$ ), 16.35 ('m',  $N = 19.8$  Hz,  $\text{PMe}_2$ ).  $^1\text{H}$ :  $\delta(\text{H}) = 1.61$ , (s, 6H,  $\text{CH}_2$ ), 0.97 (d,  $^2J(\text{PH}) = 2.4$  Hz, 18H,  $\text{PMe}_2$ ). MS (EI, 70 eV):  $m/e = 285$  ( $\text{M}^+ - \text{Me}$ , 100%), 209 ( $\text{M}^+ - \text{Me}$ ,  $- \text{PMe}_3$ , 44.58%), 75 ( $\text{CH}_2\text{PMe}_2^+$ , 93.41%). Anal. Found: C, 33.75; H, 7.36.  $\text{C}_9\text{H}_{24}\text{AsP}_3$  (300.13). Calc.: C, 36.02; H, 8.06%.

**3.1.2.3.  $\text{Sb}(\text{CH}_2\text{PMe}_2)_3$ , **2c.**** Method (c), solvent:  $\text{Et}_2\text{O}$ ,  $-78^\circ\text{C}$ . 1.02 g (4.47 mmol)  $\text{SbCl}_3$ ; 1.17 g (14.27 mmol)  $\text{LiCH}_2\text{PMe}_2$ , **1**. Yield: 1.26 g (81.3%), colorless oil.

NMR ( $\text{C}_6\text{D}_6$ ,  $+25^\circ\text{C}$ ):  $^{31}\text{P}\{^1\text{H}\}$ :  $\delta(\text{P}) = -50.46$  (s).  $^{13}\text{C}\{^1\text{H}\}$ :  $\delta(\text{C}) = 18.10$  (dt,  $^1J(\text{PC}) = 28.6$ ,  $^3J(\text{PC}) = 6.9$  Hz,  $\text{CH}_2$ ), 17.70 ('m',  $N = 16.6$  Hz,  $\text{PMe}_2$ ).  $^1\text{H}$ :  $\delta(\text{H}) = 1.50$ , (d,  $^2J(\text{PH}) = 1.0$  Hz, 6H,  $\text{CH}_2$ ), 0.97 (d,  $^2J(\text{PH}) = 2.9$  Hz, 18H,  $\text{PMe}_2$ ). MS (EI, 70 eV,  $^{121}\text{Sb}/^{123}\text{Sb}$ ):  $m/e = 331/333$  ( $\text{M}^+ - \text{Me}$ , 28.87%/21.39%), 255/257 ( $\text{M}^+ - \text{Me}$ ,  $- \text{PMe}_3$ , 11.90%/8.91%), 75 ( $\text{CH}_2\text{PMe}_2^+$ , 100%). Anal. Found: C, 29.40; H, 6.50.  $\text{C}_9\text{H}_{24}\text{P}_3\text{Sb}$  (346.97). Calc.: C, 31.16; H, 6.97%.

**3.1.2.4.  $\text{Bi}(\text{CH}_2\text{PMe}_2)_3$ , **2d.**** Method (c), solvent:  $\text{Et}_2\text{O}$ ,  $-78^\circ\text{C}$ . 1.19 g (3.77 mmol)  $\text{BiCl}_3$ ; 1.02 g (12.44 mmol)  $\text{LiCH}_2\text{PMe}_2$ , **1**. Yield: 1.54 g (94.0%), yellow oil.

NMR ( $\text{C}_6\text{D}_6$ ,  $+25^\circ\text{C}$ ):  $^{31}\text{P}\{^1\text{H}\}$ :  $\delta(\text{P}) = -47.00$  (s). (Thermolysis of **2d** (NMR tube,  $60^\circ\text{C}$ , 8 d):  $^{31}\text{P}\{^1\text{H}\}$ : mixture of **2d** (15%),  $\text{Me}_3\text{P}_\text{A}=\text{CH}-\text{P}_\text{B}\text{Me}_2$ , **3a** (43%):

$\delta(P_A) = 0.95$ ,  $\delta(P_B) = -59.58$  (AB spin system,  $^2J(P_A P_B) = 142.6$  Hz),  $Me_3P=CH_2$ , **3b** (9%);  $\delta(P) = 2.65$ , (s),  $PMe_3$ , **3c** (31%),  $\delta(P) = -62.15$ ,  $Me_2PCH_2CH_2PMe_2$ , **4** (2%);  $\delta(P) = -49.00$ .  $^{13}C\{^1H\}$ :  $\delta(C) = 21.00$  ('m',  $N = 28.2$  Hz,  $CH_2$ ), 19.35 ('m',  $N = 15.5$  Hz,  $PMe_2$ ).  $^1H$ :  $\delta(H) = 1.92$  (d,  $^2J(PH) = 1.4$  Hz, 6H,  $CH_2$ ), 0.96 (d,  $^2J(PH) = 2.5$  Hz, 18H,  $PMe_2$ ). MS (EI, 70 eV):  $m/e = 419$  ( $M^+ - Me$ , 22.53%), 209 ( $Bi^+$ , 19.81%), 75 ( $CH_2PMe_2^+$ , 100).

3.1.3. Preparation of  $R-P(CH_2PMe_2)_2$ ,  $R = Me, Ph, ^iBu, Cy_2N$ , **5a–d**

3.1.3.1. **5a**. The preparation of **5a** was described previously [18].

3.1.3.2.  $Ph-P_A(CH_2P_BMe_2)_2$ , **5b**. Method (b), solvent: THF,  $-78^\circ C$ . 1.05 ml (7.75 mmol)  $PhPCl_2$ ; 1.40 g (17.07 mmol)  $LiCH_2PMe_2$ , **1**. Yield: 2.0 g (100%), yellow oil.

NMR ( $C_6D_6$ ,  $+25^\circ C$ ):  $^{31}P\{^1H\}$ :  $\delta(P_A) = -36.09$ ,  $\delta(P_B) = -54.04$  ( $AB_2$  spin system,  $^2J(P_A P_B) = 95.6$  Hz).  $^{13}C\{^1H\}$ :  $\delta(C) = 140.27$  (dt,  $^1J(PC) = 10.5$ ,  $^3J(PC) = 5.5$  Hz, *ipso*-C), 132.82 (d,  $^2J(PC) = 20.2$  Hz, C2, C6), 129.1 (s, C4), 128.5 (d,  $^3J(PC) = 7.4$  Hz, C3, C5), 32.72 ('t'd,  $AA'BX$  spin system,  $N = 46.0$  Hz,  $^1J(PC) = 9.2$  Hz,  $CH_2$ ),  $\delta = 15.81$  ('m',  $N = 56.1$  Hz,  $PMe_2$ ).  $^1H$ :  $\delta(H) = 7.6$ – $7.1$  (m, 5H, Ph), 1.66/1.83 (d,  $^2J(HCH) = 13.6$  Hz, 4H,  $CH_2$ ), 0.88 (s, 12H,  $PMe_2$ ). MS (EI, 70 eV):  $m/e = 243$  ( $M^+ - Me$ , 100%), 75 ( $CH_2PMe_2^+$ , 62.4%). Anal. Found: C, 54.60; H, 7.96.  $C_{12}H_{21}P_3$  (258.22). Calc.: C, 55.82; H, 8.20%.

3.1.3.3.  $^iBu-P_A(CH_2P_BMe_2)_2$ , **5c**. Method (b), solvent: THF,  $-78^\circ C$ . 0.76 g (4.78 mmol)  $^iBuPCl_2$ ; 0.83 g (10.12 mmol)  $LiCH_2PMe_2$ , **1**. Yield: 1.01 g, yellow oil ( $^{31}P\{^1H\}$  NMR: mixture of  $Me_3P=CH-PMe_2$ , **3a** (10%), **5c** (70%),  $(^iBuP)_3$ , **13** (8%),  $(^iBuP)_4$ , **14** (2%) and unidentified impurities (10%).

**5c**: NMR ( $C_6D_6$ ,  $+25^\circ C$ ):  $^{31}P\{^1H\}$ :  $\delta(P_A) = -16.73$ ,  $\delta(P_B) = -53.09$  ( $AB_2$  spin system,  $^2J(P_A P_B) = 102.4$  Hz).  $^{13}C\{^1H\}$ :  $\delta(C) = 33.33$  ('t'd,  $AA'BX$  spin system,  $N = 18.1$  Hz,  $^1J(PC) = 5.0$  Hz,  $CH_2$ ), 27.31 (d,  $^2J(PC) = 13.8$  Hz,  $(CH_3)_3C-P$ ), 16.03 ('m',  $N = 29.7$  Hz,  $PMe_2$ ).

3.1.3.4.  $Cy_2N-P_A(CH_2P_BMe_2)_2$ , **5d**. Method (c), solvent: THF,  $-78^\circ C$ . 0.79 g (2.80 mmol)  $Cy_2NPCl_2$ ; 0.5 g (6.10 mmol)  $LiCH_2PMe_2$ , **1**. Yield: 0.62 g, orange oil ( $^{31}P\{^1H\}$  NMR: mixture of **5d** (75%) and unidentified impurities (25%).

**5d**: NMR ( $C_6D_6$ ,  $+25^\circ C$ ):  $^{31}P\{^1H\}$ :  $\delta(P_A) = 20.12$ ,  $\delta(P_B) = -55.68$  ( $AB_2$  spin system,  $^2J(P_A P_B) = 110.4$  Hz).  $^1H$ :  $\delta(H) = 1.17$ – $1.74$  (m, 22H,  $Cy_2N$ ), 1.06 ('m',  $N = 6.8$  Hz, 4H,  $CH_2$ ), 0.16 (s, 12H,  $PMe_2$ ).

3.1.4. Preparation of  $E(PMe_2=C(SiMe_3)_2)_3$ ,  $E = P, As, Sb$ , **7a–c**

3.1.4.1.  $P_B(P_AMe_2=C(SiMe_3)_2)_3$ , **7a**. Method (b), solvent: THF,  $-100^\circ C$ . 0.22 ml (2.52 mmol)  $PCl_3$ ; 2.41 g (8.47 mmol)  $LiC(PMe_2)(SiMe_3)_2 \cdot 0.5TMEDA$ , **6**. Yield: 1.71 g, red oil and orange crystals ( $^{31}P\{^1H\}$  NMR: mixture of **7a** (15%), **8** (26%),  $(Me_2P)PMe_2=C(SiMe_3)_2$ , **9** (18%), and  $HC(PMe_2)(SiMe_3)_2$  (41%).

**7a**: NMR ( $C_6D_6$ ,  $+25^\circ C$ ):  $^{31}P\{^1H\}$ :  $\delta(P_A) = 15.08$ ,  $\delta(P_B) = -39.09$  ( $A_3B$  spin system,  $^1J(P_A P_B) = 360.8$  Hz).  $^1H$ :  $\delta(H) = 1.75$  ('d',  $N = 10.8$  Hz, 18H,  $PMe_2$ ), 0.36 (s, 54H,  $SiMe_3$ ).

3.1.4.2.  $As(PMe_2=C(SiMe_3)_2)_3$ , **7b**. Method (b), solvent: THF,  $-100^\circ C$ . 0.20 ml (2.38 mmol)  $AsCl_3$ /2.25 g (7.91 mmol)  $LiC(PMe_2)(SiMe_3)_2 \cdot 0.5TMEDA$ , **6**. Yield: 1.23 g (70.28%), yellow crystals.

NMR ( $C_6D_6$ ,  $+25^\circ C$ ):  $^{31}P\{^1H\}$ :  $\delta(P) = 13.51$  (s) (repeated measurement of the sample after four weeks;  $^{31}P\{^1H\}$ : mixture of **7b** (10%),  $[(Me_3Si)_2C=PMe_2]_2$ , **8** (70%),  $Me_3Si-P_BMe_2=C(SiMe_3)(P_AMe_2=C(SiMe_3)_2)$ , **7'** (10%);  $\delta(P_A) = 12.84$ ,  $\delta(P_B) = -29.56$  ( $AB$  spin system,  $^2J(P_A P_B) = 84.4$  Hz) and  $HC(PMe_2)(SiMe_3)_2$  (10%).  $^{13}C\{^1H\}$ :  $\delta(C) = 6.2$ – $7.0$  (br, unresolved signal,  $SiMe_3$  and  $PMe_2$ ).  $^1H$ :  $\delta(H) = 1.7$  (br, 18H,  $PMe_2$ ), 0.28 (s, 54H,  $SiMe_3$ ). Anal. Found.: C, 41.54; H, 9.44.  $C_{27}H_{72}AsP_3Si_6$  (733.221). Calc.: C, 44.23; H, 9.89%.

3.1.4.3.  $Sb(PMe_2=C(SiMe_3)_2)_3$ , **7c**. Method (a), solvent:  $Et_2O$ ,  $-78^\circ C$ . 0.51 g (2.23 mmol)  $SbCl_3$ ; 2.07 g (7.28 mmol)  $LiC(PMe_2)(SiMe_3)_2 \cdot 0.5TMEDA$ , **6**. Yield: 1.33 g, brown oil and brown crystals ( $^{31}P\{^1H\}$  NMR: mixture of **7c** (50%), **8** (25%), and  $HC(PMe_2)(SiMe_3)_2$  (25%).

**7c**: NMR ( $C_6D_6$ ,  $+25^\circ C$ ):  $^{31}P\{^1H\}$ :  $\delta(P) = -1.11$  (s) (repeated measurement of the sample after four weeks;  $^{31}P\{^1H\}$ : mixture of **7c** (10%),  $[(Me_3Si)_2C=PMe_2]_2$ , **8** (40%),  $Me_3Si-P_BMe_2=C(SiMe_3)(P_AMe_2=C(SiMe_3)_2)$ , **7'** (10%);  $\delta(P_A) = 12.84$ ,  $\delta(P_B) = -29.56$  ( $AB$  spin system,  $^2J(P_A P_B) = 84.4$  Hz) and  $HC(PMe_2)(SiMe_3)_2$  (40%).  $^1H$ :  $\delta(H) = 1.73$  ('d',  $N = 10.3$  Hz, 18H,  $PMe_2$ ), 0.29 (s, 54H,  $SiMe_3$ ). MS (CI-VE,  $^{121}Sb/^{123}Sb$ ):  $m/e = 556/558$  ( $M^+ - HC(PMe_2)(SiMe_3)_2$ , 10.84%/9.25%), 368/370 ( $M^+ - HC(PMe_2)(SiMe_3)_2 - Me_2C(SiMe_3)_2$ , 100%/87.42%). Anal. Found: C, 41.55; H, 9.55.  $C_{27}H_{72}P_3SbSi_6$  (780.047). Calc.: C, 41.57; H, 9.30%.

3.1.5. Preparation of  $Me-P_B(P_AMe_2=C(SiMe_3)_2)_2$ , **10**  
Method (a), solvent:  $Et_2O$ ,  $-78^\circ C$ . 0.31 ml (3.46 mmol)  $MePCl_2$ ; 2.06 g (7.24 mmol)

$\text{LiC}(\text{PMe}_2)(\text{SiMe}_3)_2 \cdot 0.5 \text{ TMEDA}$ , **6**. Yield: 1.65 g, orange oil ( $^{31}\text{P}\{^1\text{H}\}$  NMR: mixture of **10** (64%), **8** (3%),  $\text{HC}(\text{PMe}_2)(\text{SiMe}_3)_2$  (19%) and unidentified impurities (14%).

NMR ( $\text{C}_6\text{D}_6$ , +25 °C):  $^{31}\text{P}\{^1\text{H}\}$ :  $\delta(\text{P}_A) = 8.18$ ,  $\delta(\text{P}_B) = -64.06$  ( $A_2B$  spin system,  $^1J(\text{P}_A\text{P}_B) = 295.7 \text{ Hz}$ ).  $^1\text{H}$ :  $\delta(\text{H}) = 2.09$  (s, 3H, PMe), 1.38 ('d',  $N = 28.3 \text{ Hz}$ , 12H, PMe<sub>2</sub>), 0.17 (s, 36H, SiMe<sub>3</sub>).

### 3.1.6. Preparation of $\text{Ph-P}_B[\text{P}_A\text{Me}_2 = \text{C}(\text{SiMe}_3)_2]_2$ , **11** and $[\text{PhP}_B\text{-P}_A\text{Me}_2 = \text{C}(\text{SiMe}_3)_2]_2$ , **12**

Method (b), solvent: THF, -100 °C. 0.49 ml (3.62 mmol)  $\text{PhPCl}_2$ ; 2.26 g (7.94 mmol)  $\text{LiC}(\text{PMe}_2)(\text{SiMe}_3)_2 \cdot 0.5 \text{ TMEDA}$ , **6**. Yield: 2.25 g, yellow oil and yellow crystals ( $^{31}\text{P}\{^1\text{H}\}$  NMR: mixture of **8** (8%), **11** (70%), **12** (8%) and  $\text{HC}(\text{PMe}_2)(\text{SiMe}_3)_2$  (14%).

**11**: NMR ( $\text{C}_6\text{D}_6$ , +25 °C):  $^{31}\text{P}\{^1\text{H}\}$ :  $\delta(\text{P}_A) = +8.5$ ,  $\delta(\text{P}_B) = -26.57$ , ( $A_2B$  spin system,  $^1J(\text{P}_A\text{P}_B) = 317.6 \text{ Hz}$ ).  $^{13}\text{C}\{^1\text{H}\}$ :  $\delta(\text{C}) = 138.14$  (dt,  $^1J(\text{PC}) = 19.3$ ,  $^3J(\text{PC}) = 6.1 \text{ Hz}$ , *ipso*-C), 130–135 (m, C2–C6), 6.72 (m,  $N = 10.5 \text{ Hz}$ , PMe<sub>2</sub>), 2.04 (s, SiMe<sub>3</sub>).  $^1\text{H}$ :  $\delta(\text{H}) = 7.3$  (m, 5H, Ph), 1.41 (br, 12H, PMe<sub>2</sub>), 0.29 (s, 36H, SiMe<sub>3</sub>).

**12**: NMR ( $\text{C}_6\text{D}_6$ , +25 °C):  $^{31}\text{P}\{^1\text{H}\}$ :  $\delta(\text{P}_{AA'}) = 12.84$ ,  $\delta(\text{P}_{BB'}) = -41.92$  ( $AA'BB'$  spin system, calc.:  $^1J(\text{P}_A\text{P}_A) = \pm 228.4$ ,  $^3J(\text{P}_B\text{P}_B) = \pm 15.7$ ,  $^1J(\text{P}_A\text{P}_B) = 294.9$ ,  $^2J(\text{P}_A\text{P}_B) = \mp 7.2 \text{ Hz}$ ).  $^{13}\text{C}\{^1\text{H}\}$ :  $\delta(\text{C}) = 128$ – $138$  (Ph), 6.51 (m,  $N = 3.9 \text{ Hz}$ , PMe<sub>2</sub>), 1.36 (s, SiMe<sub>3</sub>).  $^1\text{H}$ :  $\delta = 7.0$ – $7.7$  (m, 10H, Ph), 0.83 ('d',  $J = 11.7 \text{ Hz}$ , 12H, PMe<sub>2</sub>), 0.19 (s, 36H, SiMe<sub>3</sub>). MS (CI + VE):  $m/e = 654$  ( $M^+$ , 42%), 327 ( $M^+/2$ , 17.94%).

### 3.1.7. Preparation of $(^i\text{BuP})_3$ , **13**, and $(^i\text{BuP})_4$ , **14**

Method (b), solvent: THF, -78 °C. 0.92 g (5.78 mmol)  $^i\text{BuPCl}_2$ ; 3.62 g (12.72 mmol)  $\text{LiC}(\text{PMe}_2)(\text{SiMe}_3)_2 \cdot 0.5 \text{ TMEDA}$ , **6**. Yield: 2.05 g, orange oil ( $^{31}\text{P}\{^1\text{H}\}$  NMR: mixture of **13** (55%), **14** (5%) and  $\text{HC}(\text{PMe}_2)(\text{SiMe}_3)_2$  (40%).

**13**: NMR ( $\text{C}_6\text{D}_6$ , +25 °C):  $^{31}\text{P}\{^1\text{H}\}$ :  $\delta(\text{P}_A) = -71.0$ ,  $\delta(\text{P}_B) = -109.6$  ( $A_2B$  spin system,  $^1J(\text{P}_A\text{P}_B) = 201.1 \text{ Hz}$ ). **14**: NMR ( $\text{C}_6\text{D}_6$ , +25 °C):  $^{31}\text{P}\{^1\text{H}\}$ :  $\delta(\text{P}) = -58.1$  (s); (cf. Ref.[20]).

### 3.1.8. Preparation of $\text{Cy}_2\text{N-P}_A(\text{P}_B\text{Me}_2 = \text{C}(\text{SiMe}_3)_2)_2$ , **15**, and $\text{Cy}_2\text{N-P} = \text{C}(\text{SiMe}_3)_2$ , **16**

Method (c), solvent: Et<sub>2</sub>O, -78 °C. 0.57 g (2.02 mmol)  $\text{Cy}_2\text{NPCl}_2$ ; 1.15 g (4.04 mmol)  $\text{LiC}(\text{PMe}_2)(\text{SiMe}_3)_2 \cdot 0.5 \text{ TMEDA}$ , **6**. Yield: 1.16 g, yellow oil ( $^{31}\text{P}\{^1\text{H}\}$  NMR: mixture of  $\text{Me}_2\text{P-PMe}_2 = \text{C}(\text{SiMe}_3)_2$ , **9** (40%), **15** (20%), **16** (40%).

**15**: NMR ( $\text{C}_6\text{D}_6$ , +25 °C):  $^{31}\text{P}\{^1\text{H}\}$ :  $\delta(\text{P}_A) = 43.45$ ,  $\delta(\text{P}_B) = 13.29$  ( $AB_2$  spin system,  $^1J(\text{P}_A\text{P}_B) = 389.4 \text{ Hz}$ ). **16**: NMR ( $\text{C}_6\text{D}_6$ , +25 °C):  $^{31}\text{P}\{^1\text{H}\}$ :  $\delta(\text{P}) = 315.60$  (s). MS (CI + VE):  $m/e = 369.1$  ( $M^+$ , 10.01%).

### 3.1.9. Preparation of $\text{Ph-P}_A(\text{P}_B\text{Me}_2 = \text{C}(\text{P}_C\text{Me}_2)(\text{SiMe}_3)_2)$ , **18**, and $[(\text{Me}_2\text{P})(\text{Me}_3\text{Si})\text{C} = \text{PMe}_2]_2$ , **19**

Method (b), solvent: THF, -78 °C. 0.30 ml (2.29 mmol)  $\text{PhPCl}_2$ ; 1.05 g (4.90 mmol)  $\text{LiC}(\text{PMe}_2)_2(\text{SiMe}_3)$ , **17**. Yield: 1.05 g, yellow oil ( $^{31}\text{P}\{^1\text{H}\}$  NMR: mixture of **18** (40%), **19** (25%),  $\text{HC}(\text{PMe}_2)_2(\text{SiMe}_3)$  (25%) and unidentified impurities (10%).

**18**: NMR ( $\text{C}_6\text{D}_6$ , +25 °C):  $^{31}\text{P}\{^1\text{H}\}$ :  $\delta(\text{P}_A) = -27.59$ ,  $\delta(\text{P}_B) = 16.28$ ,  $\delta(\text{P}_C) = -38.76$  ( $ABB'CC'$  spin system; calc.:  $^1J(\text{P}_A\text{P}_B) = 307.4$ ,  $^3J(\text{P}_A\text{P}_C) = 15.0$ ,  $^2J(\text{P}_B\text{P}_C) = 176.6$ ,  $^2J(\text{P}_B\text{P}_B) = 9.0$ ,  $^4J(\text{P}_B\text{P}_C) = 10.0$ ,  $^6J(\text{P}_C\text{P}_C) = 13.0 \text{ Hz}$ ). Anal. Found: C, 49.20, H, 8.78.  $\text{C}_{22}\text{H}_{47}\text{P}_5\text{Si}_2$  (522.65). Calc.: C, 50.56; H, 9.06%.

### 3.1.10. Preparation of $\text{Me}_2\text{P}_C\text{-P}_A\text{Me}_2 = \text{C}(\text{P}_B\text{Me}_2)(\text{SiMe}_3)$ , **20**

Method (a), solvent: Et<sub>2</sub>O, -78 °C. 0.34 ml (3.79 mmol)  $\text{MePCl}_2$ ; 1.72 g (8.03 mmol)  $\text{LiC}(\text{PMe}_2)_2(\text{SiMe}_3)$ , **17**. Yield: 1.61 g, orange oil ( $^{31}\text{P}\{^1\text{H}\}$  NMR: mixture of **19** (20%), **20** (40%) and  $\text{HC}(\text{PMe}_2)_2(\text{SiMe}_3)$  (40%).

**20**: NMR ( $\text{C}_6\text{D}_6$ , +25 °C):  $^{31}\text{P}\{^1\text{H}\}$ :  $\delta(\text{P}_A) = 12.65$ ,  $\delta(\text{P}_B) = -39.01$ ,  $\delta(\text{P}_C) = -58.10$  ( $ABC$  spin system,  $^2J(\text{P}_A\text{P}_B) = 156.8$ ,  $^1J(\text{P}_A\text{P}_C) = 210.6$ ,  $^3J(\text{P}_B\text{P}_C) = 23.6 \text{ Hz}$ ). MS (CI + VE):  $m/e = 269$  ( $M^+ + 1$ , 20.57%).

### 3.1.11. Preparation of $[\mu\text{-}[\text{C}(\text{PMe}_2)_2(\text{SiMe}_3)]\text{As}_2]_2$ , **21**

Method (a), solvent: Et<sub>2</sub>O, -78 °C. 0.22 ml (2.62 mmol)  $\text{AsCl}_3$ ; 1.82 g (8.50 mmol)  $\text{LiC}(\text{PMe}_2)_2(\text{SiMe}_3)$ , **17**. Yield: 0.65 g (35%).

$^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , RT):  $\delta(\text{P}_{AA'}) = 42.20$ ,  $\delta(\text{P}_{BB'}) = 41.80$  ( $AA'BB'$  spin system, not fully resolved),  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_5\text{CD}_3$ , -90 °C): fully resolved  $AA'BB'$  spin system, calc.:  $\delta(\text{P}_{AA'}) = 43.29$ ,  $\delta(\text{P}_{BB'}) = 40.13$ ,  $^3J(\text{P}_A\text{P}_A) = \pm 51.3$ ,  $^5J(\text{P}_B\text{P}_B) = \mp 0.8$ ,  $^2J(\text{P}_A\text{P}_B) = J(\text{P}_A\text{P}_B) = \pm 110.8$ ,  $^4J(\text{P}_A\text{P}_B) = J(\text{P}_A\text{P}_B) = \pm 2.3 \text{ Hz}$ .  $^{13}\text{C}\{^1\text{H}\}$ :  $\delta(\text{C}) = 21.4$  (br, PMe<sub>2</sub>), 1.40 (s, SiMe<sub>3</sub>).

### 3.1.12. Preparation of $\overline{\text{P}_A\text{-P}_B\text{Me}_2\text{-C}(\text{SiMe}_3)\text{-P}_C\text{Me}_2\text{-C}(\text{SiMe}_3)\text{P}_B\text{Me}_2}$ , **22**

Method (b), solvent: THF, -100 °C. 0.168 ml (1.93 mmol)  $\text{PCl}_3$ ; 1.24 g (5.79 mmol)  $\text{LiC}(\text{PMe}_2)_2(\text{SiMe}_3)$ , **17**. Yield: 1.05 g, yellow oil and colorless crystals. ( $^{31}\text{P}\{^1\text{H}\}$  NMR: mixture of **20** (30%), **22** (30%) and  $\text{HC}(\text{PMe}_2)_2(\text{SiMe}_3)$  (40%).

**22**: NMR ( $\text{C}_6\text{D}_6$ , +25 °C):  $^{31}\text{P}\{^1\text{H}\}$ :  $\delta(\text{P}_A) = -140.36$ ,  $\delta(\text{P}_B) = 5.48$ ,  $\delta(\text{P}_C) = 13.50$  ( $AB_2C$  spin system  $^1J(\text{P}_A\text{P}_B) = 348.3$ ,  $^3J(\text{P}_A\text{P}_C) = 12.7$ ,  $^2J(\text{P}_B\text{P}_C) = 24.3 \text{ Hz}$ ).

### 3.1.13. Preparation of $[\overline{\text{P}_A\text{-P}_B\text{Me}_2\text{-C}(\text{SiMe}_3)\text{-P}_C\text{Me}_2\text{-C}(\text{SiMe}_3)\text{-P}_B\text{Me}_2}]^+ \text{Cl}^-$ , **23**

Method (a), solvent: THF, -100 °C. 0.24 ml (2.75 mmol)  $\text{PCl}_3$ ; 1.17 g (5.46 mmol)

LiC(PMe<sub>2</sub>)<sub>2</sub>(SiMe<sub>3</sub>), **17**. Yield: 0.61 g (46.0%), yellow solid.

NMR (C<sub>6</sub>D<sub>6</sub>, +25 °C): <sup>31</sup>P{<sup>1</sup>H}: δ(P<sub>A</sub>) = -119.26, δ(P<sub>B</sub>) = 19.45, δ(P<sub>C</sub>) = 23.24 (AB<sub>2</sub>C<sub>2</sub> spin system, <sup>1</sup>J(P<sub>A</sub>P<sub>B</sub>) = 366.5, <sup>2</sup>J(P<sub>B</sub>P<sub>C</sub>) = 8.6, <sup>3</sup>J(P<sub>A</sub>P<sub>C</sub>) = 0 Hz.

### 3.1.14. Preparation of $\overline{P_A-P_BMe_2-C(SiMe_3)-P_BMe_2}$ , **24**

Method (a), solvent: THF, -100 °C. 0.24 ml (2.75 mmol) PCl<sub>3</sub>; 1.92 g (8.96 mmol) LiC(PMe<sub>2</sub>)<sub>2</sub>(SiMe<sub>3</sub>), **17**. Yield: 1.67 g, orange oil and orange crystals (<sup>31</sup>P{<sup>1</sup>H} NMR: mixture of **19** (40%), **24** (40%) and HC(PMe<sub>2</sub>)<sub>2</sub>(SiMe<sub>3</sub>) (20%).

**24**: NMR (C<sub>6</sub>D<sub>6</sub>, +25 °C): <sup>31</sup>P{<sup>1</sup>H}: δ(P<sub>A</sub>) = -109.53, δ(P<sub>B</sub>) = 7.86 (AB<sub>2</sub> spin system, <sup>1</sup>J(P<sub>A</sub>P<sub>B</sub>) = 250.7 Hz).

### 3.1.15. Preparation of $\overline{P_A-P_BPh_2-C(SiMe_3)-P_BPh_2}$ , **26a** and (Cl)(Ph)<sub>2</sub>P<sub>A</sub> = C(P<sub>B</sub>Ph<sub>2</sub>)(SiMe<sub>3</sub>), **27**

Method (a), solvent: THF, -78 °C. 0.18 ml (2.1 mmol) PCl<sub>3</sub>; 2.66 g (4.60 mmol) LiC(PPh<sub>2</sub>)<sub>2</sub>(SiMe<sub>3</sub>) · TMEDA, **25**. Yield: 2.1 g, orange oil and orange crystals (<sup>31</sup>P{<sup>1</sup>H} NMR: mixture of **26a** (30%), **27** (30%), HC(PPh<sub>2</sub>)<sub>2</sub>(SiMe<sub>3</sub>) (20%) and unidentified impurities (20%).

**26a**: NMR (C<sub>6</sub>D<sub>6</sub>, +25 °C): <sup>31</sup>P{<sup>1</sup>H}: δ(P<sub>A</sub>) = -86.31, δ(P<sub>B</sub>) = 20.18 (AB<sub>2</sub> spin system, <sup>1</sup>J(P<sub>A</sub>P<sub>B</sub>) = 261.0 Hz). <sup>13</sup>C{<sup>1</sup>H}: δ(C) = 128.0–140.0 (m, Ph), 2.61 (t, <sup>3</sup>J(PC) = 3.3 Hz, SiMe<sub>3</sub>). <sup>1</sup>H: δ(H) = 6.9–8.0 (m, 20H, Ph), -0.03 (s, 9H, SiMe<sub>3</sub>). MS (CI + VE): *m/e* = 487 (M<sup>+</sup> + 1, 100%).

**27**: NMR (C<sub>6</sub>D<sub>6</sub>, +25 °C): <sup>31</sup>P{<sup>1</sup>H}: δ(P<sub>A</sub>) = 70.15, δ(P<sub>B</sub>) = 0.15 (AB spin system, <sup>2</sup>J(P<sub>A</sub>P<sub>B</sub>) = 164.0 Hz). <sup>1</sup>H: δ(H) = 6.60–7.90 (m, 20H, Ph), -0.22 (s, 9H, SiMe<sub>3</sub>). MS (CI + VE): *m/e* = 490 (M<sup>+</sup>, 8.17%).

### 3.1.16. Preparation of $\overline{As-PPh_2-C(SiMe_3)-PPh_2}$ , **26b** and (Cl)(Ph)<sub>2</sub>P = C(PPh<sub>2</sub>)(SiMe<sub>3</sub>), **27**

Method (b), solvent: THF, -78 °C. 0.11 ml (1.32 mmol) AsCl<sub>3</sub>; 1.76 g (3.04 mmol) LiC(PPh<sub>2</sub>)<sub>2</sub>(SiMe<sub>3</sub>) · TMEDA, **25**. Yield: 1.3 g, orange oil and solid (<sup>31</sup>P{<sup>1</sup>H} NMR: mixture of **26b** (40%), **27** (40%), HC(PPh<sub>2</sub>)<sub>2</sub>(SiMe<sub>3</sub>) (20%).

**26b**: NMR (C<sub>6</sub>D<sub>6</sub>, +25 °C): <sup>31</sup>P{<sup>1</sup>H}: δ(P) = -0.51 (s). <sup>1</sup>H: δ(H) = 6.60–7.80 (m, 20H, Ph), -0.51 (s, 9H, SiMe<sub>3</sub>). MS (CI + VE): *m/e* = 530 (M<sup>+</sup>, 100%).

### 3.1.17. Preparation of $\overline{P_A-P_BPh_2-C(SiMe_3)-P_CPh_2-C(SiMe_3)-P_BPh_2}$ , **28**

1.47 g (2.54 mmol) of LiC(PPh<sub>2</sub>)<sub>2</sub>(SiMe<sub>3</sub>) · TMEDA, **25**, in 20 ml of THF was added slowly to a solution of 0.11 ml (1.27 mmol) PCl<sub>3</sub> in 25 ml of THF at -78 °C. After warming up to room temperature, the suspension was stirred for 6 h. The solvent was replaced by pentane and, after filtration and evaporation of the pentane, an orange oil and orange crystals were obtained. Extraction

with toluene leads also to an orange oil and orange crystals. Yield: 1.23 g (<sup>31</sup>P{<sup>1</sup>H} NMR: mixture of **26a** (20%), **27** (30%), **28** (10%), HC(PPh<sub>2</sub>)<sub>2</sub>(SiMe<sub>3</sub>) (20%) and unidentified impurities (20%).

**28**: NMR (C<sub>6</sub>D<sub>6</sub>, +25 °C): <sup>31</sup>P{<sup>1</sup>H}: δ(P<sub>A</sub>) = -122.81, δ(P<sub>B</sub>) = 29.3, δ(P<sub>C</sub>) = -3.32, (AB<sub>2</sub>C spin system, <sup>1</sup>J(P<sub>A</sub>P<sub>B</sub>) = 282.4 Hz, <sup>2</sup>J(P<sub>B</sub>P<sub>C</sub>) = 64.0, <sup>3</sup>J(P<sub>A</sub>P<sub>C</sub>) = 28.5 Hz).

### 3.1.18. Preparation of $Ph_2P_C-P_APh_2=C(P_BPh_2)-SiMe_3$ , **29**

Method (a), solvent: THF, -78 °C. 0.369 ml (2.06 mmol) Ph<sub>2</sub>PCl; 1.19 g (2.06 mmol) LiC(PPh<sub>2</sub>)<sub>2</sub>(SiMe<sub>3</sub>) · TMEDA, **25**. Yield: 1.14 g, orange solid (<sup>31</sup>P{<sup>1</sup>H} NMR: mixture of **29** (85%), **29a** (7.5%) and HC(PPh<sub>2</sub>)<sub>2</sub>(SiMe<sub>3</sub>) (7.5%).

**29**: NMR (C<sub>6</sub>D<sub>6</sub>, +25 °C): <sup>31</sup>P{<sup>1</sup>H}: δ(P<sub>A</sub>) = 30.98, δ(P<sub>B</sub>) = 9.73, δ(P<sub>C</sub>) = -11.92 (ABC spin system, <sup>2</sup>J(P<sub>A</sub>P<sub>B</sub>) = 242.4, <sup>1</sup>J(P<sub>A</sub>P<sub>C</sub>) = 235.3, <sup>3</sup>J(P<sub>B</sub>P<sub>C</sub>) = 155.4 Hz). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, RT): δ(H) = 6.5–7.9 (m, 30H, Ph), -0.23 (s, 9H, SiMe<sub>3</sub>). MS (CI + VE): *m/e* = 640.1 (M<sup>+</sup>, 2.17%), 563 (M<sup>+</sup> - Ph, 2.96%), 455 (M<sup>+</sup> - PPh<sub>2</sub>, 60.15%).

**29a**: NMR (C<sub>6</sub>D<sub>6</sub>, +25 °C): <sup>31</sup>P{<sup>1</sup>H}: δ(P) = -14.55 (s). MS (CI + VE): 370 (M<sup>+</sup>, 68.77%).

### 3.1.19. Preparation of $P-PPh_2-C(SiMe_3)-PPh_2$ , **26a**

2.35 g (4.06 mmol) of LiC(PPh<sub>2</sub>)<sub>2</sub>(SiMe<sub>3</sub>) · TMEDA, **25**, in 25 ml of THF was added to 0.42 g (3.39 mmol) of P<sub>4</sub> in 20 ml of THF at -78 °C. After warming up to room temperature, the suspension was stirred for 12 h. The solvent was replaced by pentane and, after filtration and evaporation of the pentane, an orange solid remained. Yield: 1.2 g (<sup>31</sup>P{<sup>1</sup>H} NMR: mixture of **26a** (50%) and HC(PPh<sub>2</sub>)<sub>2</sub>(SiMe<sub>3</sub>) (50%).

### 3.1.20. Preparation of $P_A[(P_BPh_2)_2C(SiMe_3)]_2^+ BPh_4^-$ , **30**

To a mixture of 0.398 g (0.82 mmol) of **26a** and 0.403 g (0.82 mmol) of **27** in 35 ml of THF obtained according to Eq. (18) (E = P), 0.281 g (0.82 mmol) of NaBPh<sub>4</sub> was added at -78 °C. After warming to room temperature and stirring for 10 h, the solvent was replaced by pentane. After filtration and evaporation of pentane, traces of **27** and HC(PPh<sub>2</sub>)<sub>2</sub>(SiMe<sub>3</sub>) remained. Extraction with THF leads to an orange oil. Orange crystals were obtained after 1 week. **30**, yield: 0.40 g (39%).

<sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub> + THF, +20 °C): δ(P<sub>A</sub>) = -76.26, δ(P<sub>B</sub>) = 37.73, (AB<sub>4</sub> spin system <sup>1</sup>J(P<sub>A</sub>P<sub>B</sub>) = 137.3 Hz); (C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub> + THF, -107 °C): AB<sub>2</sub>C<sub>2</sub> spin system: δ(*i*P<sub>B</sub><sup>ax</sup>) = +44.39; δ(P<sub>C</sub><sup>eq</sup>) = +26.25; δ(P<sub>A</sub>) = -83.71; <sup>1</sup>J(P<sub>A</sub>P<sub>C</sub>) = 172.0, <sup>1</sup>J(P<sub>A</sub>P<sub>B</sub>) = 86; <sup>2</sup>J(P<sub>B</sub>P<sub>C</sub>) = 172.0 Hz. (The coupling constants have to be regarded as 'apparent coupling constants'). <sup>11</sup>B{<sup>1</sup>H} NMR(C<sub>6</sub>D<sub>6</sub> + THF, +20 °C): δ(B) = -6.47.



Table 10  
Structural data of **7b**, **12**, **18**, **21**, **22**, **26a,b** and of the cation of **30**

	<b>7b</b>	<b>12</b>	<b>18</b>	<b>21</b>	<b>22</b>	<b>26a</b>	<b>26b</b>	<b>30</b>
Molecular formula	C <sub>27</sub> H <sub>72</sub> AsP <sub>3</sub> Si <sub>6</sub>	C <sub>30</sub> H <sub>58</sub> P <sub>4</sub> Si <sub>4</sub>	C <sub>22</sub> H <sub>47</sub> P <sub>5</sub> Si <sub>2</sub>	C <sub>16</sub> H <sub>42</sub> As <sub>4</sub> P <sub>4</sub> Si <sub>2</sub>	C <sub>14</sub> H <sub>36</sub> P <sub>4</sub> Si <sub>2</sub>	C <sub>28</sub> H <sub>29</sub> P <sub>3</sub> Si	C <sub>28</sub> H <sub>29</sub> AsP <sub>2</sub> Si	C <sub>80</sub> H <sub>78</sub> BP <sub>5</sub> Si <sub>2</sub>
Molecular mass (g mol <sup>-1</sup> )	733.22	655.00	522.631	714.27	384.5	486.55	530.461	1261.261
Crystal system	triclinic	monoclinic	triclinic	monoclinic	monoclinic	triclinic	triclinic	monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>m</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>d</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.112	1.156	1.106	1.529	1.157	1.260	1.346	1.185
<i>a</i> (Å)	11.776(1)	9.399(1)	8.556(1)	14.091(1)	6.551(2)	9.606(1)	9.687(1)	14.817(1)
<i>b</i> (Å)	13.405(1)	13.516(1)	13.633(1)	8.702(1)	20.221(2)	16.227(1)	16.317(1)	18.639(1)
<i>c</i> (Å)	14.369(1)	14.827(2)	14.137(1)	13.621(1)	8.681(2)	17.172(1)	17.274(1)	25.665(2)
$\alpha$ (deg)	78.07(1)	90	88.11(1)	90	90	106.30(2)	106.35(1)	90
$\beta$ (deg)	89.50(1)	92.49(1)	89.60(1)	111.77(1)	106.30(1)	90.13(2)	90.34(1)	94.08(1)
$\gamma$ (deg)	80.90(1)	90	72.20(1)	90	90	93.12(2)	92.55(1)	90
<i>V</i> (Å <sup>3</sup> )	2190.7(3)	1881.8(4)	1569.2(2)	1551.1	1104	2564.9(9)	2616.9(3)	7070.0(8)
<i>Z</i>	2	2	2	2	2	4	4	4
$\mu$ (mm <sup>-1</sup> )	1.065	0.347	0.376	4.545	0.44	0.286	1.481	2.06
Crystal dimensions (mm <sup>3</sup> )	0.3 × 0.4 × 0.5	0.55 × 0.40 × 0.25	0.3 × 0.2 × 0.2	0.4 × 0.3 × 0.25	0.77 × 0.51 × 0.31	0.45 × 0.45 × 0.30	0.5 × 0.4 × 0.2	0.3 × 0.3 × 0.5
Data collection diffractometer	CAD4	CAD4	CAD4	CAD4	CAD4	CAD4	CAD4	CAD4
Radiation	Mo K $\alpha$ graphite monochromator	Mo K $\alpha$ graphite monochromator	Mo K $\alpha$ graphite monochromator	Mo K $\alpha$ graphite monochromator	Mo K $\alpha$ graphite monochromator	Mo K $\alpha$ graphite monochromator	Mo K $\alpha$ graphite monochromator	Mo K $\alpha$ graphite monochromator
Reciprocal space	0 ≤ <i>h</i> ≤ 14 -16 ≤ <i>k</i> ≤ 16 -17 ≤ <i>l</i> ≤ 17	-11 ≤ <i>h</i> ≤ 11 0 ≤ <i>k</i> ≤ 17 0 ≤ <i>l</i> ≤ 18	-10 ≤ <i>h</i> ≤ 10 -16 ≤ <i>k</i> ≤ 16 0 ≤ <i>l</i> ≤ 17	-17 ≤ <i>h</i> ≤ 17 0 ≤ <i>k</i> ≤ 11 0 ≤ <i>l</i> ≤ 17	0 ≤ <i>h</i> ≤ 9 0 ≤ <i>k</i> ≤ 28 -12 ≤ <i>l</i> ≤ 12	0 ≤ <i>h</i> ≤ 12 -21 ≤ <i>k</i> ≤ 20 -21 ≤ <i>l</i> ≤ 20	-11 ≤ <i>h</i> ≤ 11 -19 ≤ <i>k</i> ≤ 18 0 ≤ <i>l</i> ≤ 20	-17 ≤ <i>h</i> ≤ 17 0 ≤ <i>k</i> ≤ 22 0 ≤ <i>l</i> ≤ 30
Scan mode	$\omega$ - $\theta$	$\omega$	$\theta$ - $\theta$	$\omega$	$\omega$	$\omega$ -2 $\theta$	$\omega$ - $\theta$	$\omega$
Independent reflections	8529	4059	6682	3040	3006	11157	9108	12373
Observed reflections	7281	3558	5602	2525	3006	8849	7116	8783
Program	SHELXL-93	SHELXL-93	SHELXL-93	SHELX-76	SDP	MOLEN	SHELXL-93	SHELXL-93
Parameter	358	200	276	118	171	577	583	799
$R = \sum   F_o  -  F_c   / \sum  F_o $	0.033	0.0363	0.0306	0.0353	0.037	0.0287	0.0311	0.0403
$wR_1 = [\sum w( F_o  -  F_c )^2 / \sum w(F_o)^2]^{1/2}$				0.0357	0.031	0.0480		
$wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$	0.0857	0.1000	0.0784				0.0747	0.0950
Largest residual (e <sup>-3</sup> Å <sup>-3</sup> )	0.466	0.358	0.247	0.52	0.40	0.33	0.845	0.348

### 3.1.21. Preparation of $(Cl)(Ph)_2P=C(PPh_2)(SiMe_3)$ , **27**

Method (c), solvent: THF,  $-78^\circ\text{C}$ . 0.24 g (0.76 mmol)  $\text{BiCl}_3$ ; 1.31 g (2.26 mmol)  $\text{LiC}(\text{PPh}_2)_2(\text{SiMe}_3) \cdot \text{TMEDA}$  **25**. Yield: 0.63 g, red solid ( $^{31}\text{P}\{^1\text{H}\}$  NMR: mixture of **27** (45%) and  $\text{HC}(\text{PPh}_2)_2(\text{SiMe}_3)$  (55%)).

### 3.2. Crystal structure analysis of **7b**, **12**, **18**, **21**, **22**, **26a,b**, **30**

Crystallographic measurements were made at 293(2) K (**7b**), 217(2) K (**12**), 296(2) K (**18**), 293(2) K (**21**), 193(3) K (**22**), 153(2) K (**26a**), 205(2) K (**26b**), 205(2) K (**30**) with graphite-monochromated  $\text{Mo K}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) on an Enraf–Nonius CAD4-Turbo diffractometer. The crystals used for measurement were solids of sizes 0.30 mm  $\times$  0.40 mm  $\times$  0.50 mm (**7b**), 0.55 mm  $\times$  0.40 mm  $\times$  0.25 mm (**12**), 0.30 mm  $\times$  0.20 mm  $\times$  0.20 mm (**18**), 0.4 mm  $\times$  0.3 mm  $\times$  0.25 mm (**21**), 0.77 mm  $\times$  0.51 mm  $\times$  0.31 mm (**22**), 0.45 mm  $\times$  0.45 mm  $\times$  0.30 mm (**26a**), 0.50 mm  $\times$  0.40 mm  $\times$  0.20 mm (**26b**), 0.30 mm  $\times$  0.30 mm  $\times$  0.50 mm (**30**). For each compound, the unit-cell dimensions (Table 10) were determined by 100 reflections of high diffraction angles using values between  $\theta = 17\text{--}21^\circ$  (**7b**, **18**, **21**),  $10\text{--}13^\circ$  (**26b**, **30**),  $20\text{--}25^\circ$  (**22**),  $\theta = 9\text{--}13^\circ$  (**26a**). The intensity data were measured by continuous  $\omega\text{--}\theta$  (**7b**, **12**),  $\theta\text{--}\theta$  (**18**),  $\theta$  (**21**, **22** and **30**),  $\omega\text{--}2\theta$  (**26a**) and  $\omega\text{--}\theta$  (**26b**) scans. Measured data were corrected for Lorentz and polarization effects [48]. The structures were solved by direct methods [49]. Refinement was done by the full-matrix least squares method. The calculations were performed using SHELXL-93 (**7b**, **12**, **18**, **26b**, **30**) [50], SHELX-76 (**21**), MOLEN (**26a**) [51], SDP (**22**) [52]. Empirical absorption correction was applied using DIFABS [53] for **7b**, **12**, **18** and  $\psi$ -scan based corrections for **21**. In the structural models, all non-hydrogen atoms were assigned anisotropic displacement parameters. The coordinates of the hydrogen atoms were geometrically calculated and refined using a 'riding model' for **7b**, **12**, **18**, **26a,b**, **30**. For **21**, all hydrogen atoms were calculated in idealized geometry and included with isotropic contributions ( $U_{\text{iso}(\text{fix})} = 0.08 \text{ \AA}^2$ ). For **22**, all hydrogen atoms were found in the difference map calculated from the model containing all non-hydrogen atoms. The hydrogen positions were refined with individual isotropic temperature parameters. Tables of H atom coordinates and thermal parameters and a complete list of bond lengths and angles have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Informationen m.b.H., D-76344 Eggenstein-Leopoldshafen, under the following numbers CSD-58646 (**7b**, **18**, **22**), CSD 40436 (**12**), CSD 59325 (**26a**), CSD 59325 (**26b**), CSD 59325 (**30**). For **21**, atomic coordinates,

bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

### Acknowledgements

We thank Mr. J. Riede for X-ray data collection and Dr. M. Heckel, Dr. R. Ficker, Dr. A. Schier, Dr. E. Herdtweck, Professor Dr. W. Hiller and Professor Dr. F.E. Hahn (FU, Berlin) for structure refinements and discussions. H.H.K. thanks the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support.

### References

- [1] H.H. Karsch, *Russ. Chem. Bull.*, 42 (1993) 1937.
- [2] H.H. Karsch, B. Deubelly, U. Keller, O. Steigelmann, J. Lachmann and G. Müller, *Chem. Ber.*, 129 (1996) 67.
- [3] H.H. Karsch, B. Deubelly, U. Keller, F. Bienlein, R. Richter, P. Bissinger, M. Heckel and G. Müller, *Chem. Ber.*, 129 (1996) 759.
- [4] H.H. Karsch, R. Richter and E. Witt, *J. Organomet. Chem.*, 521 (1996) 185.
- [5] H.H. Karsch, A. Appelt, J. Riede and G. Müller, *Organometallics*, 6 (1987) 316.
- [6] H.H. Karsch, G. Ferazin, H. Kooijman, O. Steigelmann, A. Schier, P. Bissinger and W. Hiller, *J. Organomet. Chem.*, 482 (1994) 151.
- [7] H.H. Karsch, R. Richter and A. Schier, *Z. Naturforsch. Teil B:*, 48 (1993) 1533.
- [8] H.H. Karsch, U. Keller, S. Gamper and G. Müller, *Angew. Chem.*, 102 (1990) 297; *Angew. Chem. Int. Ed. Engl.*, 29 (1990) 295.
- [9] H.H. Karsch, B. Deubelly, G. Grauvogl and G. Müller, *J. Organomet. Chem.*, 459 (1993) 95.
- [10] H.H. Karsch, B. Deubelly and G. Müller, *J. Chem. Soc. Chem. Commun.*, (1988) 517.
- [11] H.H. Karsch, E. Witt, A. Schneider, E. Herdtweck and M. Heckel, *Angew. Chem.*, 107 (1995) 628; *Angew. Chem. Int. Ed. Engl.*, 34 (1995) 557.
- [12] H.H. Karsch and A. Schier, *J. Chem. Soc. Chem. Commun.*, (1994) 2703.
- [13] H.H. Karsch, E. Witt and F.E. Hahn, *Angew. Chem.*, 108 (1996) 2380; *Angew. Chem. Int. Ed. Engl.*, in press.
- [14] H.H. Karsch and H. Schmidbaur, *Z. Naturforsch. Teil B:*, 32 (1977) 762.
- [15] H. Schmidbaur and W. Tronich, *Chem. Ber.*, 101 (1968) 3545.
- [16] G. Wittig and G. Geissler, *Justus Liebigs Ann. Chem.*, 580 (1953) 44.
- [17] W. Wolfsberger and H. Schmidbaur, *Synth. Inorg. Met. Org. Chem.*, 4 (1974) 149.
- [18] H.H. Karsch, *Z. Naturforsch. Teil B:*, 37 (1982) 284.
- [19] J.B. Lambert, G.F. Jackson and D.C. Mueller, *J. Am. Chem. Soc.*, 92 (1970) 3093.
- [20] M. Baudler, J. Hahn, H. Dietsch and G. Fürstenberg, *Z. Naturforsch. Teil B:*, 31 (1976) 1305.
- [21] M. Baudler, Y. Aktalay, T. Heinlein and K.-F. Tebbe, *Z. Naturforsch. Teil B:*, 37 (1982) 299.
- [22] W.S. Sheldrick, *Acta Crystallogr. Sect. B:*, 31 (1975) 1789.
- [23] E. Fluck, G. Heckmann, W. Plass, M. Spahn and H. Borrmann, *J. Chem. Soc. Perkin Trans. I*, (1990) 1223.

- [24] (a) G. Märkl, *Angew. Chem.* 78 (1966) 907; *Angew. Chem. Int. Ed. Engl.*, 5 (1966) 846. (b) A.J. Ashe, III, *J. Am. Chem. Soc.*, 93 (1971) 3293.
- [25] G. Märkl, *Chem. Unserer Zeit*, 16 (1982) 139.
- [26] A. Schmidpeter, S. Lochschmidt and W.S. Sheldrick, *Angew. Chem.*, 97 (1985) 214; *Angew. Chem. Int. Ed. Engl.*, 24 (1985) 226.
- [27] A. Schmidpeter, F. Steinmüller and W.S. Sheldrick, *Z. Anorg. Allg. Chem.*, 579 (1989) 158.
- [28] (a) B. Neumüller and E. Fluck, *Phosphorus Sulfur*, 29 (1986) 23. (b) H.H. Karsch, T. Rupprich and M. Heckel, *Chem. Ber.*, 128 (1995) 959. (c) H. Keller, G. Maas and M. Regitz, *Tetrahedron Lett.*, 27 (1986) 1903.
- [29] P. Braunstein, R. Hasselbring, A. DeCian and J. Fischer, *Bull. Soc. Chim. Fr.*, 132 (1995) 691.
- [30] E. Witt and H.H. Karsch, unpublished results, 1996.
- [31] A. Schmidpeter and G. Burget, *Phosphorus Sulfur*, 22 (1985) 323.
- [32] A.H. Cowley, M.C. Cushner and J.S. Szobota, *J. Am. Chem. Soc.*, 100 (1978) 7784.
- [33] H.H. Karsch, H.-U. Reisacher and G. Müller, *Angew. Chem.*, 96 (1984) 619; *Angew. Chem. Int. Ed. Engl.*, 23 (1984) 618.
- [34] S.F. Gamper and H. Schmidbaur, *Chem. Ber.*, 126 (1993) 601.
- [35] K.B. Dillon, *Chem. Rev.*, 94 (1994) 1441.
- [36] H.H. Karsch, B. Deubelly, G. Hanika, J. Riede and G. Müller, *J. Organomet. Chem.*, 344 (1988) 153.
- [37] H.H. Karsch, A. Appelt and G. Müller, *Angew. Chem.*, 97 (1985) 404; *Angew. Chem. Int. Ed. Engl.*, 24 (1985) 402.
- [38] A.L. Balch and D.E. Oram, *Inorg. Chem.*, 26 (1987) 1906.
- [39] H.H. Karsch and G. Baumgartner, in preparation.
- [40] M. Sanchez, M.R. Mazières, L. Lamandé and R. Wolf, in M. Regitz and O.J. Scherer (eds), *Multiple Bonds and Low Coordination in Phosphorus Chemistry*, Thieme, Stuttgart, 1990, p. 129.
- [41] G. Bouhadir, R.W. Reed, R. Réaud and G. Bertrand, *Heteroatom Chem.*, 6 (1995) 371.
- [42] R. Weiß and S. Engel, *Angew. Chem.*, 104 (1992) 239; *Angew. Chem. Int. Ed. Engl.*, 31 (1992) 216.
- [43] F.Sh. Shagvaleev, T.V. Zykova, R.I. Tarasova, T.Sh. Sitdikova and V.V. Moskva, *J. Gen. Chem.*, 60 (1990) 1585; *Zh. Obshch. Khim.*, 60 (1990) 1775.
- [44] H.H. Karsch, H.-U. Reisacher, A. Schneider and T. Rupprich, in W.A. Herrmann (ed.), *Brauer–Herrmann: Synthetic Methods of Organometallic and Inorganic Chemistry*, Vol. 3, H.H. Karsch (ed.), *Phosphorus, Arsenic, Antimony and Bismuth*, Thieme, Stuttgart, p. 145.
- [45] H.H. Karsch, A. Appelt, B. Deubelly, K. Zellner, J. Riede and G. Müller, *Z. Naturforsch. Teil B.*, 43 (1988) 1416.
- [46] H.H. Karsch, G. Grauvogl, P. Mikulcic, P. Bissinger and G. Müller, *J. Organomet. Chem.*, 465 (1994) 65.
- [47] H.H. Karsch, R. Richter, B. Deubelly, A. Schier, M. Paul, M. Heckel, K. Angermeier and W. Hiller, *Z. Naturforsch. Teil B.*, 49 (1994) 1798.
- [48] J. Kopf and H.-C. Rübke, CADSHL V3.10, University of Hamburg, 1993.
- [49] A. Altomare, G. Cascarano, C. Giacovazzo and A. Guagliardi, *J. Appl. Crystallogr.*, 26 (1993) 343.
- [50] G.M. Sheldrick, SHELXL-93, University of Göttingen.
- [51] MolEN: *Molecular Structure Solution Procedures. Program Descriptions*, Enraf–Nonius, Delft, 1990.
- [52] B.A. Frenz, *Enraf–Nonius SDP-PLUS Structure Determination Package*, Version 4.0, Enraf–Nonius, Delft, Netherlands, 1988.
- [53] (a) N. Walker and D. Stuart, *Acta Crystallogr. Sect. A.*, 39 (1993) 1083. (b) N. Walker, DIFABS V09.0, BASF AG, 1993.