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Metalation and Oxidative Coupling of the Unique Cyclic Silylphosphanes $(i\mathrm{Pr_2Si})_3\mathrm{PH}$ and $(i\mathrm{Pr_2Si})_4\mathrm{PH}$

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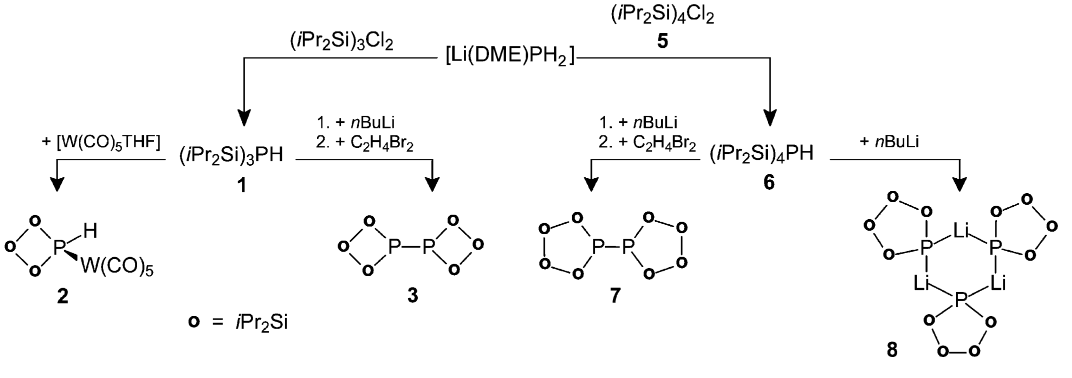
The cyclic tetrasilaphosphane $(i\mathrm{Pr_2Si})_4\mathrm{PH}$ (**6**) can be synthesised in five steps starting from diisopropylchlorsilane and $[\mathrm{Li(DME)PH_2}]$. Subsequent lithiation and oxidative coupling with dibromethane yields the diphosphane $[(i\mathrm{Pr_2Si})_4\mathrm{P}]_2$ (**7**). In an analogous manner the bicyclic diphosphane $[(i\mathrm{Pr_2Si})_3\mathrm{P}]_2$ (**3**) can be obtained from the cyclic trisilaphosphane $(i\mathrm{Pr_2Si})_3\mathrm{PH}$ (**1**). Moreover, the reaction of **1** with $[\mathrm{W(CO)_5THF}]$ yields the Lewis acid–base complex $[(i\mathrm{Pr_2Si})_3\mathrm{P(H)W(CO)_5}]$ (**2**), and the trimeric lithiumphoshpanide $[(i\mathrm{Pr_2Si})_4\mathrm{PLi}]_3$ (**8**) occurs from the reaction of **6** with *n*BuLi in heptane. All intermediate and final products are characterised by multinuclear NMR spectroscopy, IR spectroscopy and mass spectrometry. Furthermore, the crystal structures determined by X-ray diffraction are described for compounds **2**, **3**, **6**, **7** and **8**.

Introduction

Molecular compounds of group 14 and 15 elements with C–N, C–P and Si–N bonds have been the subject of investigation for many years. In 1953, Fritz and co-workers synthesised $\mathrm{H_3Si\text{-}PH_2}$, the first molecular compound with a Si–P bond.[1] Since that time, a large number of novel binary Si–P compounds with alternating silicon and phosphorus atoms have been synthesised.[2] Examples of this class of compounds are the cyclic species $[\mathrm{Me_3SiPSiMe_2}]_2$ and the heterocubane $[\mathrm{PSi}t\mathrm{Bu}]_4$.[3,4]



Scheme 1. Synthesis of the compounds **1**, **2**, **3**, **6**, **7** and **8**.

Silylphosphanes with Si–Si bonds, in contrast, have hardly been studied so far.[5] In previous studies, the four-membered ring system $(i\mathrm{Pr_2Si})_3\mathrm{PH}$ (**1**) was formed by means of the reaction of $[\mathrm{Li(DME)PH_2}]$ and isopropyl-substituted 1,3-dichlorotrisilane $(i\mathrm{Pr_2Si})_3\mathrm{Cl_2}$.[6] Subsequent research covered the functionalisation of this unique ring compound. In this paper we present the Lewis acid–base adduct $[(i\mathrm{Pr_2Si})_3\mathrm{PHW(CO)_5}]$ (**2**) obtained from the reaction of **1** with $[\mathrm{W(CO)_5THF}]$ and the product of the oxidative coupling reaction $[(i\mathrm{Pr_2Si})_3\mathrm{P}]_2$ (**3**). Moreover, the synthesis, metalation and oxidative coupling of the larger ring system $(i\mathrm{Pr_2Si})_4\mathrm{PH}$ (**6**) will be presented (Scheme 1).

Results and Discussion

To obtain information on the structure of the liquid Lewis base **1**, the Lewis acid–base complex $[(i\mathrm{Pr_2Si})_3\mathrm{PHW(CO)_5}]$ (**2**) was synthesised from the reaction of **1** with $[\mathrm{W(CO)_5(THF)}]$ in THF. After removing the solvent and recrystallisation of the residue from *n*-heptane yellow crys-

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tals of **2** were obtained, the yield being 74%. The crystal structure of **2** was solved in the monoclinic space group $P2_1/n$.

In **2** the cyclic compound $(i\mathrm{Pr}_2\mathrm{Si})_3\mathrm{PH}$ binds with its lone pair at the $\mathrm{W(CO)_5}$ fragment. Because of this coordination, a bond length reduction between the tungsten atom and the C atom of the *trans* carbonyl group [C(1)] can be noticed in comparison to the W–C(2–5) bonds (Figure 1). The $\mathrm{Si_3P}$ ring is strongly folded to a butterfly structure with a Si(2)–Si(1)–Si(3)–P angle of torsion of 141.9°. The folding of the ring is more distinct than in the compounds $[(i\mathrm{Pr}_2\mathrm{Si})_3\mathrm{PLi(DME)}]_2$ (176.5°) and $(i\mathrm{Pr}_2\mathrm{Si})_3\mathrm{PSiMe}_3$ (150.9°) described previously.[6] The ^{31}P NMR spectrum shows a doublet at δ = –225.2 ppm with a P–H coupling constant of 254 Hz. Furthermore, the spectrum reveals a P–W coupling constant of 158 Hz. Mass spectroscopy displays the molecule peak [M$^+$] at 697.9 *m*/*z* and signals that indicate the elimination of carbonyl and isopropyl groups.

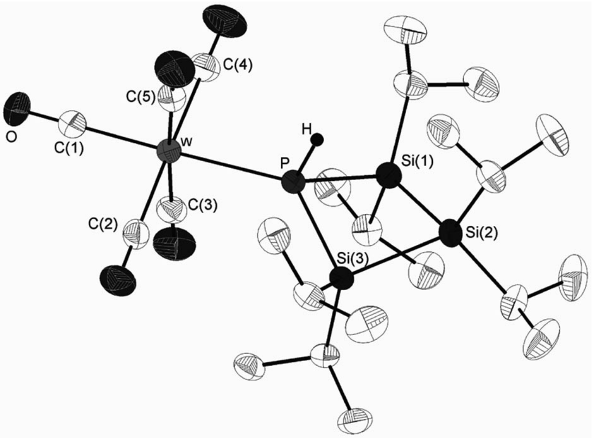


Figure 1. Molecular structure of **2**, thermal ellipsoids represent a 50% probability level, hydrogen atoms of the organic groups are not shown, selected bond lengths [pm] and angles [°]: W–P 254.8(8), W–C(1) 199.2(3), W–C(2–5) 203.3(4)–204.7(4), P–Si(1) 229.8(1), P–Si(3) 229.7(1), Si(1)–Si(2) 238.2(1), Si(2)–Si(3) 236.6(1); P–W–C(1) 178.1(1), Si(1)–P–Si(3) 87.07(4), P–Si(1)–Si(2) 87.89(4), P–Si(3)–Si(2) 88.31(4), Si(2)–Si(1)–Si(3)–P 141.9(1).

Lithiation and subsequent oxidation of $(i\mathrm{Pr}_2\mathrm{Si})_3\mathrm{PH}$ with dibromethane yield the bicyclic compound $[(i\mathrm{Pr}_2\mathrm{Si})_3\mathrm{P}]_2$ (**3**) which can be obtained as yellow crystals from benzene at a moderate yield. The structure refinement was carried out in the triclinic space group *P*-1. The molecule consists of two approximately orthogonally oriented $(i\mathrm{Pr}_2\mathrm{Si})_3\mathrm{P}$ rings bonded by a P–P bond (Figure 2). The sum of angles at the phosphorus atom is about 337°. Consequently, the p-orbital character of the lone pair should not be underestimated. The distance between P(1) and P(2) is a little shorter (217.3 pm) than in P–P bonds usually observed (219–223 pm). This probably results from the overlap of the lone pair at P(1) with the Si–P σ* orbital at P(2) and vice versa. A similar effect was described recently for noncyclic diphosphane $[(t\mathrm{BuPh}_2\mathrm{Si})_2\mathrm{P}]_2$.[7] The $\mathrm{Si_3P}$ rings in **3** are distorted with an angle of torsion along the Si(1)–Si(3) axis of 147.9° [along Si(4)–Si(6): 150.7°].

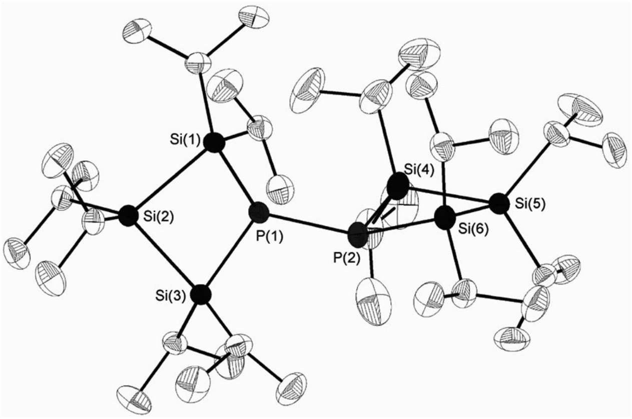


Figure 2. Molecular structure of **3**, thermal ellipsoids represent a 50% probability level, hydrogen is not shown, selected bond lengths [pm] and angles [°]: P(1)–P(2) 217.3(1), P(1)–Si(1) 225.4(1), Si(1)–Si(2) 237.6(1), Si(2)–Si(3) 237.8(2), Si(3)–P(1) 226.2(1) P(2)–Si(4) 224.1(1), Si(4)–Si(5) 237.8(1), Si(5)–Si(6) 239.3(1), Si(6)–P(2) 225.6(1); Si(1)–P(1)–Si(3) 93.16(4), P(1)–Si(1)–Si(2) 85.57(4), Si(1)–Si(2)–Si(3) 87.24(4), Si(2)–Si(3)–P(1) 85.33(4), Si(4)–P(2)–Si(6) 94.00(5), P(2)–Si(4)–Si(5) 86.14(5), Si(4)–Si(5)–Si(6) 87.16(4), Si(5)–Si(6)–P(2) 85.46(5).

The ^{31}P NMR spectrum shows a singlet at δ = –188.3 ppm with two kinds of Si satellites. In the ^{29}Si NMR spectrum, two signals in the form of a triplet can be seen (Figure 3). They represent the X parts of an AA′X spin system with a strong coupling between A and A′. In this case, it is not possible to resolve the coupling constants $J_{\mathrm{AA'}}$, J_{AX} and $J_{\mathrm{A'X}}$. However, the distance between both outer lines in these multiplets represents the sum of the J_{AX} and $J_{\mathrm{A'X}}$ coupling constants.[8]

Such signals with a "virtual coupling" can also be seen in the ^{13}C{^{1}H} NMR spectrum of **3**. There are five different signals of carbon atoms. Four of the signals exhibit such a pseudo triplet structure (Figure 3, b). Mass spectroscopy of compound **3** displays the molecule peak [M$^+$] at 746 *m*/*z*, the symmetrical disunite product [M$^+$]/2 at 373 *m*/*z*, and signals that indicate the elimination of isopropyl groups.

Five-membered ring systems, including silicon and phosphorus only are still rare.[9] Known species with a $\mathrm{Si_4P}$ backbone are $(\mathrm{Me_2Si})_4\mathrm{PPh}$ and $(\mathrm{Ph_2Si})_4\mathrm{PPh}$, but to the best of our knowledge no structural data are available.[10] We succeeded in synthesising the cyclic tetrasilaphosphane $(i\mathrm{Pr}_2\mathrm{Si})_4\mathrm{PH}$ (**6**) via the synthetic strategy shown in Scheme 2 and determined its crystal structure by X-ray diffraction.

The compound $\mathrm{H}(i\mathrm{Pr}_2\mathrm{Si})_4\mathrm{H}$ (**4**) was obtained in three steps starting from diisopropylchlorosilane as a colourless oil. ^{29}Si NMR spectroscopy displays two different signals of silicon. A doublet at δ = –10.3 ppm for the outer Si atoms ($^1J_{\mathrm{SiH}}$ = 150 Hz) and a singlet at δ = –15.5 ppm for the inner silicon atoms. The mass spectra reveal the molecule peak [M$^+$] at 457.1 *m*/*z* and signals that reflect the elimination of isopropyl groups. In a subsequent chlorination, compound $\mathrm{Cl}(i\mathrm{Pr}_2\mathrm{Si})_4\mathrm{Cl}$ (**5**) is obtained as a highly viscous oil that solidifies close to room temperature. Mass spectroscopic analysis shows the molecule peak [M$^+$] at 527.1 *m*/*z*. The reaction of two equivalents of $[\mathrm{Li(DME)PH_2}]$ and

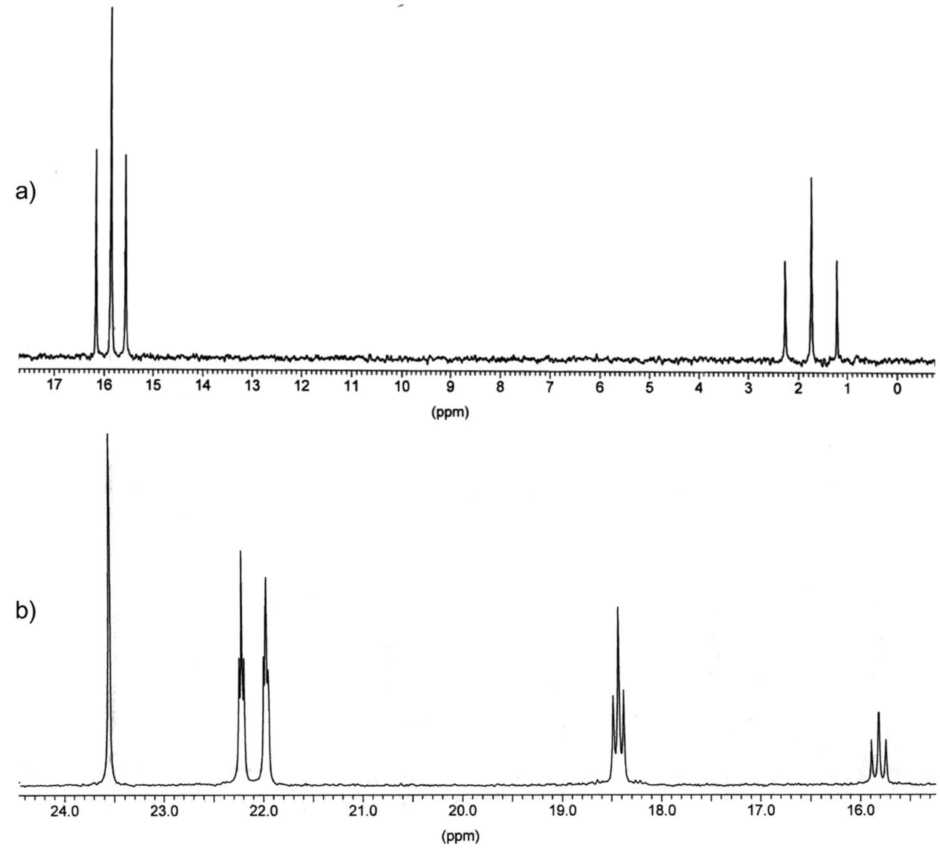
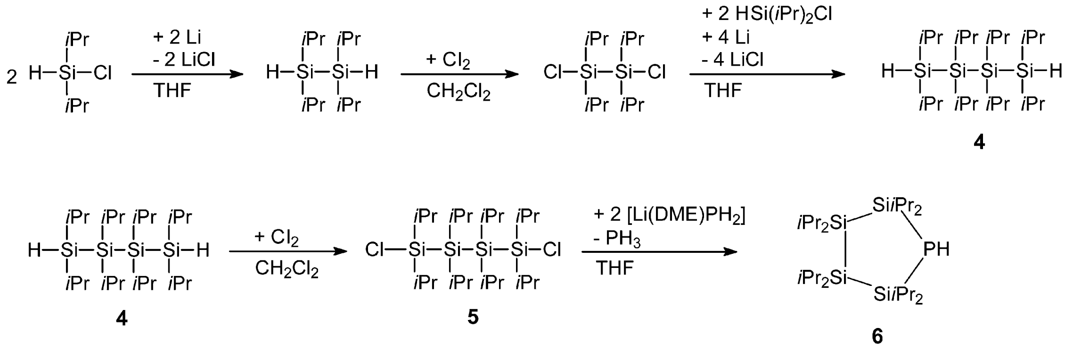


Figure 3. (a) $^{29}Si\{^1H\}$ spectrum of compound **3** in C_6D_6. (b) $^{13}C\{^1H\}$ NMR spectrum of compound **3** in C_6D_6.



Scheme 2. Synthesis of compounds **4**, **5**, and **6**.

compound **5** at 0 °C in *n*-heptane yields colourless crystals of $(iPr_2Si)_4PH$ (**6**) (monoclinic, space group $P2_1$). The Si_4P ring is distorted to an envelope structure with P, Si(1), Si(2) and Si(3) almost within a plane and an angle of torsion along the P–Si(3) axis of about 145° (Figure 4). Spectroscopic experiments confirm the information obtained from X-ray diffraction. The ^{31}P NMR spectra exhibit the expected signal in the form of a doublet at δ = –261.3 ppm with a P–H coupling constant of 185 Hz. Mass spectroscopy shows the molecule peak [M^+] at 488.1 *m*/*z* and signals indicating the elimination of isopropyl groups. The FT-IR spectrum displays the P–H vibration at 2266 cm^{-1}. This result is similar to the P–H vibration in the four-membered ring $(iPr_2Si)_3PH$ observed at 2281 cm^{-1}.[6]

In analogy to **1**, lithiation and subsequent oxidation of **6** with dibromethane yield the bicyclic compound $[(iPr_2Si)_4P]_2$ **7** which can be obtained as yellow rhombohedral crystals from benzene (Figure 5) at a yield of 38%. The structure solution and refinement were carried out in the monoclinic space group $P2_1/n$. The structure consists of two approximately orthogonally standing $[(iPr_2Si)_4P]$ rings bonded by a P–P bond. Both P atoms are virtually coordinated in a planar manner (sum of angles: 356.7°). The distance between P(1) and P(2) is a little shorter (217.6 pm)

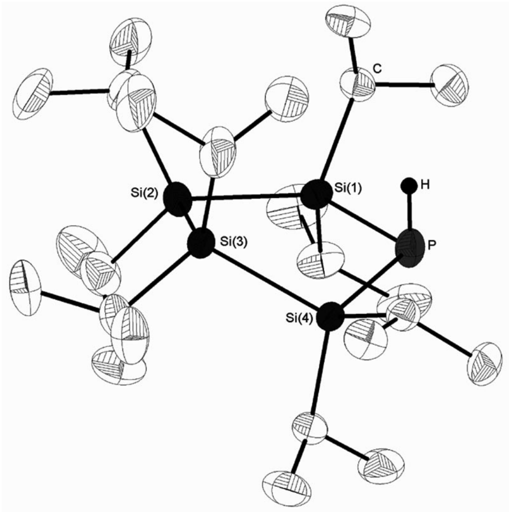


Figure 4. Molecular structure of **6**, thermal ellipsoids represent a 50 % probability level, hydrogen atoms of the organic groups are not shown, selected bond lengths [pm] and angles [°]: P–Si(1) 226.8(1), P–Si(4) 226.8(1), Si(1)–Si(2) 240.4(1), Si(2)–Si(3) 239.3(1), Si(3)–Si(4) 237.4(2); P–Si(1)–Si(2) 109.59(5), Si(1)–P–Si(4) 104.88(5), Si(1)–Si(2)–Si(3) 103.56(5), Si(2)–Si(3)–Si(4) 101.90(5), Si(3)–Si(4)–P 107.37(5).

than in P–P bonds usually observed (219–223 pm) and similar to compound **3**. Like in **6** the rings are slightly folded to an envelope structure, the angle of torsion along the Si(6)–Si(8) axis amounts to 138°, along the Si(1)–Si(3) axis 141°.

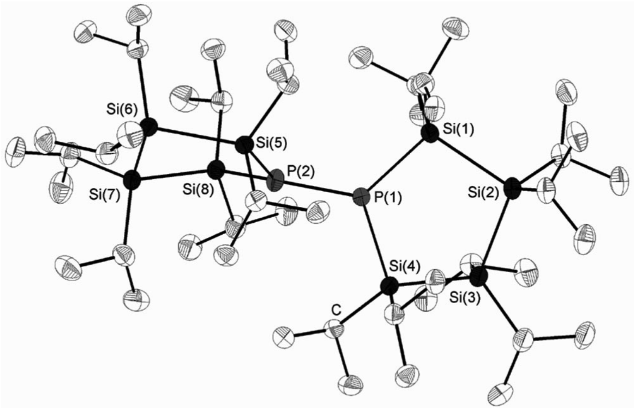


Figure 5. Molecular structure of **7**, thermal ellipsoids represent a 50 % probability level, hydrogen is not shown, selected bond lengths [pm] and angles [°]: P(1)–P(2) 217.6(1), P(1)–Si(1) 226.3(1), Si(1)–Si(2) 240.1(1), Si(2)–Si(3) 241.2(1), Si(3)–Si(4) 240.4(1), Si(4)–P(1) 226.5(1), P(2)–Si(5) 226.6(1), Si(5)–Si(6) 240.9(1), Si(6)–Si(7) 240.8(1), Si(7)–Si(8) 240.3(1), Si(8)–P(2) 226.9(1); Si(1)–P(1)–Si(4) 115.04(4), Si(1)–P(1)–Si(4) 115.04(4), Si(1)–Si(2)–Si(3) 104.4, Si(2)–Si(3)–Si(4) 102.9, Si(2)–Si(1)–Si(3)–P(1) 161.4.

The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at δ = –194.3 ppm. In the $^{29}Si\{^1H\}$ NMR spectrum, two signals in the form of a triplet can be seen. Analogously to compound **3**, these triplet signals result from the "virtual coupling" with two phosphorus atoms. Such triplet signals are also noticeable in the $^{13}C\{^1H\}$ NMR spectrum of **7**. There are six different signals of carbon atoms. Four of these show such a pseudo triplet structure. Mass spectroscopy of compound **7** displays the molecule peak [M^+] at 974.6 *m*/*z* and signals of separate isopropyl groups. Moreover, the symmetrical disunite product [M^+]/2 is found at 487.3 *m*/*z*.

Starting from **6**, the reaction with *n*BuLi in *n*-heptane yields the polycyclic compound [(iPr$_2$Si)$_4$PLi]$_3$ (**8**) in the form of colourless crystals. Structure solution and refinement were carried out in the monoclinic space group $P2_1/n$ (Figure 6). This species is composed of three (iPr$_2$Si)$_4$P rings that are bridged by three Li$^+$ ions. The central Li$_3$P$_3$ ring is planar and the three outer rings are folded slightly to an envelope structure. The coordination number of two for lithium should be noted. Usually, the Li$^+$ ion in lithium phosphanides (LiPR$_2$)$_n$ shows coordination numbers of three or four due to the solvent–molecule coordination or the formation of polycyclic oligomers. This rare coordination number is a result of the steric demand of the (iPr$_2$Si)$_4$P rings and the absence of a donor solvent. The small coordination number causes a very short Li–P bond between 244.8 pm and 248.5 pm. In the known compound [(Me$_3$Si)$_2$PLi(DME)]$_2$, for example, the P(1)–Li(1) distance is about 256 pm.[11]

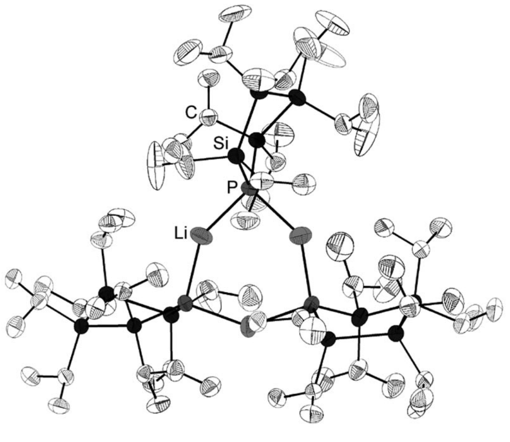


Figure 6. Molecular structure of **8**, thermal ellipsoids represent a 50 % probability level, hydrogen is not shown, selected bond lengths [pm] and angles [°]: P–Li 243.2(7)–248.5(8), P–Si 223.7(1)–224.2(2), Si–Si 238.0(2)–241.7(2); Li–P–Li 94.3(3)–99.8(3), P–Li–P 141.1(3)–147.9(4), Si–P–Si 100.79(5)–102.53(5), Si–Si–Si 97.49(6)–102.93(6).

The $^{31}P\{^1H\}$ NMR spectrum exhibits a broad signal at δ = –315.2 ppm. In the ^7Li NMR spectrum, a signal with a triplet structure at δ = 3.49 ppm reflects the binding to two phosphorus atoms.

Conclusions

The cyclic tetrasilaphosphane (iPr$_2$Si)$_4$PH (**6**) was synthesised by first building up a 1,4-dichlorterasilane chain and a subsequent cyclisation reaction with [Li(DME)PH$_2$]. Starting from **6** as well as the corresponding four-membered ring compound **1**, the bicyclic silyldiphosphanes **3**

Table 1. X-ray structure data of compounds **2**, **3**, **6**, **7** and **8**.[12]

	2	**3**	**6**	**7**	**8**
Empirical formula	$C_{23}H_{43}O_5PSi_3W$	$C_{36}H_{84}P_2Si_6$	$C_{24}H_{57}PSi_4$	$C_{48}H_{112}P_2Si_8$	$C_{72}H_{168}Li_3P_3Si_{12}$
Crystal system	monoclinic	triclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$P2_1$	$P2_1/n$	$P2_1/c$
Formula units	4	2	2	4	4
Temperature [K]	190	190	190	180	180
Unit cell dimensions	a = 1083.6(2) pm b = 2005.2(4) pm c = 1442.2(3) pm α = 90° β = 99.69(3)° α = 90°	a = 1050.6(2) pm b = 1344.1(3) pm c = 1854.9(4) pm α = 103.93(3)° β = 100.88(3)° γ = 107.85(3)°	a = 1044.1(2) pm b = 1421.8(3) pm c = 1102.3(2) pm γ = 90° β = 110.87(3)° γ = 90°	a = 1727.6(4) pm b = 1721.2(3) pm c = 2129.4(4) pm α = 90° β = 105.75(3)° α = 90°	a = 2759.1(6) pm b = 1584.0(3) pm c = 2171.4(4) pm γ = 90° β = 99.60(3)° γ = 90°
Cell volume [A^3]	30889(11)	23203(8)	15290(5)	6094(2)	9357(3)
Density [g/cm^3]	1.502	1.070	1.062	1.064	1.054
Absorption coefficient [mm^{-1}]	3.936	0.271	0.257	0.257	0.252
2Θ range [°]	3.52–51.28	3.36–51.34	3.96–51.28	3.08–51.36	2.98–49.32
Reflections measured	21100	16166	8669	22690	31429
Independent reflections	5803 (R_{int} = 0.0506)	8183 (R_{int} = 0.0400)	5706 (R_{int} = 0.0269)	10082 (R_{int} = 0.0536)	15256 (R_{int} = 0.0525)
Parameters	302	397	266	523	811
R_1 [$F_o > 4\sigma(F_o)$]	0.0234	0.0379	0.0474	0.0449	0.0612
wR_2 (all data)	0.0570	0.1084	0.1170	0.1186	0.1695
GOOF	1.111	1.030	1.021	1.010	1.029
Residual electron density	0.451	0.566	0.742	0.355	1.293

and **7** are accessible by an oxidative coupling of the lithium derivatives. These bicyclic compounds exhibit Si–Si bonds as well as one P–P bond. Because of π-interactions these P–P bonds are shortened compared to usual P–P single bonds. The lithium derivative of compound **6** exists in the solid state as well as in solution as a trimer with a central Li_3P_3 ring. The lithium ions in this compound exhibit only coordination number two. This result shows that sterically demanding cyclic secondary silylphosphanes can be used for the synthesis of main group element polycycles with novel structural motifs and coordination numbers. The subject of current research is the synthesis and characterisation of corresponding compounds of the heavy elements As and Sb as well as Ge and Sn. The crystal structures of compounds **2**, **3**, **6**, **7** and **8** are reported in Table 1.

Experimental Section

General Remarks: All manipulations were performed under rigorous exclusion of oxygen and moisture using a Schlenk line and nitrogen atmosphere. Solvents were dried and freshly distilled before use. The starting materials were prepared according to literature procedures: HSi*i*Pr$_2$Cl, [Cl$_2$(Si*i*Pr$_2$)$_2$],[13] [Li(DME)PH$_2$],[14] (*i*Pr$_2$Si)$_3$PH (**1**).[6]

Compound 2: A solution of **1** (0.42 g, 1 mmol) in THF (5 mL) was treated with a 0.08-M solution of [W(CO)$_5$THF] (12.5 mL, 1 mmol) at 0 °C. Subsequently, the yellow solution was warmed to room temperature and stirred for 12 h. After removing the solvent, the residue was dissolved in hot *n*-heptane. At –20 °C, yellow crystals of **2** were obtained after 3 d, the yield being 0.52 g (74%). $C_{23}H_{43}O_5PSi_3W$ (698.66): calcd. C 39.54, H 6.20; found C 39.69, H 5.82. ^{1}H NMR (400 MHz, C$_6$D$_6$, 25 °C): δ = 1.10 [d, $^3J_{H,H}$ = 8 Hz, 12 H, -CH$_3$], 1.14 [d, $^3J_{H,H}$ = 8 Hz, 12 H, -CH$_3$], 1.28 [d, $^3J_{H,H}$ = 8 Hz, 12 H, -CH$_3$], 1.33 [sept, $^3J_{H,H}$ = 8 Hz, 2 H, -CH], 1.35 [sept, $^3J_{H,H}$ = 8 Hz, 2 H, -CH], 1.45 [sept, $^3J_{H,H}$ = 8 Hz, 2 H, -CH], 2.33 [d, $^1J_{P,H}$ = 254 Hz, 1 H] ppm. ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ = 14.1 [d, $^3J_{P,C}$ = 3 Hz, -CH], 15.6 [d, $^2J_{P,C}$ = 7 Hz, -CH], 16.6 [d,$^2J_{P,C}$ = 9 Hz, -CH], 20.8 [dd, $^2J_{P,C}$ = 10, $^3J_{P,C}$ = 3 Hz], 21.4 [d, $^3J_{P,C}$ = 5 Hz], 22.3 [s], 23.2 [s], 198.9 [d, *cis*-$^2J_{P,C}$ = 4 Hz], 199.5 [d, *trans*-$^2J_{P,C}$ = 20 Hz] ppm. ^{29}Si{^{1}H} NMR (C$_6$D$_6$): δ = 11.1 [d, $^1J_{P,Si}$ = 21 Hz], 14.1 [s] ppm. ^{31}P NMR (C$_6$D$_6$): δ = –225.2 [d with W satellites, $^1J_{P,H}$ = 254, $^1J_{P,W}$ = 158 Hz] ppm. MS (EI, 70 eV): *m*/*z* (%) = 697.9 (95) [M]$^+$, 670 (35) [M – CO]$^+$, 642 (31) [M – 2 CO]$^+$, 614 (44) [M – 3 CO]$^+$, 599.8 (60) [M – 2 CO – C$_3$H$_6$]$^+$, 571.9 (80) [M – 3 CO – C$_3$H$_6$]$^+$. IR (KBr): $\tilde{\nu}$ = 2950 (m), 2865 (m), 2717 (w), 2362 (w), 2268 (w), 2066 (s), 1947 (vs), 1900 (vs), 1459 (m), 1389 (m), 1366 (m), 1221 (m), 1067 (m), 1009 (m), 875 (m), 771 (m), 635 (m), 597 (s), 574 (s) cm^{-1}.

Compound 3: Compound **1** (0.38 g, 1 mmol) was dissolved in *n*-heptane (10 mL) and treated with *n*BuLi (0.64 mL, 1 mmol, 1.6 M) at 0 °C while stirring. After 30 min, the solution was warmed to room temperature. After 1 h, the yellow solution was charged with dibromethane (0.043 mL, 0.5 mmol). After separation of the white LiBr precipitate, the solvent was removed and the residue was purified at 140 °C and 10^{-3} mbar. Recrystallisation from benzene (2 mL) yielded yellow crystals of **3**. Yield: 0.06 g (16% based on phosphorus). $C_{36}H_{84}P_2Si_6$ (747.52): calcd. C 57.84, H 11.33; found C 56.27, H 10.63. ^{1}H NMR (C$_6$D$_6$): δ = 1.30 [d, $^3J_{H,H}$ = 8 Hz, 12 H, -CH$_3$], 1.40 [d, $^3J_{H,H}$ = 8 Hz, 12 H, -CH$_3$], 1.45 [d, $^3J_{H,H}$ = 8 Hz, 12 H, -CH$_3$], 1.57 [sept, $^3J_{H,H}$ = 8 Hz, 2 H, -CH], 1.66 [sept overlay, $^3J_{H,H}$ = 8 Hz, 2×2 H, -CH] ppm. ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ = 15.8 [pseudo t, $^2J_{P,C}$ + $^3J_{P,C}$ = 15 Hz], 18.4 [pseudo t, $^3J_{P,C}$ + $^4J_{P,C}$ = 9 Hz], 21.9 [pseudo t, $^3J_{P,C}$ + $^4J_{P,C}$ = 5 Hz], 22.2 [pseudo t, $^3J_{P,C}$ + $^4J_{P,C}$ = 5 Hz], 23.5 [s] ppm. ^{29}Si{^{1}H} NMR (C$_6$D$_6$): δ = 1.77 [pseudo t, $^2J_{P,Si}$ + $^3J_{P,Si}$ = 42 Hz], 15.90 [pseudo t, $^1J_{P,Si}$ + $^2J_{P,Si}$ = 24 Hz] ppm. ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ = –188.3 [s with Si satellites] ppm. MS (EI, 70 eV): *m*/*z* (%) = 746.2 (68) [M]$^+$, 703.2 (12) [M – *i*Pr]$^+$, 487.1 (73) [M – 6 *i*Pr]$^+$, 373.1 (100) [M/2]$^+$, 331.1 (100) [M/2 – C$_3$H$_6$]$^+$, 289.1 (100) [M/2 – 2 C$_3$H$_6$]$^+$, 247.1 (100) [M/2 – 3 C$_3$H$_6$]$^+$, 204.9 (84) [M/2 – 4 C$_3$H$_6$]$^+$, 163.0 (51) [M/2 – 5 C$_3$H$_6$]$^+$.

IR (KBr): $\tilde{\nu}$ = 2940 (s), 2861 (vs), 2708 (w), 1459 (s), 1383 (m), 1360 (m), 1258 (m), 1071 (s), 1018 (vs), 876 (s), 800 (m), 633 (m) cm^{-1}.

Compound 4: The synthesis was carried out according to a modified description from Masamune and Tobita.[15] Lithium powder (1.40 g, 0.201 mol) was suspended in THF (100 mL). At 0 °C, a mixture of HSi*i*Pr$_2$Cl (13.3 mL, 0.076 mol), [Cl$_2$(Si*i*Pr$_2$)$_2$] (8.95 g, 0.038 mol) and THF (25 mL) was added slowly. After 1.5 h, the solution was warmed to room temperature and stirred overnight. The solution turned dark brown. The solvent was removed under low pressure and the residue was elutriated in *n*pentane (100 mL). After filtration, the solvent was removed and the residue was distilled at 164–167 °C and 10^{-3} mbar. The colourless oil of compound **4** was obtained at a yield of 7.39 g (42%). ^{1}H NMR (C$_6$D$_6$): δ = 1.26 [d, $^3J_{\mathrm{H,H}}$ = 7 Hz, -CH$_3$, 12H], 1.30 [d, $^3J_{\mathrm{H,H}}$ = 7 Hz, 12 H, -CH$_3$], 1.31 [d, $^3J_{\mathrm{H,H}}$ = 7 Hz, 12 H, -CH$_3$], 1.33 [d, $^3J_{\mathrm{H,H}}$ = 7 Hz, 12 H, -CH$_3$],1.44 [sept, $^3J_{\mathrm{H,H}}$ = 7 Hz, 4 H, -CH(CH$_3$)$_2$], 1.54 [sept, $^3J_{\mathrm{H,H}}$ = 7 Hz, 4 H, -CH(CH$_3$)$_2$], 4.10 [s, 2 H, Si-H] ppm. ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ = 14.3 [s], 15.1 [s], 21.6 [s], 22.9 [s], 23.4 [s], 24.4 [s] ppm. ^{29}Si NMR (C$_6$D$_6$): δ = –15.5 [s], –10.3 [d, $^1J_{\mathrm{Si,H}}$ = 150 Hz, Si-H] ppm. MS (EI, TOF): *m*/*z* (%) = 457.07 (1) [M]$^+$, 415.05 (18) [M – C$_3$H$_6$]$^+$, 343.04 (75) [M – Si(*i*Pr)$_2$]$^+$, 301.02 (75) [M – Si(*i*Pr)$_2$ – C$_3$H$_6$]$^+$, 258.99 (100) [M – Si(*i*Pr)$_2$ – 2 C$_3$H$_6$]$^+$, 228.03 (80) [M/2]$^+$, 216.97 (90) [M – Si(*i*Pr)$_2$ – 3 C$_3$H$_6$]$^+$, 174.96 (45) [M – Si(*i*Pr)$_2$ – 4 C$_3$H$_6$]$^+$.

Compound 5: The synthesis was carried out according to a modified description from Masamune and Tobita.[15] Silane **4** (7.39 g, 0.016 mol) was dissolved in dichloromethane (125 mL). Chlorine was passed through the solution at 0 °C. By means of ^{1}H NMR spectroscopy, the end of the reaction was defined. The solvent was removed and the remaining oil of compound **5** was obtained without any purification at a yield of 8.40 g (98%). ^{1}H NMR (C$_6$D$_6$): δ = 1.16 [d, $^3J_{\mathrm{H,H}}$ = 7 Hz, 12 H, -CH$_3$], 1.28 [d, $^3J_{\mathrm{H,H}}$ = 7 Hz, 12 H, -CH$_3$], 1.33 [d, $^3J_{\mathrm{H,H}}$ = 7 Hz, 12 H, -CH$_3$], 1.34 [d, $^3J_{\mathrm{H,H}}$ = 7 Hz, 12 H, -CH$_3$], 1.52 [sept, $^3J_{\mathrm{H,H}}$ = 7 Hz, 4 H, -CH], 1.65 [sept, $^3J_{\mathrm{H,H}}$ = 7 Hz, 4 H, -CH] ppm. ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ = 15.9 [s], 19.2 [s], 19.5 [s], 20.5 [s], 22.9 [s], 23.3 [s] ppm. ^{29}Si{^{1}H} NMR (C$_6$D$_6$): δ = –10.4 [s], 34.1 [s] ppm. MS (EI, TOF): *m*/*z* (%) = 527.08 (3) [M]$^+$, 441.03 (5) [M – 2 *i*Pr]$^+$, 398.99 (8) [M – 2 *i*Pr – C$_3$H$_6$]$^+$, 377.11 (22) [M – Si(*i*Pr)$_2$Cl]$^+$, 356.95 (12) [M – 2 *i*Pr – 2 C$_3$H$_6$]$^+$, 335.05 (35) [M – Si(*i*Pr)$_2$Cl – C$_3$H$_6$]$^+$, 293.02 (72) [M – Si(*i*Pr)$_2$Cl – 2 C$_3$H$_6$]$^+$, 250.99 (48) [M – Si(*i*Pr)$_2$Cl – 3 C$_3$H$_6$]$^+$, 221.01 (89) [M – Si(*i*Pr)$_2$Cl – C$_3$H$_6$ – Si(*i*Pr)$_2$]$^+$, 186.05 (100) [M – Si(*i*Pr)$_2$Cl – 5 C$_3$H$_6$]$^+$, 144.02 (39) [M – Si(*i*Pr)$_2$Cl – 6 C$_3$H$_6$]$^+$.

Compound 6: [Li(DME)PH$_2$] (4.18 g, 0.032 mol) was dissolved in THF (225 mL) and treated with a solution of **5** (8.40 g, 0.016 mol) in THF (50 mL) at 0 °C. The yellow suspension became pale after 16 h. The solvent was removed and the residue was suspended in *n*pentane (100 mL). After filtration, the solvent was removed and the white precipitate was dissolved in boiling *n*-heptane (20 mL). At –20 °C, colourless crystals of **6** were obtained, the yield being 4.07 g (52%). C$_{24}$H$_{57}$PSi$_4$ (489.03): calcd. C 58.95, H 11.75; found C 58.54, H 11.42. ^{1}H NMR (C$_6$D$_6$): δ = 0.72 [d, $^1J_{\mathrm{P,H}}$ = 185 Hz, 1 H], 1.27 [d, $^3J_{\mathrm{H,H}}$ = 7 Hz, 12 H], 1.30 [d, $^3J_{\mathrm{H,H}}$ = 7 Hz, 12 H], 1.33 [d, $^3J_{\mathrm{H,H}}$ = 5 Hz, 24 H], 1.35 [sept overlay, $^3J_{\mathrm{H,H}}$ = 5 Hz, 4 H], 1.36 [sept overlay, $^3J_{\mathrm{H,H}}$ = 7 Hz, 2 H], 1.54 [sept, $^3J_{\mathrm{H,H}}$ = 7 Hz, 2 H] ppm. ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ = 15.5 [s], 16.9 [d, $^2J_{\mathrm{P,C}}$ = 10 Hz], 21.8 [d, $^3J_{\mathrm{P,C}}$ = 5 Hz], 22.1 [d, $^3J_{\mathrm{P,C}}$ = 7 Hz], 23.5 [s], 23.9 [s] ppm. ^{29}Si{^{1}H} NMR (C$_6$D$_6$): δ = –13.3 [d, $^2J_{\mathrm{Si,P}}$ = 3 Hz], 6.4 [d, $^1J_{\mathrm{Si,P}}$ = 39 Hz] ppm. ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ = –261.3 [d with Si satellites; $^1J_{\mathrm{P,H}}$ = 185, $^1J_{\mathrm{P,Si}}$ = 39 Hz] ppm. MS (EI, 70 eV): *m*/*z* (%) = 488.1 (26) [M]$^+$, 445.1 (100) [M – *i*Pr]$^+$, 403.1 (32) [M – *i*Pr – C$_3$H$_6$]$^+$, 361.0 (4) [M – *i*Pr – 2 C$_3$H$_6$]$^+$, 319.0 (2) [M – *i*Pr – 3 C$_3$H$_6$]$^+$, 287.0 (20) [M – *i*Pr – C$_3$H$_6$ – Si(*i*Pr)$_2$]$^+$, 245.0 (6) [M – *i*Pr – 2 C$_3$H$_6$ – Si(*i*Pr)$_2$]$^+$. IR (KBr): $\tilde{\nu}$ = 2946 (vs), 2862 (vs), 2708 (s), 2266 (m, PH), 1457 (s), 1016 (m), 876 (s), 619 (s) cm^{-1}.

Compound 7: Compound **6** (0.476 g, 0.97 mmol) was dissolved in *n*-heptane (10 mL) and treated with *n*BuLi (0.61 mL, 0.97 mmol; 1.6 M) at 0 °C. After 30 min, the solution was warmed to room temperature. After another hour, the yellow solution was charged with dibromethane (0.042 mL, 0.48 mmol). After separation of the white LiBr precipitate, the filtrate was concentrated and yellow crystals of **7** were formed, the yield being 0.18 g (38% based on phosphorus) at 4 °C. C$_{48}$H$_{112}$P$_2$Si$_8$ (976.04): calcd. C 59.07, H 11.57; found C 58.06, H 11.81. ^{1}H NMR (C$_6$D$_6$): δ = 1.41 [d, $^3J_{\mathrm{H,H}}$ = 7 Hz, 12 H], 1.43 [d, $^3J_{\mathrm{H,H}}$ = 7 Hz, 12 H], 1.48 [d, $^3J_{\mathrm{H,H}}$ = 5 Hz, 12 H], 1.53 [d, $^3J_{\mathrm{H,H}}$ = 5 Hz, 12 H], 1.73 [sept, $^3J_{\mathrm{H,H}}$ = 7 Hz, 4 H], 1.84 [sept, $^3J_{\mathrm{H,H}}$ = 7 Hz, 4 H] ppm. ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ = 16.5 [pseudo t, $^3J_{\mathrm{P,C}}$ + $^4J_{\mathrm{P,C}}$ = 3 Hz], 19.3 [pseudo t, $^2J_{\mathrm{P,C}}$ + $^3J_{\mathrm{P,C}}$ = 5 Hz], 22.3 [pseudo t, $^3J_{\mathrm{P,C}}$ + $^4J_{\mathrm{P,C}}$ = 3 Hz], 23.0 [pseudo t, $^3J_{\mathrm{P,C}}$ + $^4J_{\mathrm{P,C}}$ = 3 Hz], 24.4 [s], 24.8 [s] ppm. ^{29}Si{^{1}H} NMR (C$_6$D$_6$): δ = –15.6 [pseudo t, $^2J_{\mathrm{P,Si}}$ + $^3J_{\mathrm{P,Si}}$ = 14 Hz], 7.7 [pseudo t, $^1J_{\mathrm{P,Si}}$ + $^2J_{\mathrm{P,Si}}$ = 29 Hz] ppm. ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ = –194.3 [s] ppm. MS (EI, 70 eV): *m*/*z* (%) = 974.1 (55) [M]$^+$, 931.1 [M – *i*Pr]$^+$, 488.1 (100) [M/2]$^+$, 444.9 (73) [M/2 – *i*Pr]$^+$, 402.9 (89) [M/2 – *i*Pr – C$_3$H$_6$]$^+$, 287.0 (85) [M/2 – *i*Pr – C$_3$H$_6$ – Si(*i*Pr)$_2$]$^+$. IR (KBr): $\tilde{\nu}$ = 2946 (vs), 2864 (vs), 1462 (s), 1384 (m), 1361 (m), 1262 (m), 1067 (m), 1019 (vs), 879 (m), 802 (vs), 616 (m), 488 (m), 463 (m) cm^{-1}.

Compound 8: Compound **7** (0.206 g, 0.42 mmol) was dissolved in *n*-heptane (10 mL) and treated with *n*BuLi (0.26 mL, 0.42 mmol; 1.6 M) at 0 °C. After 30 min, the solution was warmed to room temperature. Subsequently, the solution was concentrated and colourless crystals of **8** were obtained, the yield being 0.26 g (42%) at 4 °C. C$_{72}$H$_{168}$Li$_3$P$_3$Si$_{12}$ (1484.89): calcd. C 58.24, H 11.40; found C 57.14, H 11.31. ^{1}H NMR (C$_6$D$_6$): δ = 1.28 [d, $^3J_{\mathrm{H,H}}$ = 7 Hz, 12 H], 1.31 [d, $^3J_{\mathrm{H,H}}$ = 7 Hz, 12 H], 1.38 [d, $^3J_{\mathrm{H,H}}$ = 5 Hz, 12 H], 1.45 [d, $^3J_{\mathrm{H,H}}$ = 5 Hz, 12 H], 1.55 [sept, $^3J_{\mathrm{H,H}}$ = 7 Hz, 4 H], 1.67 [sept, $^3J_{\mathrm{H,H}}$ = 7 Hz, 4 H] ppm. ^{7}Li NMR (C$_6$D$_6$): δ = 3.49 [t, $^1J_{\mathrm{P,Li}}$ = 74 Hz] ppm. ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ = 16.1 [s], 17.0 [s], 22.9 [s], 24.2 [s], 24.7 [s] ppm. ^{29}Si{^{1}H} NMR (C$_6$D$_6$): δ = –16.7 [s], 14.6 [d, $^1J_{\mathrm{Si,P}}$ = 38. Hz].^{31}P{^{1}H} NMR (C$_6$D$_6$): δ = –315.2 [s] ppm. MS (EI, 70 eV): *m*/*z* (%) = 488.1 (66) [(*i*Pr$_2$Si)$_4$P]$^+$, 444.9 (100) [(*i*Pr$_2$Si)$_4$P – *i*Pr]$^+$, 402.9 (93) [(*i*Pr$_2$Si)$_4$P – *i*Pr – C$_3$H$_6$]$^+$, 287.0 (85) [(*i*Pr$_2$Si)$_4$P – *i*Pr – C$_3$H$_6$ – Si(*i*Pr)$_2$]$^+$. IR (KBr): $\tilde{\nu}$ = 2946 (vs), 2864 (vs), 1461 (s), 1383 (m), 1361 (m), 1262 (s), 1096 (vs), 1018 (vs), 878 (m), 802 (vs), 621 (m), 499 (m), 450 (m) cm^{-1}.

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[1] G. Fritz, *Z. Naturforsch., Teil B* **1953**, *8*, 776.

[2] G. Fritz, P. Scheer, *Chem. Rev.* **2000**, *100*, 3341.

[3] G. Fritz, W. Hölderich, *Z. Anorg. Allg. Chem.* **1977**, *431*, 76.

[4] G. Fritz, K. Stoll, *Z. Anorg. Allg. Chem.* **1986**, *538*, 78.

[5] a) C. von Hänisch, *Z. Anorg. Allg. Chem.* **2008**, *634*, 23; b) G. Tekautz, J. Baumgartner, A. Dransfeld, K. Hassler, *Eur. J. Inorg. Chem.* **2007**, 4071; c) C. von Hänisch, E. Matern, *Z. Anorg. Allg. Chem.* **2005**, *631*, 1655; d) M. Driess, I. Hyla-Kryspin, H. Lange, R. Gleiter, *Chem. Eur. J.* **1997**, *3*, 874.

[6] C. v. Hänisch, S. Traut, S. Stahl, *Z. Anorg. Allg. Chem.* **2007**, *633*, 2199.

[7] C. v. Hänisch, D. Nikolova, *Eur. J. Inorg. Chem.* **2006**, 4770.

[8] a) H. Günther, *NMR-Spektroskopie*, 3rd ed., Georg Thieme Verlag, Stuttgart, **1992**; b) R. Radeglia, *J. Prakt. Chem.* **1989**, *331*, 863.

[9] G. M. Kollegger, U. Katzenbeisser, K. Hassler, C. Krüger, D. Bauer, R. Gielen, *J. Organmet. Chem.* **1997**, *543*, 103.

[10] a) R. T. Oakley, D. A. Stanislawski, R. West, *J. Organomet. Chem.* **1978**, *157*, 389; b) E. Hengge, U. Brychey, *Monatsh. Chem.* **1966**, *97*, 1309.

[11] G. Becker, H.-M. Hartmann, W. Schwarz, *Z. Anorg. Allg. Chem.* **1989**, *577*, 9.

[12] STOE-IPDS2 (Mo-K_α radiation, $\lambda = 0.71073$ A). The structure was resolved by direct methods and refined against F^2 by the full-matrix least-squares technique (Li, C, O, Si, P and W were refined anisotropically, H atoms at the phosphorus atoms were refined isotropically, all other H atoms were calculated at ideal positions). CCDC-701023 (for **2**), -701024 (for **3**), -701025 (for **6**), -701026 (for **7**), -701027 (for **8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[13] H. Gilman, R. N. Clark, *J. Am. Chem. Soc.* **1947**, *69*, 1499.

[14] H. Schäfer, G. Fritz, W. Hölderlich, *Z. Anorg. Allg. Chem.* **1977**, *428*, 222.

[15] S. Masamune, H. Tobita, *J. Am. Chem. Soc.* **1983**, *105*, 6524.

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