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Synthesis of a "Half"-Parent Phosphasilene $R_2Si{=}PH$ and Its Metalation to the Corresponding *P*-Zinciophosphasilene $[R_2Si{=}PM]$**

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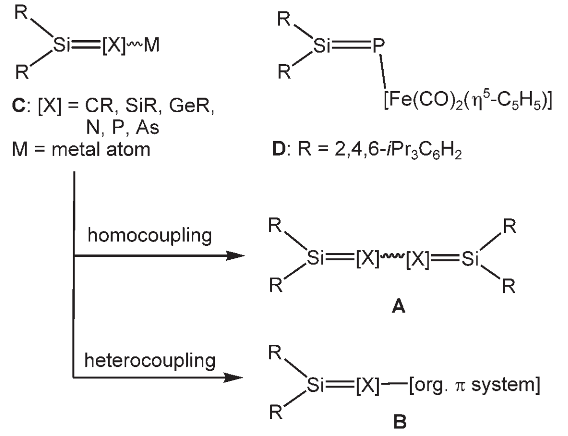
Dedicated to Professor Hansgeorg Schnöckel on the occasion of his 65th birthday

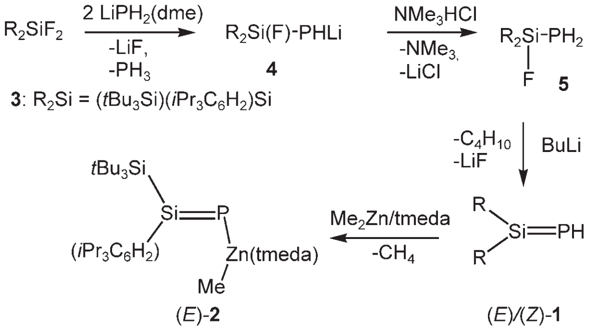
The isolation of compounds with low-coordinate silicon atoms,[1–3] in other words, silicon homologues of olefins, and more recently the synthesis of the first inert disilyne, an alkyne analogue with a silicon–silicon triple bond,[4] are major breakthroughs in contemporary silicon chemistry. Unsaturated silicon compounds with Si=X bonds (X = elements from Groups 14,[1] 15,[2] or 16 [3]) show an intriguing reactivity toward both electrophiles and nucleophiles, and are valuable building blocks for the synthesis of electronically unusual silicon compounds by means of addition reactions.

Another challenge is to use functional groups containing low-coordinate silicon atoms for the synthesis of novel conjugated heteroatom systems **A** and **B** by homo- and heterocoupling reactions of metal-substituted Si=X building blocks **C** (X = elements from Groups 14 or 15; Scheme 1). However, compounds of type **C** suitable as reagents for a nucleophilic transfer of intact Si=X moieties are still very rare. While lithium disilenylide derivatives of the type $R_2Si{=}SiR(Li)$, that is, disila analogues of vinyllithium, have been reported very recently,[5] related metal-substituted heterosilenes of the type $R_2Si{=}[X]M$ and $(M)RSi{=}[X]R$ are currently unknown, except for the *P*-ferrio-substituted phosphasilene $R_2Si{=}P[Fe(CO)_2(\eta^5\text{-}C_5H_5)]$ **D** (R = 2,4,6-iPr$_3$C$_6$H$_2$; Scheme 1).[6] Lithium disilenylides have been shown to undergo homocoupling to give the corresponding tetrasilabuta-1,3-dienes.[7]

P-metalated phosphasilenes of the type $R_2Si{=}PM$ should be easily accessible through metalation of "half"-parent phosphasilenes of the type $R_2Si{=}PH$; however, such a phosphasilene derivative is hitherto unknown. We report here the synthesis of the first isolable phosphasilene **1** with a PH group and its P-metalation with Me_2Zn in the presence of *N,N,N′,N′*-tetramethylethylenediamine (tmeda) to afford the crystalline *P*-zinciophosphasilene **2** in 87% yield (Scheme 2).



Scheme 1. The ferrio-substituted phosphasilene **D** and the conversion of X-metalated silenes **C** into **A** and **B**.



Scheme 2. Synthesis of **1** and **2** via the difluorosilane **3** and the (fluorosilyl)phosphanes **4** and **5**, respectively. dme = dimethoxyethane.

Phosphasilene **1** is easily accessible by a modified procedure analogous to the preparation of P-silyl-substituted phosphasilenes,[2f,g,i,k] starting from the bulky substituted difluorosilane $(tBu_3Si)RSiF_2$ **3** (R = 2,4,6-iPr$_3$C$_6$H$_2$) and $[LiPH_2(dme)]$ in the molar ratio of 1:2 (Scheme 2). The first step of this reaction leads solely to the corresponding lithium (fluorosilyl)phosphanide **4** (characterized by ^{31}P and ^{29}Si NMR spectroscopy, see the Supporting Information) along with PH_3 and LiF. Unexpectedly and in contrast to other lithium (fluorosilyl)phosphanides,[2l,8] solutions of **4** in THF already undergo LiF elimination above 30 °C, affording a mixture of the *Z* and *E* isomers of **1** in moderate yield (^{31}P NMR) besides several side-products, which could not be separated from **1**. However, compound **1** is surprisingly simple to prepare in quantitative yield by a modified procedure using LiF-free samples of **4** in hexane solutions at ambient temperature. This can be achieved by P-lithiation of purified (fluorosilyl)phosphane **5** with BuLi in hexane solution, and **5** is in turn easily accessible by mild protonation of **4** with NMe_3HCl (Scheme 2). Compound **5** can be isolated

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[**] M = {Zn(tmeda)Me}; tmeda = *N,N,N′,N′*-tetramethylethylenediamine.

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in 91 % yield in the form of colorless crystals, which have been characterized by NMR spectroscopy and elemental analysis (see the Supporting Information).

Phosphasilene **1** was isolated in the form of greenish yellow crystals in 88 % yield, and its composition was confirmed by EIMS (*m*/*z* 462) and C,H analysis. The product consists of a 1:1.5 mixture of the *Z* and *E* isomers as proven by its ^{1}H, ^{31}P, and ^{29}Si NMR spectra. Thus, the ^{31}P NMR spectrum shows two doublet signals with ^{29}Si satellites at $\delta = 123.1$ ($^{1}J(\mathrm{P,H}) = 123$, $^{1}J(^{31}\mathrm{P},^{29}\mathrm{Si}) = 157$ Hz) and 134.2 ppm ($^{1}J(\mathrm{P,H}) = 131$, $^{1}J(^{31}\mathrm{P},^{29}\mathrm{Si}) = 130$ Hz). Accordingly, the ^{1}H NMR spectrum of the *E*/*Z* mixture exhibits two doublets for the protons of the PH groups at $\delta = 5.14$ ($^{1}J(^{31}\mathrm{P},^{1}\mathrm{H}) = 131$ Hz) and 5.20 ppm ($^{1}J(^{31}\mathrm{P},^{1}\mathrm{H}) = 123$ Hz), respectively. Based on selective NOE ^{1}H NMR experiments, one can assign the NMR resonances at $\delta = 5.14$ (^{1}H) and 123 ppm (^{31}P) to the *E* isomer ($t\mathrm{Bu_3Si}$,PH), while the signals at $\delta = 5.20$ (^{1}H) and 134.2 ppm (^{31}P) belong to the *Z* form.

Interestingly, the $^{1}J(\mathrm{P,H})$ coupling constants are approximately 80 Hz smaller than the characteristic values observed for secondary phosphanes $\mathrm{R_2PH}$ (R = alkyl, aryl, silyl) and significantly smaller than those of phosphaalkenes with a PH group ($^{1}J(^{31}\mathrm{P},^{1}\mathrm{H}) = 140$–208 Hz).[9] This indicates that the phosphorus atom in **1** prefers more 3p character in the P–H bond. As expected, the ^{31}P nucleus in **1** is less shielded than those in P-silylated phosphasilenes of the type $\mathrm{R_2Si{=}PSiR_3}$ ($\delta = -33$ to 28 ppm)[2k,i] but almost identical with the values reported for P-organo-substituted Si=P compounds ($\delta = 65$–136 ppm).[2k,i,o] The ^{29}Si resonance for the low-coordinate Si atom in **1** shows for each isomer a doublet at characteristically low field with a typical scalar ^{29}Si-^{31}P coupling constant. The signal at $\delta = 248.9$ ppm ($^{1}J(^{29}\mathrm{Si},^{31}\mathrm{P}) = 130$ Hz) can be assigned to the *Z* isomer and that at $\delta = 249.8$ ppm ($^{1}J(^{29}\mathrm{Si},^{31}\mathrm{P}) = 157$ Hz), to the *E* form.

A single-crystal X-ray diffraction analysis[10] confirms that the low-coordinate silicon atom adopts the trigonal-planar coordination geometry (Figure 1). The Si1–P1 distance of 209.4(5) pm is about 7 % shorter than a Si–P single bond but only marginally longer (ca. 3 pm) than the respective value in P-silyl-substituted phosphasilenes.[2k,i] This indicates a shallow potential of the Si=P bond on the potential energy surface.[2n,o] The Si1–Si2 bond length of 239.8(5) pm is comparable to the values of other $t\mathrm{Bu_3Si}$-substituted silicon compounds.[11]

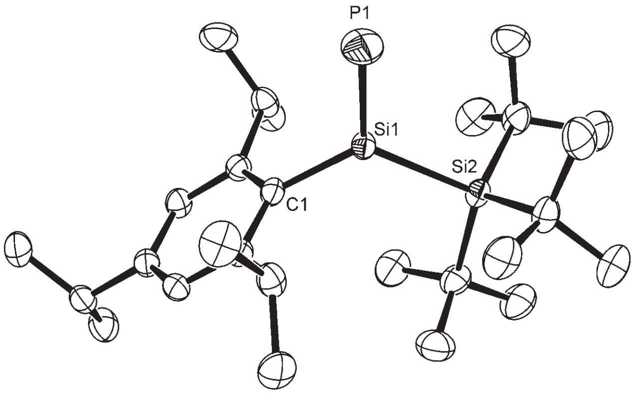

Figure 1. X-ray crystal structure of **1** (ellipsoids drawn at the 50% probability level; hydrogen atoms omitted for clarity). Selected distances [pm] and angles [°]: Si1–P1 209.4(5), Si1–Si2 239.8(5), Si1–C1 188.0(12); Si2-Si1-P1 121.5(2), C1-Si1-Si2 120.3(4), C1-Si1-P1 118.2(4); sum of the bond angles at Si1: 359.9°.

Although the substituents at the phosphorus atom are not very bulky, compound **1** survives heating in boiling toluene solution for several days. Since the Si=P bond appears to be sufficiently protected, we decided to use **1** as the starting material for the formation of an isolable, nucleophilic P-metal-subsituted phosphasilene. While lithiation of **1** with BuLi in nonpolar or polar donor solvents (ether, tmeda) at −78 °C did not lead to the desired P-lithiated phosphasilene as indicated by the ^{31}P NMR spectrum of the reaction mixture (no low-field resonances), its metalation with $\mathrm{Me_2Zn}$ in the presence of tmeda proceeded cleanly at −78 °C and furnished solely the desired *P*-zinciophosphasilene **2** (low-field $\delta(^{31}\mathrm{P})$ and $\delta(^{29}\mathrm{Si})$ signals). Alternatively, **2** was also accessible in high yield by a one-pot procedure, starting from **5** (see the Supporting Information).

P-zinciophosphasilene **2** was isolated in the form of orange crystals in 87 % yield, and its composition and constitution was proven by EIMS (*m*/*z* 658), C,H analysis, and NMR spectroscopy. Because of the dominantly covalent character of the Zn–P bond, **2** does not dissociate in solutions in aromatic hydrocarbons and in ethers, as proven by cryoscopic measurements. Not only that, the steric demand of the {ZnMe(tmeda)} group at the phosphorus atom favors the *E* configuration as the lowest energy configuration; this was proven by variable-temperature (VT) ^{1}H, ^{31}P and ^{29}Si NMR spectroscopy. Thus, solutions of **2** in toluene exhibit in the temperature range from −80 to 80 °C only one singlet resonance signal in the ^{31}P NMR spectrum at unusual low field ($\delta = 227$ ppm). The extremely low-field resonance of the ^{31}P nucleus, which is roughly 100 ppm lower than that observed for (*Z*)- and (*E*)-**1** represents the least shielded chemical shift hitherto reported for a phosphasilene.[2j,k]

In contrast to the deshielding of the ^{31}P nucleus, the low-coordinate ^{29}Si atom in **2** ($\delta = 203$ ppm) is more shielded than that in (*Z*)/(*E*)-**1** ($\Delta\delta = 42$ ppm). This can be explained by stabilization of the n orbital at phosphorus through $n(\mathrm{P}) \rightarrow \sigma^*(\mathrm{Si{-}Si})$ hyperconjugation which, apparently, is more efficient in **2** than in **1** as a result of the higher negative partial charge at the phosphorus atom (Figure 2).[12] Similar shielding effects have been observed for related alkali-metal-substituted disilenylides ("disilavinyls") of the type $[\mathrm{M(R_3Si)Si{=}Si(SiR_3)_2}]$ (M = Li, Na, K),[5b,7b] which show extremely low-field signals for the metal-substituted silicon atoms. Accord-

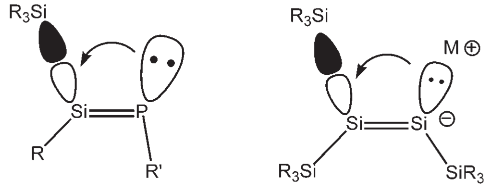

Figure 2. Proposed negative hyperconjugation $n(\mathrm{P}) \rightarrow \sigma^*(\mathrm{Si{-}Si})$ in **2** (left) and the analogous hyperconjugation $\sigma(\mathrm{Si{-}M}) \rightarrow \sigma^*(\mathrm{Si{-}Si})$ in isoelectronic silyl-substituted alkali-metal disilenylide compounds (right).[5b, 7b]

ingly, the resonance signal of the other low-coordinate ^{29}Si type is shifted to higher field as a result of $\sigma(\text{Si}-\text{M})\rightarrow\sigma^*(\text{Si}-\text{Si})$ negative hyperconjugation (Figure 2).

The *E* configuration of **2** was confirmed by X-ray diffraction analysis.[10] This also proved that the Si1 atom has trigonal-planar geometry and that the Si1–P1 distance of 206.4(1) pm is significantly shorter than that in **1** (Figure 3).

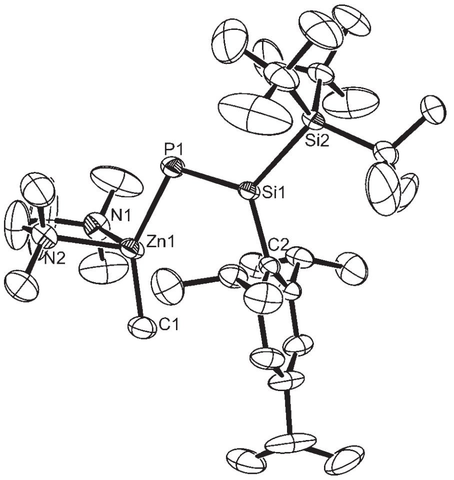

Figure 3. X-ray crystal structure of **2** (ellipsoids drawn at the 50% probability level; hydrogen atoms omitted for clarity). Selected distances [pm] and angles [°]: Si1–P1 206.4(1), Si1–Si2 240.2(1), Si1–C2 190.3(4), P1–Zn1 234.9(1), C1–Zn1 199.5(4); Si2-Si1-P1 118.10(6), Si2-Si1-C2 120.2(1), C2-Si1-P1 121.7(1), Si1-P1-Zn1 103.20(5); sum of the bond angles at Si1: 360°.

The shortening of the Si=P bond, the slight elongation of the Si1–Si2 bond, and the smaller P1-Si1-Si2 angle are consistent with the presence of hyperconjugative interactions as depicted in Figure 2. As expected, the Zn1 atom has tetrahedral coordination geometry and the value of the P1–Zn1 distance is typical for that of zincphosphanides.[13]

In summary, we have prepared the first phosphasilene derivatives with terminal hydrogen and zinc substituents at phosphorus by an unexpectedly simple procedure. These compounds represent a novel type of thermally robust building blocks in the chemistry of unsaturated silicon–phosphorus compounds. Investigations on the use of **1** and **2** for the synthesis of novel conjugated, electron-rich π systems of types **A** and **B** (see Scheme 1) by homo- or hetero-cross-coupling reactions are currently underway.

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[10] **1**: Triclinic, space group $P\bar{1}$, $a = 8.488(2)$, $b = 9.388(2)$, $c = 18.944(4)$ Å, $\alpha = 78.627(17)$, $\beta = 84.363(18)$, $\gamma = 81.652(18)°$, $V = 1460.4(6)$ Å^3, $Z = 2$, $\rho_{\text{calcd}} = 1.053\ \text{mg m}^{-3}$, $\mu(\text{Mo}_{K\alpha}) = 0.19\ \text{mm}^{-1}$, 11516 collected reflections, 5122 crystallographically independent reflections [$R_{\text{int}} = 0.0359$], 5121 reflections with $I > 2\sigma(I)$, $\theta_{\max} = 25.00°$, 271 refined parameters, $R(F_o) = 0.0459$ ($I > 2\sigma(I)$, $wR(F_o^2) = 0.1179$ (all data). **2**: Monoclinic, space group $P2_1/c$, $a = 14.6883(4)$, $b = 12.5931(3)$, $c = 24.4109(7)$ Å, $\beta = 101.7130(10)°$, $V = 4421.3(2)$ Å^3, $Z = 4$, $\rho_{\text{calcd}} = 1.076\ \text{mg m}^{-3}$, μ-$(\text{Mo}_{K\alpha}) = 0.67\ \text{mm}^{-1}$, 26671 collected reflections, 7772 crystallographically independent reflections [$R_{\text{int}} = 0.0448$], 5757 reflections with $I > 2\sigma(I)$, $\theta_{\max} = 25.00°$,419 refined parameters, $R(F_o) = 0.0580$ ($I > 2\sigma(I)$), $wR(F_o^2) = 0.1476$ (all data). Each of the crystals were mounted on a glass capillary in perfluorinated oil and measured in a cold N_2 flow. The data of **1** were collected on a STOE IPDS 2T diffractometer with an area detector at 173 K ($\text{Mo}_{K\alpha}$ radiation, $\lambda = 0.71073$ Å) and those of **2** on a Bruker-AXS SMART CCD diffractometer at 173(2) K ($\text{Mo}_{K\alpha}$ radiation, $\lambda = 0.71073$ Å). The structures were solved by direct methods and were refined on F^2 with the SHELX-97[14] software package. The positions of the H atoms were calculated and considered isotropically according to a riding model. Absorption corrections were conducted using the SADABS program.[15] CCDC 289280 (**1**) and CCDC 289281 (**2**) contains 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.

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