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A Persistent 1,2-Dihydrophosphasilene Adduct

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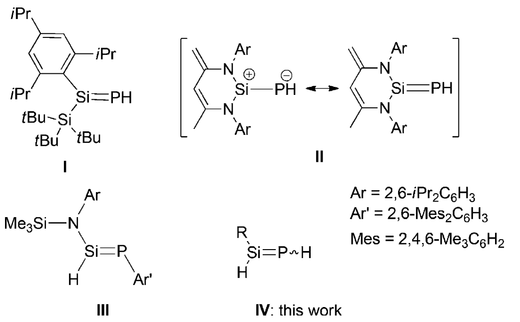
Dedicated to Professor Herbert W. Roesky on the occasion of his 80th birthday

Abstract: *The reaction of the arylchlorosilylene–NHC adduct ArSi(NHC)Cl [$Ar=2,6\text{-}Trip_2\text{-}C_6H_3$; $NHC=(MeC)_2(NMe)_2C$] **1** with one molar equiv of $LiPH_2{\cdot}dme$ (dme = 1,2-dimethoxyethane) affords the first 1,2-dihydrophosphasilene adduct **2** (ArSi(NHC)(H)=PH). The latter is labile in solution and can undergo head-to-tail dimerization to give $[ArSi(H)PH]_2$ **3** and “free” NHC. Further stabilization of **2** by complexation with {$W(CO)_5$} affords the isolable 1,2-dihydrophosphasilene–tungsten complex **4** [$ArSi(NHC)(H)=P(H)W(CO)_5$]. Additionally, the new 1-silyl-2-hydrophosphasilene $ArSi(NHC)(H)=PSiMe_3$ **5** could be synthesized and structurally characterized. DFT studies confirmed that the Si=P bond in **2** and **4** is mostly zwitterionic with drastically decreased double-bond character.*



Scheme 1. Phosphasilenes bearing a hydrogen atom at the Si and/or P center. Compounds of type **IV** are currently unknown.

The parent phosphasilene $H_2Si=PH$ has not been isolated and was only observed some years ago in a matrix-spectroscopic study through the reaction of atomic silicon with phosphane.[1] If one compares different isomers with the formula H_3SiP, the generated parent phosphasilene $H_2Si=PH$ in an argon matrix at 10 K is the most stable isomer, as calculations have suggested.[2–4] Spectroscopic evidence for the first stable phosphasilene with a Si=P bond with bulky aryl substituents at the phosphorus and silicon atoms was reported 30 years ago by Bickelhaupt et al.[5] Since then, several further species bearing a Si=P moiety have been reported. These species and related low-valent Group 14 compounds are stabilized either by taking advantage of steric congestion through the presence of bulky substituents and/or by push–pull electronic effects.[6–27] Only recently, the first isolable “half-parent” phosphasilenes **I**,[28] **II**,[29,30] and **III**[31] of the type $R_2Si=PH$ or $R(H)Si=PR$ could be realized (Scheme 1). However, a 1,2-dihydrophosphasilene **IV** with hydrogen atoms at silicon and phosphorus $R(H)Si=PH$, which are closer to the parent system, has not been reported to date.

In contrast, isolable 1,2-dihydrodisilene derivatives have been known since 2001.[32] In 2002, Tokitoh and co-workers reported the successful isolation of a 1,2-dihydrodisilene, which is kinetically stabilized by very bulky aryl groups.[33] Apparently, 1,2-dihydrophosphasilenes are more difficult to realize because of the marked polarity of the Si=P bond induced by the higher electronegativity of phosphorus versus silicon and because of the absence of steric bulk at the phosphorus center.[10,12]

Herein we report the synthesis of the first 1,2-dihydrophosphasilene adduct and the isolation and structural characterization of its $R(H)Si=P(H)\rightarrow W(CO)_5$ complex. Furthermore, through the use of the same ligand at the silicon center, a 1-silyl-2-hydrophosphasilene could be prepared and fully characterized.

The reaction of the NHC adduct of arylchlorosilylene[34] **1** with one molar equiv of $LiPH_2{\cdot}dme$ (dme = 1,2-dimethoxyethane) at room temperature in THF afforded, after 18 h, the 1,2-dihydrophosphasilene **2**, presumably through tautomerization of its elusive phosphanylsilylene isomer (Scheme 2). The ^{31}P NMR spectrum of **2** shows a doublet of doublets with ^{29}Si satellites at $\delta(^{31}P)=-301.4$ ppm ($^{1}J(P,H)=132.0$ Hz, $^{2}J(P,H)=11.3$ Hz, $^{1}J(Si,P)=120.7$ Hz). The $^{1}J(P,H)$ coupling constant is 12 Hz smaller than that of the Me_4-NHC-stabilized form of **II** (NHC-**II**),[30] indicating lower 3s character of the P–H bond. The ^{31}P signal of **2** is shifted to higher field compared with the resonance of NHC-**II** ($\delta(^{31}P)=-259.8$ ppm) and is even more shielded than signals of existing “half-parent” phosphasilenes. The upfield-shifted ^{29}Si signal ($\delta(^{29}Si)=-25.6$ ppm, $^{1}J(Si,P)=120.7$ Hz) is similar to the ^{29}Si resonance signal of **III** ($\delta(^{29}Si)=-21.1$ ppm).[31] In the ^{1}H NMR spectrum the signal for the hydrogen nucleus at the phos-

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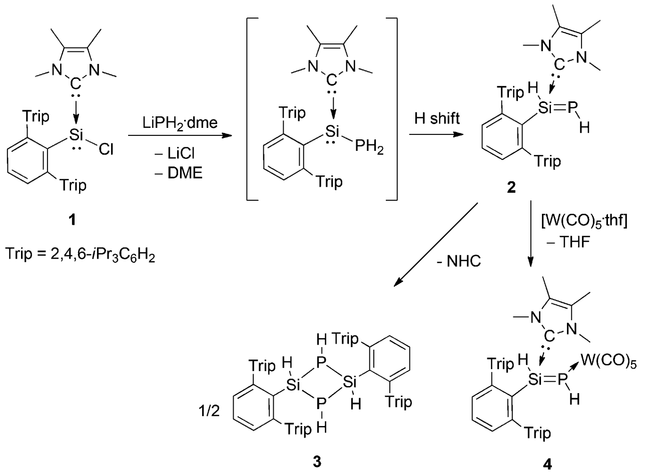


Scheme 2. Synthesis of the 1,2-dihydrophosphasilenes **2** and **4** and dimer **3**.

phorus appears at $\delta = -1.38$ ppm and is split into a doublet of doublets ($^{1}J(\mathrm{P,H}) = 132.0$ Hz, $^{3}J(\mathrm{H,H}) = 5.8$ Hz). The Si–H signal with ^{29}Si satellites is split into a doublet of doublet as well and can be found at $\delta = 5.95$ ppm ($^{1}J(\mathrm{Si,H}) = 192.8$ Hz, $^{2}J(\mathrm{P,H}) = 11.3$ Hz, $^{3}J(\mathrm{H,H}) = 5.8$ Hz).

Unfortunately, 1,2-dihydrophosphasilene is relatively labile in solution. In an NMR-scale experiment, the decomposition of **2** in [D$_8$]THF at room temperature is relatively slow but at 50 °C it takes only a few hours. Single crystals of the head-to-tail dimer **3** suitable for X-ray diffraction analysis could be obtained from the decomposition mixture in concentrated *n*-hexane solutions upon storage at 7 °C. Regrettably, its structure cannot be discussed due to poor crystal quality.[35] The high-resolution atmospheric-pressure chemical ionization mass spectrum (HR-APCI-MS) clearly proves the composition of **3**.

In fact, density functional theory (DFT) calculations indicate that the formation of **3**, under the loss of the NHC donor, is thermodynamically slightly favorable by $\Delta G = -5.7\ \mathrm{kcal\,mol^{-1}}$. For a consecutive path in which the NHC is first removed, the Gibbs free energy of activation is $\Delta G^{\#} = 16.9\ \mathrm{kcal\,mol^{-1}}$. In contrast, for a concerted mechanism, the Gibb free energy of the transition state is $\Delta G^{\#} = 12.1\ \mathrm{kcal\,mol^{-1}}$.[35] These results imply that the formation of the dimer can occur even at room temperature.

Furthermore, DFT studies at the B97-D/6-31G(d) level of theory were performed to elucidate the bonding situation in **2** and in its NHC-free form **2′** (Table 1). The Wiberg bond index (WBI) of the Si–P bond of donor-free 1,2-dihydrophosphasilene ArSi(H)=PH (**2′**; Ar = 2,6-Trip$_2$-C$_6$H$_3$) is 1.83. The natural bond orbital (NBO) analysis shows that the Si–P moiety has σ and π bonds. Compared to the "half-parent" phosphasilene **II** the s character of the σ bond of the silicon center is lower and shows sp^2 hybridization (36.8 % s, 62.7 % p, 0.4 % d; for **II**: 64.6 % s, 35.1 % p, 0.3 % d). The π bond is polarized to 63 % towards the phosphorus atom and exhibits only p character. The Si–P bond in the NHC-stabilized 1,2-dihydrophosphasilene **2** has a reduced WBI of 1.26 which is even lower than that of NHC-**II** (1.34). The calculated Si–P bond length in **2** equals 217.5 pm and is 7 pm larger than that in the NHC-free 1,2-dihydrophosphasilene ($d(\mathrm{Si,P}) = 210.6$ pm). An optimized molecular structure of compound **2** is shown is in Figure 1. The NBO analysis indicated only one σ-type bond between the Si and P atoms and two lone pairs residing on the phosphorus center. The NPA charges (Si: +1.05; P: −0.60) and the natural resonance theory (NRT) analysis (Si–P: 78.9 %, Si=P: 21.1 %) reflect this bonding situation. These computational results and the high-field-shifted ^{31}P resonance suggest that the zwitterionic resonance structure **2B** is the dominant contribution to the electronic features of **2** (Scheme 3).

Table 1: Calculated Si–P distances [pm], WBI values, atomic charges, and NRT analysis of the Si=P bond in H$_2$Si=PH, H$_2$Si(NHC)=PH, ArSi(H)=PH (Ar = 2,6-Trip$_2$-C$_6$H$_3$; NHC = (MeC)$_2$(NMe)$_2$C), **2**, and **4**.

Compound	d(Si–P) [pm]	WBI	Charges	NRT
H$_2$Si=PH	209.6	1.97	Si: +0.58 P: −0.29	Si=P: 100 %
H$_2$Si(NHC)=PH	217.1	1.29	Si: +0.74 P: −0.62	Si–P: 76.3 % Si=P: 23.7 %
ArSi(H)=PH (**2′**)	210.6	1.83	Si: +0.85 P: −0.32	Si–P: 3.9 % Si=P: 96.1 %
2	217.5	1.26	Si: +1.05 P: −0.60	Si–P: 78.9 % Si=P: 21.1 %
4	221.7	1.09	Si: +1.11 P: −0.20	Si–P: 89.9 % Si=P: 10.1 %

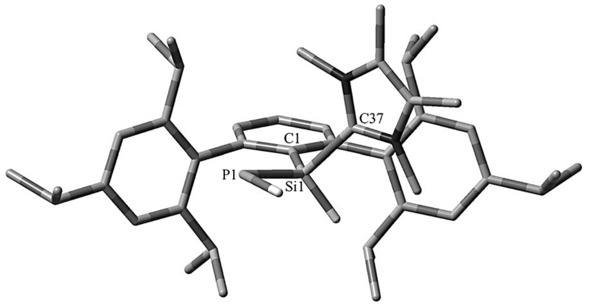
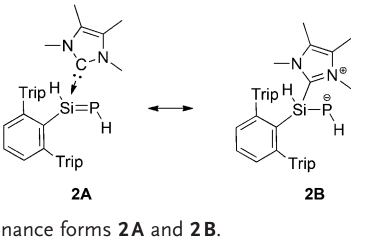


Figure 1. Stick model of the DFT-derived molecular structure of **2**. Hydrogen atoms, except for those on Si1 and P1, have been omitted for clarity.



Scheme 3. Resonance forms **2A** and **2B**.

These differences in the Si–P bonding situation can also be observed in the parent compounds H$_2$Si=PH and H$_2$Si(NHC)=PH (Table 1). Here, the Si–P bond length in the donor-free compound is greater than that in the NHC-stabilized phosphasilene by 7.5 pm. The WBI is almost 2 for $H_2Si{=}PH$ but merely 1.29 for $H_2Si(NHC){=}PH$. The NBO analysis shows, compared to the parent compound, that the Si–P bond in $H_2Si(NHC){=}PH$ consists only of a σ-type bond between the Si and P atoms and two lone pairs residing on the phosphorus center. As the atomic charges affirm, the Si–P σ-bond in the NHC-stabilized form is strongly polarized towards the phosphorus center. The NRT analysis reveals that in the parent phosphasilene the resonance structure with a Si=P bond is the main form, whereas in $H_2Si(NHC){=}PH$, a resonance structure with a Si–P single bond is the major form (76.3 %).

To stabilize the 1,2-dihydrophosphasilene, compound **2** was treated with freshly prepared $[W(CO)_5{\cdot}thf]$ (Scheme 2), affording the desired 1,2-dihydrophosphasilene–tungsten complex **4** in good yields. The $^{31}P\{^1H\}$ signal with ^{183}W satellites is shifted 13 ppm to higher field ($\delta(^{31}P) = -314.0$ ppm, $^1J(W,P) = 71.8$ Hz). However, in the ^1H NMR spectrum the doublet of the P–H signal is shifted to lower field ($\delta = -0.65$ ppm). The $^1J(P,H)$ coupling constant increased by 62.4 Hz, which is typical for complexes where the phosphorus binds to a σ-acceptor such as a transition metal.[36] The $^{29}Si\{^1H\}$ NMR spectrum displays a doublet at $\delta(^{29}Si) = -22.1$ ppm ($^1J(Si,P) = 79.0$ Hz). The $^1J(Si,P)$ coupling constant decreased by 42 Hz, indicating reduced Si=P bond character.

The molecular structure of **4** has been confirmed by X-ray diffraction analysis (Figure 2). The Si1–P1 distance of 221.05(4) pm, which is in a good agreement with the calculated Si–P distance (Table 1), is much longer than those found in NHC-**III** and in other structurally characterized phosphasilenes (ca. 205.3–216.5 pm) and is in the typical range of Si–P single bonds (average 225 pm).[31] The WBI of the Si1–P1 bond is only 1.09 and NRT analysis indicates that a zwitterionic resonance form similar to **2B** is the most important structure of **4**.

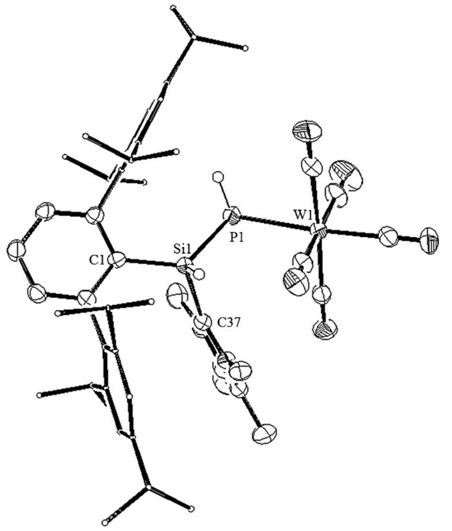
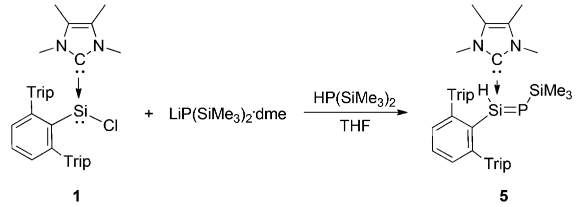


Figure 2. ORTEP representation of the molecular structure of **4**. Thermal ellipsoids at 50% probability; hydrogen atoms, except for those on Si1 and P1, have been omitted for clarity.. Selected distances (pm) and angles (°) of **4**: Si1-P1 221.05(14), Si1-C1 191.11(4), Si1-C37 192.1(4), P1-W1 263.65(10); C1-Si1-P1 122.50(12), C37-Si1-P1 98.78(12), Si1-P1-W1 105.59(5).

The IR spectrum of **4** displays two weak bands at $\nu_{PH} = 2322\ cm^{-1}$ and $\nu_{SiH} = 2170\ cm^{-1}$ corresponding to the stretching vibration of the PH and SiH groups, respectively. The characteristic stretching vibrations of the CO ligands are located at $\nu_{CO} = 2044$, 1948, 1893, and 1852 cm^{-1}.

The reaction of **1** and $LiP(SiMe_3)_3$ results in the new 1-silyl-2-hydrophosphasilene **5**, which could be isolated and fully characterized. The yield of **5** could be improved by adding one molar equivalent of bis(trimethylsilyl)phosphane to the reaction mixture, leading to full conversion of **1** to **5** (Scheme 4). The ^{31}P NMR spectrum of the reaction mixture reveals, beside the signal for the product at high field ($\delta(^{31}P) = -331.7$ ppm), the signal corresponding to $P(SiMe_3)_3$ at $\delta(^{31}P) = -253.4$ ppm. It is known that HPR_2 compounds are able to disproportionate into H_2PR and PR_3.[37] Therefore we propose that **1** reacts with the in situ formed $H_2P(SiMe_3)$, affording the corresponding NHC adduct of the phosphanylsilylene $Ar(NHC)SiP(H)SiMe_3$, which undergoes tautomerization to **5**. This proposed mechanism is supported by the clean reaction of **1** with $H_2P(SiMe_3)$ in the presence of Et_3N as a base.[35]



Scheme 4. Synthesis of the 2-hydrophosphasilene **5**.

The $^{29}Si\{^1H\}$ NMR spectrum of **5** shows two doublets at $\delta(^{29}Si) = -27.5$ ppm (Si=P, $^1J(Si,P) = 130.8$ Hz) and $\delta(^{29}Si) = 1.65$ ppm ($SiMe_3$, $^1J(Si,P) = 71.5$ Hz), respectively. The latter coupling constant is in the range typical for *P*-silyl-phosphasilenes.[10] Compared to the 1,2-dihydrophosphasilene **2**, the $^1J(Si,P)$ coupling constant in **5** is increased by 10.1 Hz, indicating increased Si–P double-bond character. This effect has already been described for the parent phosphasilenes $H_2Si{=}PH$ and $H_2Si{=}P(SiH_3)$. Computations show that the Si–P π-bond strength in the parent *P*-silyl-phosphasilene is increased and the Si–P bond length is shortened by hyperconjugation effects due to the silyl substituent at phosphorus.[12,30] The stronger σ-donor ability of the silyl group is also demonstrated by the upfield-shifted ^{31}P resonance signal in **5** ($\delta(^{31}P) = -331.7$ ppm) compared to that in **2** ($\delta(^{31}P) = -301.4$ ppm).

The molecular structure of **5** can be found in the Supporting Information. The silicon center is four-coordinated and adopts a distorted tetrahedral geometry. The Si1–P1 bond length of 214.59(17) pm is in the range typical of Si=P bonds and is shorter than the P1–Si2 distance (220.68(18) pm).

In summary, we have synthesized the first 1,2-dihydrophosphasilene adduct **2**, which is labile in solution and slowly dimerizes to give **3**. Compound **2** could be further stabilized by complexation of $\{W(CO)_5\}$ at the phosphorus atom to afford the 1,2-dihydrophosphasilene–tungsten complex **4**. Additionally, the new 1-silyl-2-hydrophosphasilene **5** has been synthesized which, similar to the formation of **2**, resulted from the tautomerization of the corresponding elusive phosphanylsilylene–NHC adduct.

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