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A Donor-Stabilized Zwitterionic "Half-Parent" Phosphasilene and Its Unusual Reactivity towards Small Molecules

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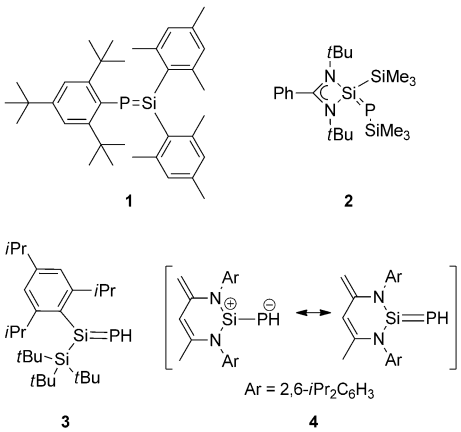
Dedicated to Professor Peter Hildebrandt

Abstract: The stabilization of the labile, zwitterionic "half-parent" phosphasilene **4** L′Si=PH (L′ = CH[(C=CH_2)CMe(NAr)$_2$]; Ar = 2,6-*i*Pr$_2$C$_6$H$_3$) could now be accomplished by coordination with two different donor ligands (4-dimethylaminopyridine (DMAP) and 1,3,4,5-tetramethylimidazol-2-ylidene), affording the adducts **8** and **9**, respectively. The DMAP-stabilized zwitterionic "half-parent" phosphasilene **8** is capable of transferring the elusive parent phosphinidene moiety (:PH) to an unsaturated organic substrate, in analogy to the "free" phosphasilene **4**. Furthermore, compounds **4** and **8** show an unusual reactivity of the Si=P moiety towards small molecules. They are capable of adding dimethylzinc and of activating the S–H bonds in H_2S and the N–H bonds in ammonia and several organoamines. Interestingly, the DMAP donor ligand of **8** has the propensity to act as a leaving group at the phosphasilene during the reaction. Accordingly, treatment of **8** with H_2S affords, under liberation of DMAP, the unprecedented thiosilanoic phosphane LSi=S(PH_2) **16** (L = HC(CMe[2,6-*i*Pr$_2$C$_6$H$_3$N])$_2$). Compounds **4** and **8** react with ammonia both affording L′Si(NH_2)PH_2 **17**, respectively. In addition, the reaction of **8** with isoproylamine, *p*-toluidine, and pentafluorophenylhydrazine lead to the corresponding phosphanylsilanes L′Si(PH_2)NHR (R = *i*Pr **18a**; R = C_6H_5–CH_3 **18b**, R = NH(C_6F_5) **18c**), respectively.

Introduction

Spectroscopic evidence for the first phosphasilene **1** bearing a Si=P functional group with bulky aryl substituents at the phosphorus and silicon atoms (Scheme 1) was reported nearly 30 years ago by Bickelhaupt et al.[1] Since this landmark discovery, it took almost a decade for the first isolation of a crystalline phosphasilene, which was reported by Niecke et al.[2] Since then, only a few other structurally characterized compounds featuring a silicon–phosphorus double bond could be realized,[3,4] representing heteroatomic Si=P species that break the "double-bond rule".[5,6] Unlike the Si=Si bond in disilenes, the Si=P functional group with three-coordinate silicon and two-coordinate phosphorus is slightly polar due to the higher electronegativity of phosphorus versus silicon.[7,8] Nevertheless, the highly reactive Si=P bond can be stabilized by taking advantage of donor–acceptor effects and/or steric congestion through the presence of bulky substituents.

Comparisons between the parent phosphasilenes H_2Si=PH and H_2Si=P(SiH_3), on the basis of computations, show that the Si–P π-bond strength in the latter compound is increased and the Si–P bond length is shortened by hyperconjugation effects due to the silyl substituent at phosphorus.[9] The latter strong influence of a silyl substituent could be experimentally verified by us.[4,9,10] In addition, the pronounced σ-donor ability of the silyl group at the phosphorus atom causes a large shielding effect for the ^{31}P nucleus, while the divalent ^{29}Si atom is deshielded. Thermodynamic stabilization of a Si=P system could



Scheme 1. Some examples of isolable phosphasilenes.

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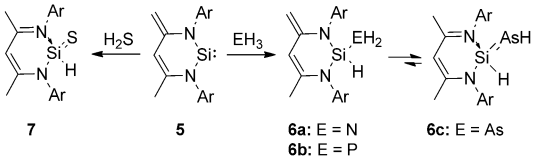
also be accomplished by employing intramolecular donor coordination of an amino group at the sp^2-silicon center, as shown in 1991 by Corriu et al.[11] Due to the large shielding of the respective ^{31}P and ^{29}Si nuclei in the NMR spectra, the latter phosphasilene is better described by a λ^4-Si^+—P^- betaine resonance structure. In contrast, a "push–pull" phosphasilene with electron-donating silyl groups on the low-coordinate (λ^3) silicon atom and electron-accepting aryl groups at the phosphorus reported by Sekiguchi et al.[12] does not show a reverse polarization of the Si=P double bond,[13] but instead both nuclei are extremely deshielded resulting from a paramagnetic contribution.[14] To gain insights into the electronic properties of conjugated Si=P functional group, Tamao et al. investigated a series of π-conjugated phosphasilenes and they established, on the basis of UV/Vis spectroscopy, that a Si=P moiety can conjugate with carbon π-electron systems.[15] Interestingly, these systems bearing the bulky Eind group (Eind = 1,1,3,3,5,5,7,7,-octaethyl-*s*-hydrindacen-4-yl) are even stable in air for months in the solid state. It appeared that the steric protection of λ^3-coordinate silicon is more important than that of λ^2-coordinate phosphorus.[7] Proof for this assertion was reported in 2006 by our group, when the first "half-parent" phosphasilenes **3** bearing a PH group was synthesized, which is stabilized by n(P)→σ*(Si–Si) hyperconjugation.[16] Besides, "half-parent" phosphasilenes bearing a naked PH moiety, a phosphasilene bearing a hydride ligand and an amino group on the silicon atom, which is stable with or without a coordinated N-heterocyclic carbene (NHC) at the silicon center, also exists. The amino group in this compound is responsible for a substantial N–Si–P π-conjugation and concomitant stabilization.[17] One of the N-donor-stabilized phosphasilenes, compound **2**[18,19] with a low-valent, λ^4-coordinate silicon atom, was synthesized in 2011 by some of us and Inoue et al.[19] in which an N→Si donor coordination favors a strong polarization of the Si=P π-bond and leads to a predominant ylide-like Si^+—P^- character. Even more recently, we reported a combination of these latter described compounds: the zwitterionic, ylide-like "half-parent" phosphasilene **4**,[20] bearing a low-valent, λ^3-coordinated Si atom (Scheme 1), which is fragile in solutions at room temperature and undergoes homolytic cleavage to form "free" silylene L′Si: **5** (L′ = CH[(C=CH_2)CMe(NAr)$_2$]; Ar = 2,6-*i*$Pr_2C_6H_3$) and parent phosphinidene (:PH); the latter of which undergoes oligomerization to $(PH)_n$ clusters. In the presence of an NHC as a :PH trapping agent, however, it was shown that **4** in fact acts as a transfer reagent of the :PH moiety resulting in the formation of a phosphaalkene bearing a terminal PH group, again with concomitant formation of **5**.

Within our ongoing research program focusing on small-molecule bond-activation reactions, mediated by low-valent silicon species,[21–26] we became interested in potentially stabilizing **4** and exploring its reactivity towards small molecules with a view of potentially uncovering new and useful reactivity patterns through donor–acceptor stabilization of **4**.

The activation of small molecules, particularly that of the N–H- and S–H-containing compounds has been a topic of organoelement chemistry due to the potential of generating new organic and/or pharmaceutical compounds.[21,22,27–54] The first example of the oxidative addition of ammonia by a transition-metal complex was published only a few years ago by Hartwig et al. Thereby, an iridium(I) pincer complex inserts into an N–H bond of ammonia, affording a stable monomeric amido hydride complex.[38] A recent example of N–H bond activation in ammonia by iridium and rhodium complexes was reported by Oro et al.[52] Low-valent main-group elements are also capable of activating N–H and S–H bonds, as shown for the first time in 2007 by Bertrand et al.[41] In 2009 and 2010, respectively, several N-heterocyclic silicon-containing compounds, which could activate N–H and/or S–H bonds, were reported.[21,22,46,55] For example, the zwitterionic N-heterocyclic silylene (NHSi) **5** undergoes the addition of ammonia affording the 1,1-insertion product **6a**. Compound **5** is also capable of activating the more Brønsted acidic heavier group 15 hydrides EH_3 (E = P, As).[56] In analogy to ammonia, phosphane engages in a 1,1-addition over the λ^3-Si center. In contrast, the reaction of AsH_3 with **5** yields the donor-stabilized arsasilene **6c**. Moreover, the reaction of **5** with H_2S gas results in the formation of the donor-stabilized silathioformamide **7** (Scheme 2).[21,24,57]

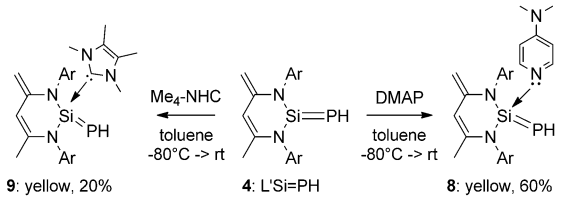


Scheme 2. Reaction of the silylene **5** toward EH_3 and H_2S (E = N, P, As).

Herein, we report the stabilization of the labile zwitterionic "half-parent" phosphasilene **4** by filling the formally empty 3p-orbital of the λ^3 silicon center with electron density with the aid of DMAP and a small NHC donor (1,3,4,5-tetramethylimidazol-2-ylidene). Furthermore, we describe the unusual reactivity of these adducts of **4** towards a variety of small molecules: $ZnMe_2$, H_2S, NH_3, *i*$PrNH_2$, $H_2N(C_6H_4)(CH_3)$, and $H_2NNH(C_6F_5)$, which is very different to that of **4** and other isolable phosphasilenes.

Results and Discussion

The highly ylidic but nevertheless surprisingly fragile phosphasilene **4** with two essentially localized lone pairs residing on the phosphorus atom could be described as an adduct of the silylene **5** and the parent phosphinidene with an empty 3p orbital at the λ^3-coordinate Si atom.[20] Therefore, it seemed reasonable to fill this empty 3p orbital at silicon with electron density and thereby stabilize this otherwise coordinatively unsaturated molecule. In fact, stabilization of the labile phosphasilene **4** could be accomplished by using the two different donor ligands 4-dimethylaminopyridine (DMAP) and 1,3,4,5-tetramethylimidazol-2-ylidene (Me_4–NHC). In both reactions, compound **4** was synthesized in situ in Et_2O according to the literature procedure[20] and extracted with toluene at which time one of these two ligands were added at low temperature af-



Scheme 3. Synthesis of the donor-stabilized phosphasilenes **8** and **9**.

fording the desired new Si=P adducts **8** and **9**, respectively, isolated in low to moderate yields (Scheme 3).

Compounds **8** and **9** were isolated as yellow solids and characterized by NMR spectroscopy, high-resolution electrospray ionization mass spectrometry (HR-ESI-MS) or electron impact mass spectrometry (EI-MS) and elemental analysis, IR spectroscopy, and by single-crystal X-ray diffraction (XRD) analysis. Compared with **4**, the stabilized phosphasilenes **8** and **9** are insoluble in *n*-hexane. Surprisingly, compound **8** is also insoluble in benzene but slightly soluble in toluene and well soluble in THF. Compound **9** is only slightly soluble in benzene, toluene, and THF. Strikingly, in contrast to the highly labile compound **4**, compounds **8** and **9** are perfectly stable in solution at room temperature for several months. Even after heating **8** for several hours at 60 °C in THF, no decomposition occurs. However, after heating compound **9** for 4 h at 50 °C and 2 h at 70 °C in C_6D_6, 20% of the ligand LH (L = HC(CMe[2,6-*i*Pr$_2$C$_6$H$_3$N])$_2$) is generated as a decomposition product. Despite the stabilization with the donor ligands, the compounds **8** and **9** are air sensitive and on contact with air turn colorless. The ^{29}Si signals of **8** and **9** are shifted considerably to higher field ($\Delta\delta$ = 93.1 to 108.5 ppm) in comparison with **4** (Table 1) but are in the same range as the Me$_4$–NHC→**5** (δ(^{29}Si) = −12.0 ppm) and dmap→**5** (δ(^{29}Si) = 37.4 ppm) adducts, synthesized in our group.[46,58] This indicates that the formally empty 3p orbital of the silicon center is filled with electron density and the silicon atom is more shielded in comparison with the donor-free phosphasilene **4**, in accordance with expectations. The ^{31}P chemical shifts of **9** (δ(^{31}P) = −259.8 ppm) is shifted to low field, whereas that of compound **8** (δ(^{31}P) = −331.9 ppm) is shifted to high field compared with the resonance of **4** δ(^{31}P) = −293.9 ppm. The explanation of this phenomenon could be that the Me$_4$–NHC is a better π-acceptor than DMAP and this trend is in addition reflected in the ^{1}H NMR spectrum for the proton at the phosphorus atom. According to this, the ^1J(Si,P) coupling constant of **9** is smaller than that of **8** and they are even smaller still in compound **4** because the ^1J coupling constants are proportional to the s character in the bonding (Table 1).[59]

The molecular structures of **8** and **9** were confirmed by using single-crystal XRD analysis[60] (Figure 1). The atoms of the C_3N_2 backbone of **8** and **9** are nearly co-planar, which is a common feature of this ligand. In comparison with the

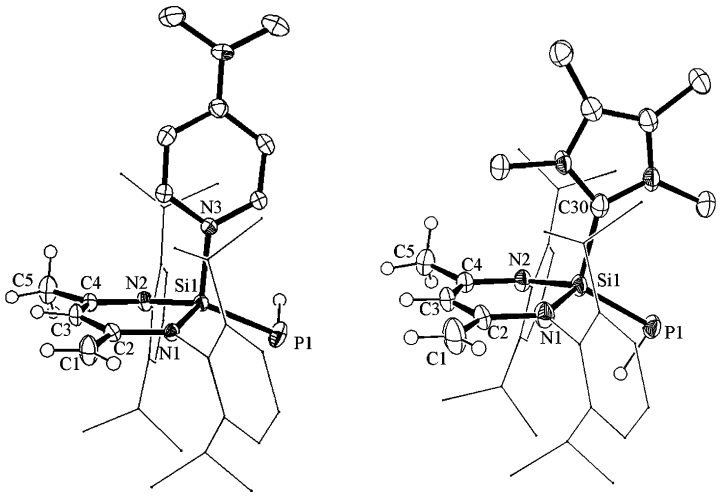


Figure 1. ORTEP representation of the molecular structure of **8** (left) and **9** (right); thermal ellipsoids are shown with 50% probability; hydrogen atoms are omitted for clarity, except those of C1, C3, C5, and P1). Selected distances (pm) and angles (deg) of **8**: Si1–P1, 212.05(1); Si1–N1, 174.82(1); Si1–N2,175.51(1); Si1–N3, 188.07(1); C1–C2, 138.76(1); C4–C5, 145.22(1); N1-Si1-N2, 102.5(1); N1-Si1-N3, 104.1(1); N2-Si1-N3, 100.9(1). Selected distances (pm) and angles (deg) of **9**: Si1–P1, 214.31(10); Si1–N1, 176.4(2); Si1–N2, 177.0(2); Si1–C30, 197.0(3); C1–C2, 137.8(4); C4–C5, 146.8(4); N1-Si1-N2, 100.81(12); N1-Si1-C30, 105.58(11); N2-Si1-C30, 106.15(12).

Table 1. Selected NMR data of **4**, **8**, and **9**.

NMR data	**4**[a]	**8**[b]	**9**[b]
^{1}H (PH) [δ, ppm]	−0.66	−2.62	−1.55
^{31}P [δ, ppm]	−293.9	−331.7	−259.8
^1J(P,H) [Hz]	143.0	144.1	144.1
^{29}Si{^{1}H} [δ, ppm]	101.5	8.4	−7.0[c]
^1J(Si,P) [Hz]	186.4	131.8	116.4

[a] [D$_6$]C$_6$H$_6$, 25 °C. [b] [D$_8$]THF, 25 °C. [c] C$_6$H$_5$F, lock capillary: [D$_6$]C$_6$H$_6$, 25 °C.

"naked" phosphasilene **4**, in which the silicon atom adopts a trigonal-planar coordination geometry, the silicon centers of both complexes **8** and **9** are coordinated in a distorted-tetrahedral fashion and they are out of the mean plane of the ligand backbone by 34.8 (**8**) and 20.1 pm (**9**), respectively. The angle between the plane of the DMAP and the ligand backbone plane in **8** is about 101.3 °, whereas the Me$_4$–NHC plane is nearly perpendicular to the ligand backbone plane (93 °). The Si–P bond lengths in **8** (212.05(1) pm) and **9** (214.31(10) pm) are slightly longer (2.4% for **8** and 3.5% for **9**) than in the phosphasilene **4** (207.12(10) pm) corresponding to the different degrees of polarization in the Si–P bond in these three phosphasilenes. The Si–C30(carbene) distance of 197.0(3) pm in **9** is significantly longer than the typical Si–C single bond

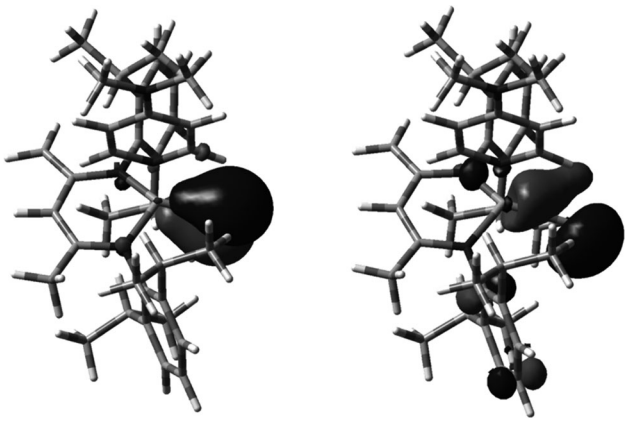


Figure 2. HOMO (left) and HOMO-8 (right) of **8**.

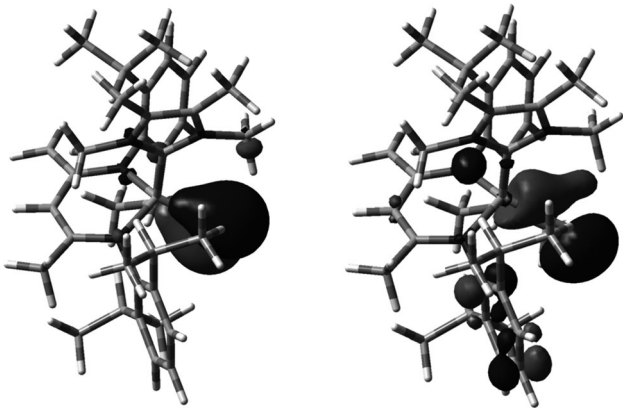
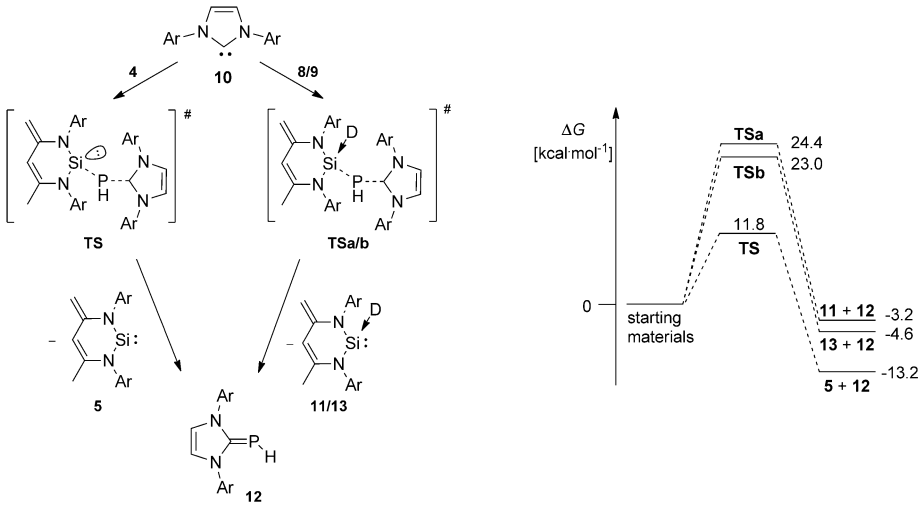


Figure 3. HOMO (left) and HOMO-8 (right) of **9**.

length in organosilanes (187 pm) but similar to the Si–C distance (201.6(3) pm) of the Me_4–NHC→**5** adduct.[58] The Si–N3(DMAP) bond length of 188.08(1) pm is almost 7% longer than the Si–N1 and Si–N2 bond lengths of the ligand. However, the Si–N3 bond length in **8** is much shorter than that of Si–N3 in the dmap→**5** adduct (200.5(2) pm),[46] indicating a stronger interaction of the P–Si–N3 subunit in **8**.

DFT calculations at the B97-D/cc-pVTZ(PCM=Benzene)//B97-D/6-31G* level of theory reveals that the formation of **8** and **9** are thermodynamically favored by $\Delta G = -11.3$ kcal mol^{-1} and -20.0 kcal mol^{-1}, respectively. Natural Bond Orbital (NBO) and Wiberg Bond Index (WBI) analyses show the change of the electronic structure of the Si=P subunit in **8** and **9** in comparison with the "donor-free" phosphasilene **4**. As a consequence of the electron donation of DMAP and Me_4–NHC, the weak double-bond character of **4**[20] (WBI of Si=P in **4** is 1.68) is completely eliminated and only the phosphinidene–silylene character remains. NBO analysis[60] indicated only one σ-type bond between the Si and P atoms, which corresponded to the donation of the lone pair of the silylene moiety **5** to the phosphinidene moiety, and two lone pairs on the P atom both in the case of **8** and **9**. WBIs suggest the same conclusion. In the DMAP-containing compound **8**, the WBI of the Si–P bond is 1.44, whereas in the stronger σ-donor Me_4–NHC-substituted compound **9**, the WBI of the Si–P bond is even lower (1.34). These bond indices are also reflected in Si–P distances of **8** and **9** (see above). NBO analysis also reveals that the σ-donor ability of the silylene moiety is enhanced by the donation of DMAP and Me_4–NHC and therefore the σ-bond is polarized toward the P atom. In **4**, the Si and P atoms contribute equally to the σ-bond (50.00%),[20] whereas in **8** and **9** the contribution of the phosphorus atom is 54.78 and 56.00%, respectively. In Figures 2 and 3, the HOMO-8's illustrate these Si–P σ-bonds, with an interaction of the hydrogen atom and the lone pair of the phosphorus, whereas the HOMOs represent the phosphinidene–silylene character.

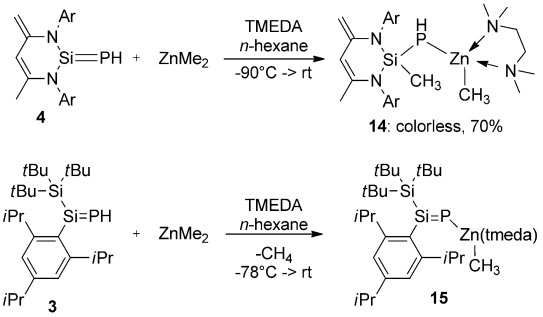
Due to the fact that the phosphasilene **4** is able to transfer the PH moiety to a bulky NHC,[20] we were interested if the stabilized phosphasilenes (**8** and **9**) could still act as a PH transfer agent. DFT studies revealed that the formation of the phosphaalkene is thermodynamically slightly favorable by $\Delta G = -3.2$ and -4.6 kcal mol^{-1}, respectively, but the Gibbs free energy of the transition states **TSa** and **TSb** are as expected to be much higher (Scheme 4). Therefore, harsher reaction conditions are required to obtain the desired phosphaalkene **12** by using **8** or **9** as a starting material. This was corroborated experimentally: After heating a solution of **8** and **10** in toluene



Scheme 4. Left: [+PH]-Transfer from the phosphasilenes **4**, **8**, and **9** to the NHC carbene center of **10** to give, under liberation of **5**, **11**, and **13**, the phosphaalkene **12**, respectively. Right: Calculated Gibbs free energy of these reactions. Ar = 2,6-diisopropylphenyl; **TSa**, **11**: D = DMAP; **TSb**, **13**: D = Me_4–NHC.

for 5 h at 90 °C, almost complete conversion to **12** was observed.[1] Unfortunately, due to these harsh reaction conditions the obtained product **11** could not be observed and decomposes into free ligand LH (L = HC(CMe[2,6-*i*Pr$_2$C$_6$H$_3$N])$_2$). Nevertheless, the stabilized phosphasilene **8** can act as a PH transfer agent, in analogy to **4**.

To compare the reactivity of **4** to the "half-parent" phosphasilene **3**, we carried out the reactions of **4** with $ZnMe_2$ in presence of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA). The ylide-like structure of **4** favors the 1,2-addition product **14**, in contrast to the analogous reaction with **3**, affording the P-zincophosphasilene **15** (Scheme 5).[16] The reaction of the DMAP-



Scheme 5. 1,2-Addition of dimethylzinc to the Si=P bond of **4** to give **14** versus the analogous reaction of **3** with dimethylzinc, affording the P-metallated phosphasilene **15**.

stabilized phosphasilene **8** with $ZnMe_2$ and TMEDA affords the same product **14** but only with a prolonged reaction time, which is required for the full conversion. Accordingly, DMAP has the propensity to be eliminated at the phosphasilene during the reaction as supported by results of DFT calculations (see the Supporting Information, Figure S16). The ^{31}P NMR spectrum of **14** reveals a doublet at $\delta = -303.4$ ppm (^1J(P,H) = 173.1 Hz), whereas the ^{29}Si signal at $\delta = 7.5$ ppm is also split into a doublet (^1J(Si,P) = 29.8 Hz). This small ^1J(Si,P) coupling constant is typical for Si–P single bonds[9] and indicates that both Si and P are coordinatively saturated. Suitable crystals of **14** for single-crystal XRD analysis[60] were obtained from a concentrated *n*-hexane solution upon storage at −30 °C for several days (Figure 4). The Si center exhibits a distorted tetrahedral coordination geometry. The methyl group at the silicon atom is positioned nearly orthogonal to the plane defined by the ligand backbone. The Si–P distance of 220.22(1) pm is 6.3% longer then the Si=P bond in **4** and is in the characteristic range of a Si–P bond.[61] The Zn atom is coordinated in a distorted-tetrahedral fashion and the value of the P–Zn bond length of 236.70(2) pm is typical for that of zincophosphanides.[16,62] Attempts to observe the $[M+H]^+$ peak in the HR-ESI spectra were unsuccessful despite several attempts. Instead,

[1] *Compound* ***12*** *could be synthesized independently by an alternative synthetic route to compare the NMR data: One equiv of* N,N′*-1,3-bis(2,6-diisopropylphenyl)-2,2-dichloroimidazol-2-ylidene*[74] *was reacted with two equiv of lithiumphosphite to afford* ***12*** *after workup.*[60]

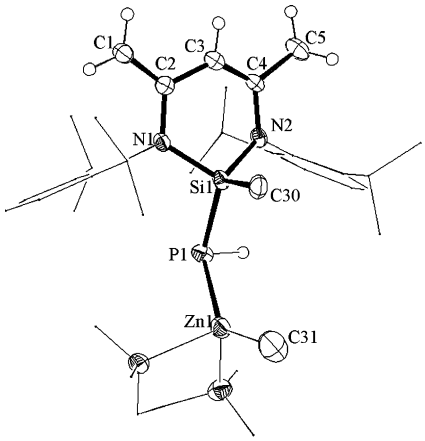
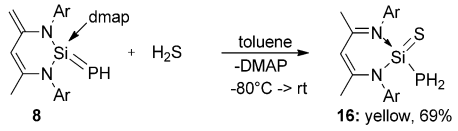


Figure 4. ORTEP representation of the molecular structure of **14** (thermal ellipsoids show 50% probability; hydrogen atoms are omitted for clarity, except those of C1, C3, C5, and P1). Selected distances (pm) and angles (deg) of **14**: Si1–P1, 220.22(1); Si1–N1, 175.62(1); Si1–N2, 177.03(1); Si1–C30, 186.99(1); Zn1–C31, 199.02(1); P1–Zn1: 236.70(2), C1–C2, 135.5(6); C4–C5, 149.7(5); N1-Si1-N2, 106.5(1); N1-Si1-C30, 107.24(17); N2-Si1-C30, 107.99(18); Si1-P1-Zn1, 106.66(6).

only the $[M$–TMEDA–ZnMe + 2H$]^+$ peak was observed, most likely due to the lability of the P–Zn bond.

The reaction of **8** with one equiv of H_2S gas at low temperature resulted in the selective formation of the donor-stabilized thiosilanoic phosphane **16** in analogy to compound **7** (Scheme 2 and 6).[21] The protons of H_2S undergo a 1,5-addition



Scheme 6. Synthesis of the first thiosilanoic phosphane **16**.

over the phosphasilene and protonate the methylene group of the backbone ligand. In the ^{1}H NMR spectrum, the characteristic signals of the exocyclic methylene groups disappeared and only one singlet at $\delta = 1.53$ ppm, corresponding to six chemically equivalent protons is observed. In the ^{31}P NMR spectrum, a triplet resonance signal with ^{29}Si satellites at $\delta = -221.2$ ppm (^1J(P,H) = 191.7 Hz) is observed, which is less shielded compared with **4** and **5**. The doublet of the ^{29}Si chemical shift at $\delta = -4.0$ ppm (^1J(Si,P) = 15.0 Hz) is in the same range as with **7** (δ(^{29}Si) = 16.8 ppm).[21] The molecular structure of **16** could be elucidated by single-crystal XRD analysis[60] (Figure 5). The bond lengths of C1–C2 = 1.5063(1) and C4–C5 = 1.4996(1) pm additionally prove that the exocyclic methylene group of **8** is converted into a methyl group in **16**. The silicon atom has a distorted tetrahedral coordination geometry and is out of the ligand backbone plane by 76.3 pm. The Si–P bond length of 224.00(2) pm is similar to that observed in **14** and characteristic for a Si–P single bond. The Si–S distance of 199.58(1) pm is only 1 pm longer then the Si–S bond length in **7**[21] and significantly shorter than Si–S single bonds.[63]

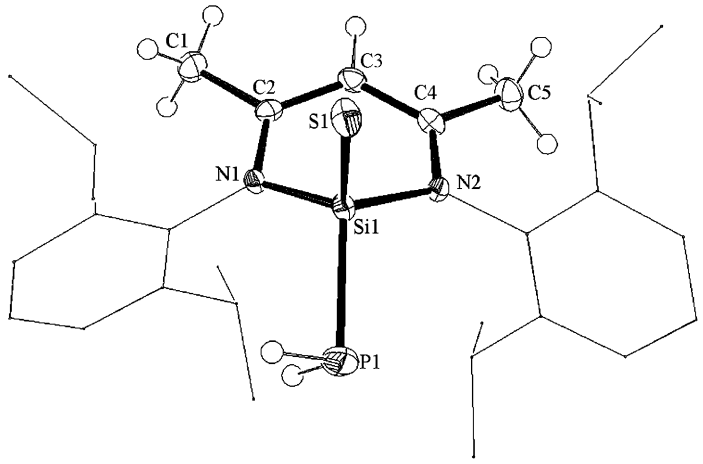
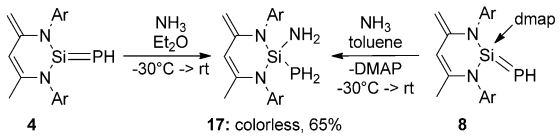


Figure 5. ORTEP representation of the molecular structure of **16** (thermal ellipsoids show 50% probability; hydrogen atoms are omitted for clarity, except those of C1, C3, C5, and P1). Selected distances (pm) and angles (deg) of **14**: Si1–P1, 224.00(2); Si1–N1, 182.72(1); Si1–N2, 180.62(1); Si1–S1, 199.58(1); C1–C2, 150.63(1); C4–C5, 149.96(1); N1-Si1-N2, 97.0(1); Si1-P1-S1, 115.24(6).

Beside the activation of $ZnMe_2$ and H_2S, compounds **4** and **8** are also capable of activating the N–H bonds in ammonia, organoamines (*i*PrNH$_2$, $H_2N(C_6H_4)(CH_3)$), and pentafluorophenylhydrazine ($H_2NNH(C_6F_5)$). Accordingly, an excess of ammonia gas was bubbled through a diethyl ether solution of **4** and a toluene solution of **8** at low temperature, respectively (Scheme 7). The formation of the colorless 1,2-addition product



Scheme 7. Synthesis of the 1,2-aminophosphinosilane **17**.

17 occurs after 30 min at room temperature. Once again, the DMAP donor ligand acts as a leaving group during the reaction, affording the desired products. In the ^{1}H NMR spectrum of **17**, each proton at the phosphorus atom reveals a doublet of doublets at $\delta = 0.99$ and 1.03 ppm, respectively, with a large ^1J(P,H) coupling constant of 189.3 Hz and a small ^2J(H,H) coupling constant of 12.1 Hz. Thus, the two protons at the phosphorus atom are not chemical equivalent, but the difference in the chemical shift between these two protons is so small that the roof effect is observed at a spectrometer frequency of 400.13 MHz. To prove this coupling pattern and the roof effect, the ^{1}H NMR spectrum was measured at different spectrometer frequencies. At a spectrometer frequency of 200.13 Hz, the two protons reveal a single resonance, whereas at a frequency of 700.17 Hz, the two resonances exhibit only a small roof effect with the same coupling constants. The protons at the nitrogen atom reveal a broad signal at $\delta = 0.86$ ppm in the ^{1}H NMR spectrum. The proton-coupled ^{31}P NMR spectrum shows at $\delta = -252.8$ ppm a triplet of triplets (^1J(P,H) = 189.3, ^3J(P,H) = 2.7 Hz), in which the latter corresponds to the coupling to the protons at the nitrogen atom. The ^{29}Si{^{1}H} spectrum exhibits a doublet at $\delta = -26.5$ ppm (^1J(Si,P) = 7.9 Hz), which is shifted by $\Delta\delta = 18.5$ ppm to low field in comparison with the chemical shift of **6a**.[22] The IR spectrum of **17** displays one weak sharp band at $\tilde{\nu} = 2285$ cm^{-1} for the P–H bond and two weak sharp bands corresponding to the symmetric and asymmetric vibration of the NH$_2$ group ($\tilde{\nu} = 3482$ and 3397 cm^{-1}).[64] The composition of **17** could be confirmed by HR-ESI mass spectrometry (m/z = 494.31148; 0.02 ppm deviation). Suitable crystals of **17** for single-crystal XRD analysis[60] were obtained from a concentrated *n*-hexane solution upon storage at −30 °C for several weeks (Figure 6). In one asymmetric unit, there are four independent molecules. The following metric parameters are all averaged over all four molecules. The silicon atom exhibits a distorted tetrahedral coordination geometry and is

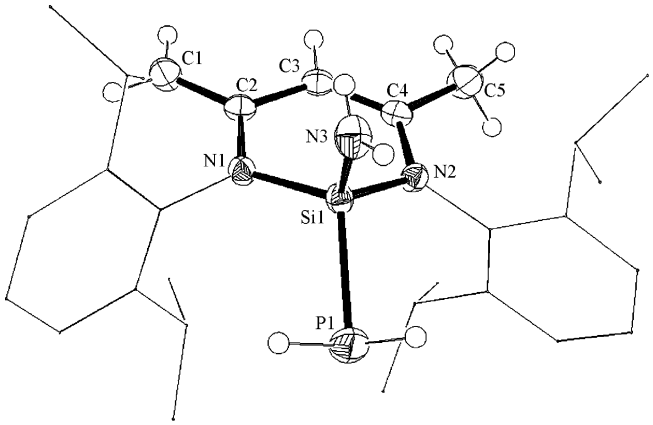
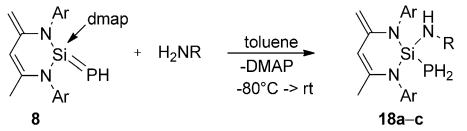


Figure 6. ORTEP representation of the molecular structure (one of four) of **17** (thermal ellipsoids show 50% probability; hydrogen atoms are omitted for clarity, except those of C1, C3, C5, P1, and N3). Selected distances (pm) and angles (deg; average values) of **17**: Si1–P1, 223.75; Si1–N1/N2, 173.71; Si1–N3, 170.00; C1–C2, 136.6; C4–C5, 147.8; N1-Si1-N2, 102.88.

out of the ligand backbone plane by 48.5 pm. The Si–P bond length of 224.15 pm is similar to that observed in **16** and characteristic for a Si–P single bond. The NH$_2$ group at the silicon atom is positioned nearly orthogonal to the plane defined by the ligand backbone. The Si–N3 bond length of 170.00 pm is 2.2% shorter than the Si–N1/N2 bond length of the ligand.

Treatment of **8** with isopropylamine, *p*-toluidine, and pentafluorophenylhydrazine in toluene at low temperature yields in the corresponding L′Si(PH$_2$)NHR (L′ = CH[(C=CH$_2$)CMe(NAr)$_2$]; Ar = 2,6-*i*Pr$_2$C$_6$H$_3$) compounds **18a–c** with a small amount of the free ligand LH (Scheme 8). In the ^{1}H NMR spectra of **18a–c**, each proton at the phosphorus atom reveals a doublet of doublets with a pronounced roof effect, as observed in compound **17** (Table 2). The ^{31}P{^{1}H} resonance signals as well as the ^{29}Si{^{1}H} resonance signals are rather similar to **17**. Unfortunately the ^1J(Si,P) of **18c** is not visible. Corresponding to secondary amines, the IR spectrum of **18a–c** reveals for the N–H bond



Scheme 8. Synthesis of the 1,2-addition products **18a–c. 18a**: R = *i*Pr; **18b**: R = tolyl; **18c**: R = NH(C_6F_5).

Table 2. Selected NMR data of **17** and **18a–c**.

NMR Data	**17**[a]	**18a**[a]	**18b**[a]	**18c**[a]
^{1}H(P*H*H′) [ppm]	0.99	1.80	0.84	1.21
^{1}H(PH*H*′) [ppm]	1.03	1.86	0.88	1.23
^1J(P,H) [Hz]	189.3	190.2	188.8	191.5
^2J(H′,H) [Hz]	12.1	11.6	12.0	11.7
^{31}P [ppm]	−252.8	−254.7	−254.3	−264.0
^{29}Si{^{1}H} [ppm]	−26.5	−27.7	−31.4	−23.1
^1J(Si,P) [Hz]	7.9	4.0	6.4	–

[a] [D_6]C_6H_6, 25 °C.

one sharp vibration (**18a**: $\tilde{\nu}$ = 3391 cm^{-1}, **18b**: $\tilde{\nu}$ = 3401 cm^{-1}, and **18c**: $\tilde{\nu}$ = 3351 cm^{-1}).[64]

Conclusion

The fragile zwitterionic "half-parent" phosphasilene **4** could be drastically stabilized by using DMAP and 1,3,4,5-tetramethylimidazol-2-ylidene, which coordinate to the low-coordinate silicon center. The latter coordination results in a substantial decrease in the bond order of the Si=P bond compared with the "donor-free" compound **4** and virtually no π-bonding exists between Si and P in **8** and **9**. Essentially, compounds **8** and **9** can be thought of as donor-stabilized silylene–phosphinidene adducts. Remarkably, compounds **8** and **9** are still capable of acting as transfer reagents of parent phosphinidene (:PH) to unsaturated organic substrates (bulky NHC) at relatively harsh reaction conditions. Furthermore, compounds **4** and **8** show striking reactivity towards a variety of small molecules and were shown to add dimethylzinc and activate the S–H bonds in H_2S and the N–H bonds in ammonia and in several organoamines to give unprecedented thiosilanoic phosphane and phosphanylsilane derivatives.

Experimental Section

General considerations

All experiments and manipulations were conducted under dry anaerobic nitrogen using standard Schlenk techniques or in an MBraun inert atmosphere dry box containing an atmosphere of purified nitrogen. Solvents were dried by standard methods and freshly distilled prior use. The starting material L′SiPH **4** (L′ = CH[(C=CH_2)CMe(NAr_2)]; Ar = 2,6-*i*PrC_6H_3) were prepared according to literature procedures.[20] Solution ^{1}H, ^{13}C, ^{31}P, and ^{29}Si NMR spectra were recorded on Bruker Avance II 400 MHz (^{1}H: 400.13, ^{13}C: 100.61; ^{29}Si: 79.49 MHz), Bruker Avance II 200 MHz (^{1}H: 200.13, ^{13}C: 50.32 MHz), or on Bruker Avance III 700 MHz (^{1}H: 700.17 MHz) spectrometers. The NMR signals are reported relative to the residual solvent peaks (^{1}H: [D_6]C_6H_6: 7.16; ^{13}C: [D_6]C_6H_6: 128.0 ppm), or an external standard (^{19}F: CCl_3F: 0.0, ^{31}P: 85% H_3PO_4: 0.0; ^{29}Si: TMS: 0.0 ppm). EI mass spectra were recorded on a Finnigan MAT95S, ESI- and APCI mass spectra on LTQ Orbitrap XL and the raw data evaluated using the XCalibur computer program. IR spectra were recorded on a PerkinElmer Spectrum 100 FTIR. UV/Vis spectra were recorded with an Analytik Jena Specord S600 Spectrometer in 10 mm quartz cuvettes. Elemental analyses were performed with a Thermo Finnigan Flash EA 1112 Series. Crystals were mounted on a glass capillary in perfluorinated oil and measured in a cold N_2 flow. The data were collected on an Oxford Diffraction Xcalibur S Sapphire at 150 K ($Mo_{K\alpha}$ radiation, λ = 0.71073 Å). The structures were solved by direct methods and refined on F^2 with the SHELX-97 software package.[65] The positions of the H atoms were calculated and considered isotropically according to a riding model. For the final refinement on compound **9**, the contributions of disordered solvent molecules were removed from the diffraction data with SQUEEZE in PLATON.[66,67]

Syntheses

Compound 8: A solution of DMAP (86.1 mg, 0.70 mmol) in toluene (5 mL) at −90 °C was added through a teflon cannula to a stirred solution of **4** (336 mg, 0.70 mmol) in toluene (50 mL) at −90 °C. The resulting yellow solution was allowed to warm up to room temperature and stirred for a further 30 min. All volatiles were removed in vacuo and the residue was washed three times with *n*-hexane (10 mL). The obtained yellow residue was extracted three times with toluene (50 mL) and the filtrate was concentrated to 10 mL and left at −30 °C for three days to the afford a yellow crystalline product, which was separated from the mother liquor by filtration and dried in vacuo for 30 min. Yield: 253 mg (60%). ^{1}H NMR (400.13 MHz, [D_8]THF, 25 °C): δ = −2.62 (d, ^1J(P,H) = 144.1, ^2J(Si,H) = 13.2 Hz, 1H, P*H*), 0.49, 0.73, 0.94, 0.98, 1.17, 1.20, 1.38, 1.43 (each d, ^3J(H,H) = 6.8 Hz, 3H, CHMe_2), 1.51 (s, 3H, NC*Me*), 2.47 (sept, ^3J(H,H) = 6.9 Hz, 2H, C*H*Me_2), 2.89 (s, 1H, NCC*H*H′), 3.20 (s, 6H, NMe_2), 3.65 (s, 1H, NCCH*H*′), 3.92 (sept, ^3J(H,H) = 6.9 Hz, 2H, C*H*Me_2), 5.35 (s, 1H, γ-C*H*), 6.77 (d, ^3J(H,H) = 7.0 Hz, 1H, DMAP), 7.04 (d, ^3J(H,H) = 7.0 Hz, 1H, DMAP), 6.90–7.25 (m, 6H, 2×2,6-*i*$Pr_2C_6H_3$), 9.03 (d, ^3J(H,H) = 7.0 Hz, 1H, DMAP), 9.52 ppm (br, 1H, DMAP); ^{13}C{^{1}H} NMR (100.61 MHz, [D_8]THF, 25 °C): δ = 23.2 (NC*Me*); 24.4, 25.0, 25.4, 25.6, 25.8, 25.9 (d, ^6J(C,P) = 3.3 Hz), 26.1, 26.5 (CHMe_2); 29.0, 29.2, 29.6, 29.7 (C*H*Me_2); 39.6 (NMe_2), 86.3 (NCCH_2); 105.0 (γ-*C*); 123.8, 124.1, 124.7, 125.1, 127.2, 128.9, 129.6, 139.8, 140.3, 148.3, 148.8, 149.2, 150.4, 157.5 (N*C*, 2,6 *i*$Pr_2C_6H_3$). 144.6, 150.6 ppm (DMAP); ^{29}Si{^{1}H} NMR (39.76 MHz, [D_8]THF, 25 °C): δ = 8.4 ppm (d, ^1J(Si,P) = 131.8 Hz); ^{31}P{^{1}H} NMR (161.97 MHz, [D_8]THF, 25 °C): δ = −331.7 ppm (s, ^1J(P,Si) = 131.8 Hz); ^{31}P NMR (161.97 MHz, [D_8]THF, 25 °C): δ = −331.7 ppm (dd, ^1J(P,H) = 144.1, ^4J(P,H) = 3.9, ^1J(P,Si) = 131.8 Hz; MS (EI 70 eV): *m/z* (%) = 476 (16, [*M*−DMAP]$^+$), 461 (100, [*M*−DMAP−Me]$^+$), 433 (29, [*M*−DMAP−*i*Pr]$^+$); elemental analysis (%) calcd for $C_{36}H_{51}N_4PSi$: C 72.20, H 8.58, N 9.36; found: C 71.65, 8.65, N 9.20; UV/Vis (toluene): λ_{max} = 294, 345 nm.

Compound 9: A solution of 1,3,4,5-tetramethylimidazol-2-ylidene (86.1 mg, 0.70 mmol) in toluene (5 mL) at −90 °C was added through a teflon cannula to a stirred solution of **4** (336 mg,

0.70 mmol) in toluene (50 mL) at −90 °C. The resulting yellow solution was warmed to room temperature and stirred for further 30 min. All volatiles were removed in vacuo and the residue was washed three times with *n*-hexane (10 mL). The obtained yellow residue was extracted three times with toluene (50 mL) and the filtrate was concentrated to 10 mL and left at −30 °C for three days to afford the yellow crystalline product, which was separated from the mother liquor by filtration and dried in vacuo for 30 min. Yield: 84.1 mg (20%). ^{1}H NMR (200.13 MHz, [D$_8$]THF, 25 °C): $\delta = -1.55$ (d, ^1J(P,H) = 144.1 Hz, 1H, P*H*), 0.40, 0.66, 1.05, 1.07, 1.16, 1.20, 1.37, 1.40 (each d, ^3J(H,H) = 6.8 Hz, 3H, CH*Me*$_2$), 1.50 (s, 3H, NC*Me*), 2.11, 2.32 (each s, 3H, NHC (C(4,5)-*Me*)), 2.57, 2.72 (each sept, ^3J(H,H) = 6.9 Hz, 1H, C*H*Me$_2$), 2.82 (s, 1H, NCC*H*H′), 3.58 (s, 1H, NCCH*H*′), 3.75, 4.15 (each s, 3H, NHC (N(1,3)-*Me*)) 3.80, 3.83 (each sept, ^3J(H,H) = 6.9 Hz, 1H, C*H*Me$_2$), 5.37 (s, 1H, γ-C*H*), 6.86–7.28 ppm (m, 6H, 2×2,6-*i*Pr$_2$C$_6$*H*$_3$); ^{13}C{^{1}H} NMR (100.61 MHz, C$_6$H$_5$F, lock-capillary: [D$_6$]C$_6$H$_6$, 25 °C): $\delta = 7.7$, 8.0 (C(4,5)-*Me*); 24.6 (NC*Me*); 22.8, 23.4, 24.1, 24.6 (d, ^6J(C,P) = 3.7 Hz), 24.7, 25.5, 26.2, 26.5 (CH*Me*$_2$); 27.9, 28.4, 29.3, 29.6 (*C*HMe$_2$);33.5, 36.0 (N(1,3)-*Me*); 87.4 (NC*C*H$_2$); 106.7 (γ-*C*); 113.9–116.7, 121.9–125.4, 126.0, 126.8, 127.0, 127.3–131.6, 139.9, 141.3, 142.7, 143.6, 146.7, 147.4, 149.6, 150.0, 155.2, 161.5–164.9 ppm (*C*$_6$H$_5$F, N*C*, 2,6 *i*Pr$_2$*C*$_6$H$_3$, N*C*N, C(4,5)); ^{29}Si{^{1}H} NMR (79.49 MHz, C$_6$H$_5$F, lock-capillary: [D$_6$]C$_6$H$_6$, 25 °C): $\delta = -7.0$ ppm (d, ^1J(Si,P) = 116.4 Hz); ^{31}P{^{1}H} NMR (81.01 MHz, [D$_8$]THF, 25 °C): $\delta = -259.8$ ppm (s, ^1J(P,Si) = 116.4 Hz); ^{31}P NMR (81.01 MHz, [D$_8$]THF, 25 °C): $\delta = -289.8$ ppm (d, ^1J(P,H) = 144.1 Hz); ESI-MS: *m/z* calcd for C$_{36}$H$_{54}$N$_4$PSi: 601.3850 $[M+H]^+$; found: 601.3840.

Compound 14: A solution of **4** (122 mg, 0.24 mmol) in *n*-hexane (10 mL) at −90 °C was treated with TMEDA (42.9 μL) and subsequently a solution of ZnMe$_2$ (0.22 mL, 1.2 M in toluene) was added dropwise. After stirring for 10 min, the solution was warmed to room temperature and stirred for further 90 min. The resulting orange solution was filtered and all volatiles of the filtrate were removed in vacuo. The residue was dissolved in Et$_2$O (2 mL) and left at −30 °C for three days to afford a colorless crystalline product, which was separated from the mother liquor by filtration and dried in vacuo for 30 min. Yield: 115 mg (70%). ^{1}H NMR (400.13 MHz, [D$_6$]C$_6$H$_6$, 25 °C): $\delta = -1.03$ (d, ^1J(P,H) = 173.1 Hz, 1H, P*H*), −0.71 (s, 3H, Zn*Me*), 0.94, 1.26, 1.38, 1.45, 1.47, 1.56, 1.63, 1.65 (each d, ^3J(H,H) = 6.8 Hz, 3H, CH*Me*$_2$), 1.19 (s, 3H, Si-*Me*), 1.47 (4H, NC*H*$_2$C*H*$_2$N), 1.62 (s, 3H, NC*Me*), 1.99 (br, 12H, N*Me*$_2$); 3.26 (s, 1H, NCC*H*H′); 3.67, 3.70 (each sept, ^3J(H,H) = 6.9 Hz, 1H, C*H*Me$_2$), 4.00 (s, 1H, NCCH*H*′), 4.19, 4.25 (each sept, ^3J(H,H) = 6.9 Hz, 1H, C*H*Me$_2$), 5.56 (s, 1H, γ-C*H*), 7.03–7.36 ppm (m, 6H, 2×2,6-*i*Pr$_2$C$_6$*H*$_3$); ^{13}C{^{1}H} NMR (100.61 MHz, [D$_6$]C$_6$H$_6$, 25 °C): $\delta = -9.8$ (d, ^2J(C,P) = 10.8 Hz, Zn*Me*); 8.6 (d, ^2J(C,P) = 1.2 Hz, Si*Me*); 22.8 (NC*Me*); 23.0, 23.7, 24.5, 25.3, 26.2, 26.4, 26.4, 26.5 (CH*Me*$_2$); 28.0, 28.0, 29.2, 29.4 (*C*HMe$_2$); 46.5 (N*Me*$_2$), 56.4 (NC*H*$_2$C*H*$_2$N), 84.2 (NC*C*H$_2$); 105.8 (γ-*C*); 123.7, 124.1, 124.3, 124.9, 126.9, 126.9, 140.1, 140.9, 142.2, 148.6, 149.5, 149.7, 149.9, 149.9 ppm (N*C*, 2,6 *i*Pr$_2$*C*$_6$H$_3$); ^{29}Si{^{1}H} NMR (79.49 MHz, [D$_6$]C$_6$H$_6$, 25 °C): $\delta = 7.6$ ppm (d, ^1J(Si,P) = 29.7 Hz); ^{31}P{^{1}H} NMR (161.97 MHz, [D$_6$]C$_6$H$_6$, 25 °C): $\delta = -304.6$ ppm (s, ^1J(P,Si) = 29.7 Hz); ^{31}P NMR (161.97 MHz, [D$_6$]C$_6$H$_6$, 25 °C): $\delta = -304.6$ ppm (d, ^1J(P,H) = 173.1, ^1J(P,Si) = 29.7 Hz); ESI-MS: *m/z* calcd for C$_{30}$H$_{46}$N$_2$PSi: 493.31624; found: 493.31503 $[M-\text{TMEDA}-\text{ZnMe}+2\text{H}]^+$; MS (EI 70 eV): *m/z* (%) = 492 (12, $[M-\text{TMEDA}-\text{ZnMe}+\text{H}]^+$), 477 (32, $[M-\text{TMEDA}-\text{ZnMe}-\text{Me}+\text{H}]^+$), 449 (43, $[M-\text{TMEDA}-\text{ZnMe}-i\text{Pr}+\text{H}]^+$), 58 (100, 1/2 TMEDA: $[\text{Me}_2\text{NCH}_2]^+$).

Compound 16: Gaseous H$_2$S (2.57 mL, 0.11 mmol) was added though a syringe to a stirred solution of **8** (59.6 mg, 0.10 mmol) in toluene (10 mL) at −80 °C. After stirring for 90 min, the solution was warmed to room temperature and stirred for further 30 min. All volatiles were removed in vacuo and the residue was washed three times with *n*-hexane (5 mL). The obtained yellow residue was extracted three times with toluene (10 mL) and the filtrate was concentrated to 5 mL and left at −30 °C for three days to afford a yellow crystalline product, which was separated from the mother liquor by filtration and dried in vacuo for 30 min. Yield: 35.2 mg (69%). ^{1}H NMR (400.13 MHz, [D$_8$]Tol, 25 °C): $\delta = 0.92$, 1.16, 1.30, 1.61 (each d, ^3J(H,H) = 6.8 Hz, 6H, CH*Me*$_2$); 1.62 (d, ^1J(P,H) = 191.7 Hz, 2H, P*H*$_2$); 1.53 (s, 6H, NC*Me*); 3.06, 4.41 (each sept, ^3J(H,H) = 6.9 Hz, 2H, C*H*Me$_2$); 5.10 (s, 1H, γ-C*H*), 6.95–7.20 ppm (m, 6H, 2×2,6- *i*Pr$_2$C$_6$*H*$_3$); ^{13}C{^{1}H} NMR (100.61 MHz, [D$_8$]Tol, 25 °C): $\delta = 23.6$ (NC*Me*); 24.2 (d, ^6J(C,P) = 4.1 Hz), 24.6, 25.0, 28.0 (CH*Me*$_2$); 29.3, 29.6 (d, ^5J(C,P) = 4.5 Hz) (*C*HMe$_2$), 101.9 (γ-*C*); 124.2, 126.5, 137.3, 144.1, 148.6, 168.5 ppm (N*C*, 2,6 *i*Pr$_2$*C*$_6$H$_3$); ^{29}Si{^{1}H} NMR (39.76 MHz, [D$_8$]Tol, 25 °C): $\delta = -4.0$ ppm (d, ^1J(Si,P) = 15.0 Hz); ^{31}P{^{1}H} NMR (161.97 MHz, [D$_8$]Tol, 25 °C): $\delta = -221.2$ ppm (s, ^1J(P,Si) = 15.0 Hz); ^{31}P NMR (161.97 MHz, [D$_8$]Tol, 25 °C): $\delta = -221.2$ ppm (t, ^1J(P,H) = 191.7, ^1J(P,Si) = 15.0 Hz); UV/Vis (toluene): $\lambda_{max} = 356$ nm; ESI-MS: *m/z* calcd for C$_{29}$H$_{44}$N$_2$PSSi: 511.2727 $[M+H]^+$; found: 511.2715.

Compound 17: A solution of **8** (30.4 mg, 0.05 mmol) in toluene (10 mL) at −25 °C was placed in a Schlenk tube and degassed by a freeze–pump–thaw cycle. The reaction vessel was charged with NH$_3$ of normal pressure. After stirring for 30 min, the solution was warmed to room temperature and stirred for a further 30 min. All volatiles were removed in vacuo and the residue was extracted three times with *n*-hexane (5 mL). The obtained colorless filtrate was concentrated to 5 mL and left at −30 °C for three days to afford colorless crystalline product, which was separated from the mother liquor by filtration and dried in vacuo for 30 min. Yield: 16 mg (65%). ^{1}H NMR (400.13 MHz, [D$_6$]C$_6$H$_6$, 25 °C): $\delta = 0.86$ (br, N*H*$_2$); 0.99, 1.03 (each dd, ^1J(P,H) = 189.3 Hz, ^2J(H,H) = 12.1 Hz, 1H, P*HH*′); 1.17, 1.20, 1.23, 1.24, 1.37, 1.39, 1.43, 1.44 (each d, ^3J(H,H) = 6.8 Hz, 3H, CH*Me*$_2$); 1.50 (s, 3H, NC*Me*); 3.31 (s, 1H, NCC*H*H′); 3.40, 3.56, 3.63, 3.70 (each sept, ^3J(H,H) = 6.9 Hz, 1H, C*H*Me$_2$); 3.94(s, 1H, NCC*H*H′); 5.40 (s, 1H, γ-C*H*), 7.04–7.25 ppm (m, 6H, 2×2,6- *i*Pr$_2$C$_6$*H*$_3$); ^{13}C{^{1}H} NMR (100.61 MHz, [D$_6$]C$_6$H$_6$, 25 °C): $\delta = 22.0$ (NC*Me*); 24.3 (d, ^6J(C,P) = 5.5 Hz), 24.6, 24.9, 25.0, 25.1 (d, ^6J(C,P) = 3.2 Hz) 25.5, 26.2, 26.7 (CH*Me*$_2$); 28.2, 25.6, 28.8 (d, ^5J(C,P) = 2.0 Hz), 29.1 (d, ^5J(C,P) = 4.2 Hz) (*C*HMe$_2$); 86.1 (NC*C*H$_2$); 106.2 (γ-*C*); 124.5, 124.5, 124.9, 125.0, 127.8, 128.3, 136.9, 138.0, 141.3, 148.3, 148.6, 148.7, 149.9, 149.0 ppm (N*C*, 2,6 *i*Pr$_2$*C*$_6$H$_3$); ^{29}Si{^{1}H} NMR (39.76 MHz, [D$_6$]C$_6$H$_6$, 25 °C): $\delta = -26.5$ ppm (d, ^1J(Si,P) = 7.9 Hz). ^{31}P{^{1}H} NMR (161.97 MHz, [D$_6$]C$_6$H$_6$, 25 °C): $\delta = -253.8$ ppm (s, ^1J(P,Si) = 7.9 Hz); ^{31}P NMR (161.97 MHz, [D$_6$]C$_6$H$_6$, 25 °C): $\delta = -253.8$ ppm (t, ^1J(P,H) = 189.3, ^1J(P,Si) = 7.9 Hz); IR (KBr): $\tilde{\nu} = 3482$ (w, N–H), 3397 (w, N–H), 3056 (w), 2960 (s), 2924 (m), 2868 (m), 2286 (w, P–H), 1640 (m), 1540 (w), 1467 (m), 1438 (m), 1384 (s), 1351 (s), 1308 (m) 1257 (m), 1243 (m), 1195 (m), 1110 (w), 1098 (w), 1063 (m), 1054 (m),976 (w), 803 (s), 758 (m), 591 (w), 554 (w), 516 cm^{-1} (w); ESI-MS: *m/z* calcd for C$_{29}$H$_{45}$N$_3$PSi: 494.3115 $[M+H]^+$; found: 494.3115.

Compound 18a: *i*PrNH$_2$ (9.30 μL, 6.41 mg, 0.11 mmol) was added through a syringe to a stirred solution of **8** (65.0 mg, 0.11 mmol) in toluene (10 mL) at −80 °C. After stirring for 30 min, the solution was warmed to room temperature and stirred for further 60 min. All volatiles were removed in vacuo and the residue was extracted three times with *n*-hexane (5 mL). All volatiles were removed in vacuo and the residue was dissolved in [D$_6$]C$_6$H$_6$ for NMR measurements. Afterwards, again all volatiles were removed and dried in vacuo for further characterization analyses. ^{1}H NMR (400.13 MHz, [D$_6$]C$_6$H$_6$, 25 °C): $\delta = 0.43$, 0.44 (each d, ^3J(H,H) = 6.2 Hz, 3H, NCH*Me*$_2$); 0.82 (dd, ^3J(H,H) = 10.5, ^3J(P,H) = 3.4 Hz, 1H, N–H); 1.20, 1.23, 1.32, 1.33, 1.34, 1.37, 1.40, 1.44 (each d, ^3J(H,H) = 6.8 Hz, 3H, CH*Me*$_2$); 1.49 (s, 3H, NC*Me*);1.80, 1.86 (each dd, ^1J(P,H) = 190.2, ^2J(H,H) = 11.6, ^2J(Si,H) = 7.73 Hz, 1H, P*HH*′); 2.88 (m, 1H, NC*H*Me$_2$);

3.34 (s, 1H, NCC*H*H'); 3.47, 3.58, 3.61, 3.81 (each sept, ^3J(H,H) = 6.9 Hz, 1H, C*H*Me$_2$); 3.98 (s, 1H, NCC*H*H'); 5.46 (s, 1H, γ-C*H*), 7.04–7.25 ppm (m, 6H, 2×2,6-*i*Pr$_2$C$_6$*H*$_3$); ^{13}C{^{1}H} NMR (100.61 MHz, [D$_6$]C$_6$H$_6$, 25 °C): δ = 22.5 (NC*Me*); 23.8, 24.9, 24.9, 25.4, 25.7 (d, ^6J(C,P) = 5.9 Hz), 26.2 (d, ^6J(C,P) = 3.2 Hz), 26.4, 26.9, 27.0, 27.2 (CH*Me*$_2$, NCH*Me*$_2$); 28.5 (d, ^5J(C,P) = 4.5 Hz), 28.3, 28.3, 28.9 (d, ^5J(C,P) = 5.0 Hz) (*C*HMe$_2$); 43.8 (d, ^3J(C,P) = 5.4 Hz) (NCHMe$_2$); 87.5 (NCCH$_2$); 107.6 (γ-*C*); 124.2, 124.3, 124.6, 125.5, 127.5, 127.9, 136.9, 138.0, 141.4, 148.2, 148.5, 148.7, 148.9, 149.0 ppm (N*C*, 2,6 *i*Pr$_2$C$_6$H$_3$); ^{29}Si{^{1}H} NMR (79.49 MHz, [D$_6$]C$_6$H$_6$, 25 °C): δ = −27.7 ppm (d, ^1J(Si,P) = 4.0 Hz); ^{31}P{^{1}H} NMR (161.97 MHz, [D$_6$]C$_6$H$_6$, 25 °C): δ = −254.7 ppm (s); ^{31}P NMR (161.97 MHz, [D$_6$]C$_6$H$_6$, 25 °C): δ = −254.7 ppm (t, ^1J(P,H) = 190.2 Hz); IR (KBr): $\tilde{\nu}$ = 3391 (w, N–H), 3113 (w), 3056 (w), 2962 (s), 2925 (m), 2862 (m), 2284 (w, P-H), 1635 (m), 1535 (w), 1462 (m), 1439 (m), 1380 (s), 1353 (s), 1306 (m) 1252 (m), 1238 (m), 1198 (m), 1176 (m), 1165 (m), 1128 (m), 1111 (w), 1098 (w), 1060 (m), 1044 (m), 1031 (w), 976 (w), 926 (m), 918 (w), 804 (s), 774 (m), 757 (m), 591 (w), 596 (w), 509 cm^{-1} (w); ESI-MS: *m/z* calcd for C$_{32}$H$_{51}$N$_3$PSi: 536.3584 [*M*+H]$^+$; found: 536.3583.

Compound 18b: A solution of *p*-toluidine (6.08 mg, 0.06 mmol) in toluene (5 mL) at −70 °C was added through a teflon cannula to a stirred solution of **8** (34 mg, 0.06 mmol) in toluene (10 mL) at −70 °C. After stirring for 60 min, the solution was warmed to room temperature and stirred for further 3 h. All volatiles were removed in vacuo and the residue was extracted three times with *n*-hexane (5 mL). All volatiles were removed in vacuo and the residue was dissolved in [D$_6$]C$_6$H$_6$ for NMR measurements. Afterwards, again all volatiles were removed and dried in vacuo for further characterization analyses. ^{1}H NMR (400.13 MHz, [D$_6$]C$_6$H$_6$, 25 °C): δ = 0.84, 0.88 (each dd, ^1J(P,H) = 188.8, ^2J(H,H) = 12.0, ^2J(Si,H) = 8.4 Hz 1H, P*H*H'); 0.89, 0.99, 1.02, 1.18, 1.28, 1.46, 1.47, 1.48 (each d, ^3J(H,H) = 6.8 Hz, 3H, CH*Me*$_2$); 1.51 (s, 3H, NC*Me*); 2.12 (s. 3H, Ph-C*H*$_3$); 3.32 (s, 1H, NCC*H*H'); 3.34, 3.43, 3.64, 3.81 (each sept, ^3J(H,H) = 6.9 Hz, 1H, C*H*Me$_2$); 3.96 (s, 1H, NCC*H*H'); 3.78 (br, 1H, N–H); 5.54 (s, 1H, γ-C*H*), 6.74 (d, ^3J(H,H) = 8.1 Hz, 2H, NCC*H*CH); 6.97 (d, ^3J(H,H) = 8.1 Hz, 2H, NCCHC*H*); 7.00–7.26 ppm (m, 6H, 2×2,6-*i*Pr$_2$C$_6$*H*$_3$); ^{13}C NMR (100.61 MHz, [D$_6$]C$_6$H$_6$, 25 °C): δ = 20.1 (Ph–*C*H$_3$) 22.1 (NC*Me*); 24.4, 24.5, 24.6, 24.9 (d, ^6J(C,P) = 5.0 Hz), 25.2, 25.2, 25.8, 26.5 (CH*Me*$_2$); 27.1, 27.8, 29.1, 29.2 (d, ^5J(C,P) = 4.3 Hz, *C*HMe$_2$); 86.8 (NCCH$_2$); 105.6 (γ-*C*); 118.1 (NCCH$_2$CH$_2$); 129.8 (NCCH$_2$*C*H$_2$);124.5, 124.8, 124.8, 125.3, 127.9, 128.1, 129.9, 136.8, 137.8, 142.2, 142.9, 148.1, 149.0, 149.0, 149.2, 150.3 ppm (NCCH$_2$CH$_2$*C*, N*C*, 2,6 *i*Pr$_2$C$_6$H$_3$); ^{29}Si{^{1}H} NMR (39.76 MHz, [D$_6$]C$_6$H$_6$, 25 °C): δ = −31.4 ppm (d, ^1J(Si,P) = 6.4 Hz); ^{31}P{^{1}H} NMR (161.97 MHz, [D$_6$]C$_6$H$_6$, 25 °C): δ = −254.3 ppm (s, ^1J(Si,P) = 6.4 Hz); ^{31}P NMR (161.97 MHz, [D$_6$]C$_6$H$_6$, 25 °C): δ = −254.3 ppm (t, ^1J(P,H) = 188.8 Hz); IR (KBr): $\tilde{\nu}$ = 3401 (w, N–H), 3176 (w), 3153 (w), 3054 (w), 3013 (w), 2961 (s), 2925 (m), 2918 (m), 2865 (m), 2285 (w, P–H), 1638 (m), 1603 (s), 1515 (s), 1462 (m), 1438 (m), 1372 (s), 1352 (s), 1306 (m), 1279 (s), 1252 (w), 1240 (w), 1226 (m), 1199 (m), 1177 (m), 1165 (m), 989 (w), 926 (m), 900 (w), 805 (s), 760 (m), 588 (w), 559 (w), 540 (w), 519 cm^{-1} (w); ESI-MS: *m/z* calcd for C$_{36}$H$_{51}$N$_3$PSi: 584.3584 [*M*+H]$^+$; found: 584.3575.

Compound 18c: A solution of pentafluorophenylhydrazine (7.84 mg, 0.04 mmol) in toluene (5 mL) at −70 °C was added through a teflon cannula to a stirred solution of **8** (23.7 mg, 0.04 mmol) in toluene (10 mL) at −70 °C. After stirring for 60 min, the solution was warmed to room temperature and stirred for further 3 h. All volatiles were removed in vacuo and the residue was extracted three times with *n*-hexane (5 mL). All volatiles were removed in vacuo and the residue was dissolved in [D$_6$]C$_6$H$_6$ for NMR measurements. Afterwards, again all volatiles were removed and dried in vacuo for further characterization analyses. ^{1}H NMR (400.13 MHz, [D$_6$]C$_6$H$_6$, 25 °C): δ = 1.21,1.23 (each dd, ^1J(P,H) = 191.5, ^2J(H,H) = 11.7 Hz, 1H, P*H*H');1.09, 1.18, 1.21, 1.29, 1.30, 1.34, 1.36, 1.39 (each d, ^3J(H,H) = 6.8 Hz, 3H, CH*Me*$_2$); 1.49 (s, 3H, NC*Me*); 3.37 (s, 1H, NCC*H*H'); 3.44, 3.47, 3.59, 3.61 (each sept, ^3J(H,H) = 6.9 Hz, 1H, C*H*Me$_2$); 3.97 (s, 1H, NCC*H*H'); 4.01 (br, N–H); 4.78 (br, N–H); 5.43 (s, 1H, γ-C*H*); 6.95–7.27 ppm (m, 6H, 2×2,6-*i*Pr$_2$C$_6$*H*$_3$); ^{13}C NMR (100.61 MHz, [D$_6$]C$_6$H$_6$, 25 °C): δ = 21.9 (NC*Me*); 24.0, 24.3 (d, ^6J(C,P) = 5.3 Hz), 24.9, 25.1, 25.1 (d, ^6J(C,P) = 2.5 Hz), 25.2, 26.5, 26.9 (CH*Me*$_2$); 28.3, 28.4, 28.6, 29.1 (d, ^5J(C,P) = 3.6 Hz) (*C*HMe$_2$); 87.8 (NCCH$_2$); 107.3 (γ-*C*); 124.6, 124.8, 125.1, 125.3, 127.5, 127.8, 128.1, 128.3, 128.3, 128.4, 136.1, 137.1, 142.2, 148.0, 148.4, 148.5, 148.5, 148.8 ppm (*C*$_6$F$_5$, N*C*, 2,6 *i*Pr$_2$C$_6$H$_3$); ^{19}F{^{1}H} NMR (188.31 MHz, [D$_6$]C$_6$H$_6$, 25 °C): δ = −156.2 (br d, ^3J(F,F) = 22.5 Hz, 2F, *ortho*-F); −164.5 (2×t, ^3J(F,F) = 22.3 Hz, 2F, *meta*-F), −167.7 ppm (tt, ^3J(F,F) = 22.2, ^4J(F,F) = 4.3 Hz, 1F, *para*-F); ^{29}Si{^{1}H} NMR (79.49 MHz, [D$_6$]C$_6$H$_6$, 25 °C): δ = −23.1 ppm; ^{31}P{^{1}H} NMR (161.97 MHz, [D$_6$]C$_6$H$_6$, 25 °C): δ = −263.9 ppm (t, ^6J(P,F) = 7.5 Hz); ^{31}P NMR (161.97 MHz, [D$_6$]C$_6$H$_6$, 25 °C): δ = −263.9 ppm (tt, ^1J(P,H) = 191.5, ^6J(P,F) = 7.5 Hz); IR (KBr): $\tilde{\nu}$ = 3351 (w, N–H), 3059 (w), 2963 (s), 2921 (m), 2864(m), 2290 (w, P–H), 1621 (s), 1551 (s), 1526 (s), 1518 (s), 1461 (m), 1439 (m), 1380 (s), 1361 (w), 1323 (m), 1275 (m), 1253 (w), 1176 (m), 1100 (m), 1059 (m), 1018 (m), 992 (m), 963 (w), 932 (w), 804 (m), 759 cm^{-1} (m); APCI-MS: *m/z* calcd for C$_{36}$H$_{51}$N$_3$PSi: 675.3066 [*M*+H]$^+$; found: 675.3067.

Computational methods

DFT calculations were performed at the B97-D/cc-pVTZ(PCM=Benzene)//B97-D/6-31G* level of theory.[68–72] Stationary points on the potential energy surface (PES) were characterized by harmonic vibrational frequency calculations. Transition states, with one imaginary frequency, were confirmed by intrinsic reaction coordinate (IRC) calculations. Calculations were carried out using Gaussian 09 program.[73]

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