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A Fragile Zwitterionic Phosphasilene as a Transfer Agent of the Elusive Parent Phosphinidene (:PH)

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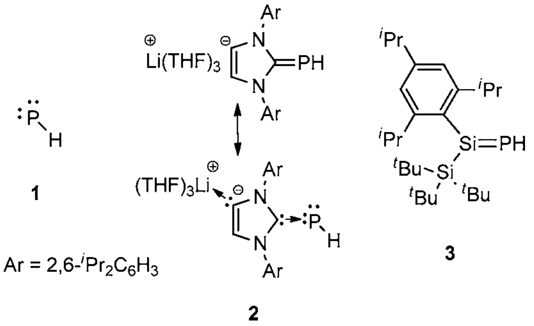
Supporting Information

ABSTRACT: The simplest parent phosphinidene, :PH (**1**), has been observed only in the gas phase or low temperature matrices and has escaped rigorous characterization because of its high reactivity. Its liberation and transfer to an unsaturated organic molecule in solution has now been accomplished by taking advantage of the facile homolytic bond cleavage of the fragile Si═P bond of the first zwitterionic phosphasilene LSi=PH (**8**) (L = CH-[(C═CH$_2$)CMe(NAr)$_2$]; Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$). The latter bears two highly localized lone pairs on the phosphorus atom due to the LSi═PH ↔ LSi$^+$−PH$^-$ resonance structures. Strikingly, the dissociation of **8** in hydrocarbon solutions occurs even at room temperature, affording the N-heterocyclic silylene LSi: (**9**) and **1**, which leads to oligomeric [PH]$_n$ clusters in the absence of a trapping agent. However, in the presence of an N-heterocyclic carbene as an unsaturated organic substrate, the fragile phosphasilene **8** acts as a :PH transfer reagent, resulting in the formation of silylene **9** and phosphaalkene **11** bearing a terminal PH moiety.

The elusive parent phosphinidene :PH (**1**) has escaped isolation and has been observed only transiently in the gas phase or in low temperature matrices.[1] Only scant examples of isolated compounds featuring the PH group exist.[2] In analogy to the parent carbene (:CH$_2$), **1** has a triplet electronic ground state with a singlet−triplet energy gap of −32.9 kcal·mol^{-1} (vs a singlet−triplet energy gap of only −9.05 kcal·mol^{-1} for :CH$_2$),[3] which highlights its immense reactivity. Derivatives of **1** of the type PR, where R is a bulky substituent that affords kinetic stabilization, have emerged as a crucial class of compounds in contemporary chemistry, as exemplified by the seminal work of Lammertsma and Lappert[1,4−6] and numerous further examples.[7,8] However, because of the short lifetime and lability of "free" **1**,[1] the ability of an isolable molecule bearing a PH moiety to act as a phosphinidene transfer reagent has never been demonstrated. The synthetic potential of such a reagent would enable new vistas in the synthesis of organophosphorus compounds, such as phospholes[9−11] or other compounds featuring a PH functionality that represent versatile ligands in coordination chemistry.[12,13]

In 1983, Issleib et al.[14] reported the phosphaalkene [(CH$_3$)$_2$N]$_2$C═PH, which could be described as an acyclic diaminocarbene−parent phosphinidene adduct, and the first lithiated N-heterocyclic carbene (NHC)−parent phosphinidene adduct **2** was recently reported by Robinson and coworkers.[15] To date, only one phosphasilene with a PH group has been reported, namely, the "half-parent" phosphasilene **3**, which was recently synthesized in our group[16] (Scheme 1).

Scheme 1. "Free" Parent Phosphinidene 1, Its Lithiated NHC Adduct 2, and "Half-Parent" Phosphasilene 3



However, the few examples of PH-containing compounds (Scheme 1) are rather stable and unsuitable for liberation of the reactive :PH species at ambient temperature in solution. Inspired by the facile homolytic Si═Si bond cleavage reactions of some disilenes, R^{1}R^{2}Si═SiR^{1}R^2, to afford the corresponding "free" silylenes R^{1}R^{2}Si: (R^1 = 2,4,6-tris[bis(trimethylsilyl)-methyl]phenyl; R^2 = 2,4,6-trimethylphenyl),[17−20] which feature a large singlet−triplet energy gap, we reasoned that the very stable zwitterionic silylene LSi: (L = CH[(C═CH$_2$)CMe-(NAr)$_2$]; Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$)[21] could be a particularly suitable leaving group to liberate **1** through homolytic dissociation of the corresponding phosphasilene LSi═PH (**8**) in solution. Herein we report the facile synthesis and isolation of **8**, the first fragile "half-parent" phosphasilene, which contains a three-coordinate silicon atom and features the most shielded PH moiety reported to date as a result of its strikingly zwitterionic character. In fact, its ability to facilely transfer :PH toward an NHC has been shown.

The desired phosphasilene **8** was synthesized in a straightforward manner by a sequence of substitution and

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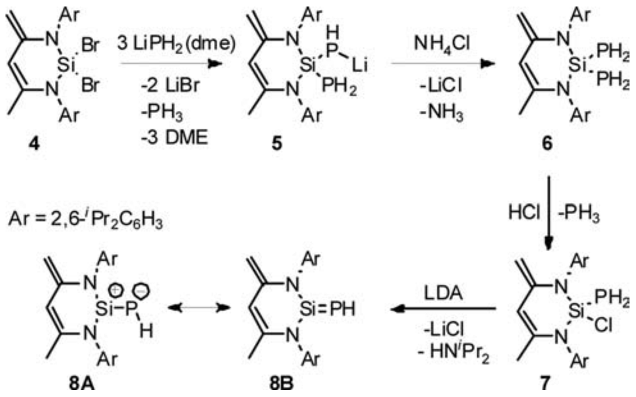
subsequent elimination reactions (Scheme 2). Starting with the Si(IV) precursor **4**,[21] the reaction with LiPH$_2$·dme (dme = 1,2-dimethoxyethane) afforded lithiated bis(phosphido)silane **5**. The bis(phosphido)silane intermediate **6** competes with unconverted LiPH$_2$·dme and is deprotonated immediately. Therefore, 3 equiv of LiPH$_2$·dme and a mild proton source (NH$_4$Cl) were needed to form **6** as a key starting material (Scheme 2). The following synthetic step involved the replacement of one PH$_2$ group by chlorine. Accordingly, the reaction of **6** with HCl afforded the product LSi(Cl)PH$_2$ (**7**) by PH$_3$ elimination. Compounds **6** and **7** were isolated as colorless crystals and characterized by NMR spectroscopy, electron impact mass spectrometry (EI-MS), elemental analysis, IR spectroscopy, and single-crystal X-ray diffraction (XRD).[22] Subsequently, treatment with lithium diisopropylamide (LDA) enabled the base-assisted dehydrochlorination of **7**, affording the desired phosphasilene **8** at low temperature as a colorless solid in 35% yield (Scheme 2). Notably, the ^{31}P NMR spectrum of **8** shows a doublet signal at −293.9 ppm with ^{29}Si satellites [^1J(P,H) = 143.0 Hz, ^1J(Si,P) = 186.4 Hz], which is by far the most shielded signal for a PH-containing compound reported to date and provides strong evidence for its formulation as a highly ylidic phosphasilene.[23] In comparison with the "half-parent" phosphasilene **3** [δ(^{31}P) = 123.1 pm], the ^{31}P signal of compound **8** is shifted dramatically by 417 pm toward higher field, indicative of a more covalent bonding situation in the former compound. Accordingly, the ^{1}H NMR spectrum exhibits a high-field doublet at −0.7 ppm with ^{29}Si satellites [^1J(P,H) = 143.0 Hz, ^2J(Si,H) = 18.3 Hz] for the proton of the PH moiety. The small ^1J(P,H) coupling constant indicates that the P 3s character of the P−H bond is decreased and therefore that the phosphorus atom adopts a large 3p character in the P−H bond. The ^{29}Si{^{1}H} NMR spectrum exhibits a low-field doublet at 101.5 ppm [^1J(Si,P) = 186.4 Hz], which is characteristic for coordinatively unsaturated λ^3-Si atoms.[24] The large ^1J(Si,P) coupling constant of 186.4 Hz is typical for phosphasilenes with three-coordinate silicon and results from the increase in the s character of the Si−P bond. These NMR results, particularly the chemical shift in the ^{31}P NMR spectrum, reveal that phosphasilene **8** is highly ylidic and that the Si−P double bond is strongly polarized to the phosphorus atom (resonance form **8A** in Scheme 2).

Scheme 2. Synthesis of Compounds 5−8



Single-crystal XRD analysis revealed that the silicon atom adopts a trigonal-planar coordination geometry (Figure 1). The Si−P bond distance of 207.12(10) pm is ~8% shorter than the Si−P single bond in compound **6** and slightly (2.3 pm) shorter than the Si−P bond length in phosphasilene **3** [209.4(5) pm].

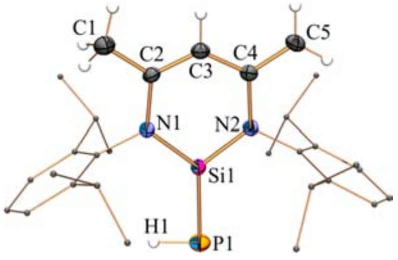


Figure 1. ORTEP representation of the molecular structure of **8** (thermal ellipsoids show 50% probability; H atoms have been omitted for clarity, except those of C1, C3, C5, and P1). Selected bond distances (pm) and angles (deg) in **8**: Si1−P1, 207.12(10); Si1−N1, 169.4(2); Si1−N2, 170.1(2); C1−C2, 140.9(4); C4−C5, 142.8(4); N1−Si1−N2, 106.50(11); Si1−P1−H1, 86(2).

To further elucidate the bonding situation in the highly ylidic system of **8**, density functional theory (DFT) studies at the B3LYP/6-31G(d) level were performed. Natural bond orbital (NBO) analysis showed that the Si−P bond consists of a σ bond and a π bond. The Si and P atoms each contribute 50% to the σ bond. For this bonding, the orbital of the silicon atom mainly has strong s character (64.58% s, 35.15% p, 0.27% d), whereas the orbital of the phosphorus atom exhibits high p character. In Figure 2, the HOMO−7 illustrates this Si−P σ bond, with an interaction of the hydrogen atom and the lone pair of the phosphorus, which has strong s character (69.58% s, 30.38% p, 0.04% d). In contrast to the σ bond, the π bond (HOMO−1) is strongly polarized to the phosphorus atom (73.45%), which explains the dramatic high-field shift of the ^{31}P NMR resonance and provides further evidence for its formulation as the highly ylidic phosphasilene **8A** (Scheme 2) with two essentially localized lone pairs residing on the phosphorus atom (Figure 2). The Wiberg bond index (WBI) of the Si−P bond of **8** is 1.68. These computational results demonstrate that the π bond between the silicon and phosphorus atoms is not predominant and further supports the importance of the zwitterionic resonance structure **8A** for the description of the bonding situation in **8**.

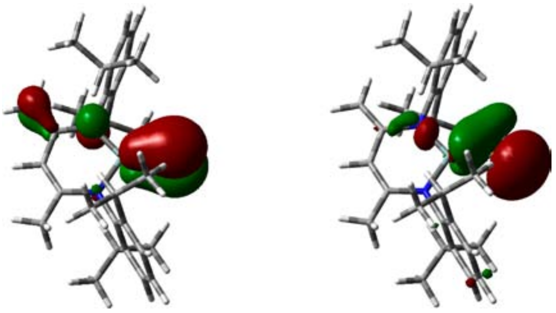
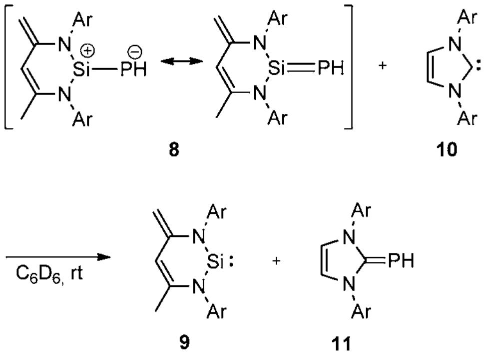


Figure 2. (left) HOMO−1 and (right) HOMO−7 of **8**.

Remarkably, phosphasilene **8** was unstable in solution at room temperature. After a few hours in C$_6$D$_6$, it dissociated into silylene **9** [δ(^{29}Si) = 88.5 ppm][21] and an insoluble red-brown solid. The solid-state ^{31}P NMR analysis of the latter revealed broad signals between +150 and −300 ppm, potentially corresponding to polyphosphanes of large [PH]$_n$ clusters.[25] According to DFT calculations [B97-D/cc-pVTZ-(PCM=Benzene)//B97-D/6-31G*], the Gibbs free energy associated with the dissociation of **8** into silylene **9** and the parent phosphinidene **1** is rather high (ΔG = +42.4 kcal·mol^{-1}).[22] However, the formation of the [PH]$_4$ oligomer, for example, is thermodynamically favorable (ΔG = −3.9 kcal·mol^{-1}), suggesting that the formation of larger [PH]$_n$ clusters is likely even more favorable. In light of the experimentally observed lability of the PH moiety in **8**, supported by the aforementioned calculations, we tested the propensity of **8** to act as a :PH transfer agent. In this context, 1 molar equiv of NHC **10** was added into an NMR tube with phosphasilene **8** in C_6D_6 at room temperature. Immediately, the :PH species of **8** was transferred to **10** with concomitant liberation of silylene **9** (Scheme 3), demonstrating facile :PH transfer for the first time.

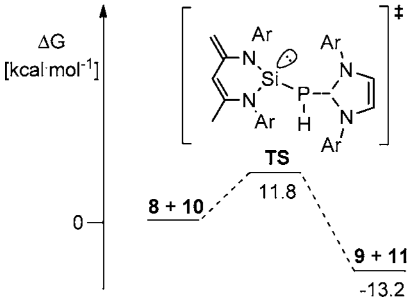
Scheme 3. Transfer of :PH from phosphasilene 8 to NHC 10 (Ar = 2,6-diisopropylphenyl)



The formation of phosphaalkene **11** was confirmed by high-resolution electrospray ionization mass spectrometry (HR-ESI-MS) (m/z 421.27606, 1.5 ppm deviation) and ^{1}H, ^{31}P, and ^{13}C{^{1}H} NMR spectroscopy. The ^{31}P NMR spectrum shows a doublet at −134.3 ppm [^1J(P,H) = 165.5 Hz]. The ^{1}H NMR spectrum exhibits a doublet for the proton of the PH group at 1.9 ppm [^1J(P,H) = 165.5 Hz]. In the ^{13}C{^{1}H} NMR spectrum, the doublet for the carbon atom bound to the phosphorus atom is at 180.5 ppm [^1J(P,C) = 85.0 Hz]. These analytical data, particularly that of the ^{31}P NMR spectrum, are quite similar to those of compound **2** [$\delta(^{31}$P) = −143.0 ppm, ^1J(P,H) = 171.0 Hz].[15]

This astonishingly facile :PH transfer reaction to an unsaturated organic substrate (NHC) is certainly facilitated by the zwitterionic nature of **8**. The reaction mechanism, according to DFT studies at the B97-D/cc-pVTZ-(PCM=Benzene)//B97-D/6-31G* level,[22] is a one-step reaction. The Gibbs free energy of activation of the transition state **TS** ($\Delta G^\ddagger$ = 11.8 kcal·mol^{-1}) is low enough that the reaction can proceed at room temperature, resulting in thermodynamically stable products (**9** + **11**, ΔG = −13.2 kcal·mol^{-1}) (Scheme 4). In the transition state (**TS**), the silicon atom is pyramidalized and adopts a silylene character while the Si−P bond is elongated to 235.4 pm and the NHC **10** attacks the phosphorus center (C−P bond distance = 225.2 pm). The carbon atom in compound **11** has a stronger σ-donor capacity than the silicon atom in phosphasilene **8**. Therefore, it can form a stronger interaction with the PH moiety. The WBI of phosphaalkene **11** (1.36) indicates that it has a lower double-bond character than **8** (WBI = 1.68). In addition to the NBO analysis, these partial Si−P and C−P double-bond characters are suggested by transition-state calculations on the rotational barrier of the P−H moiety about the C−P and Si−P axes. The rotation is almost free when the bond character is close to phosphinidene with a charge-transfer double bond, while for standard double bonds the rotation barrier is very high [$\Delta G(H_2C{=}CH_2)$ = 65 kcal·mol^{-1}].[26,27] For phosphaalkene **11** and phosphasilene **8**, these barriers are ΔG = 14.0 and 11.3 kcal·mol^{-1}, respectively. These low free energy barriers demonstrate once more that the π bond between the silicon and phosphorus atoms in **8** and that between the carbon and the phosphorus atoms in **11** are not predominant, again highlighting the ylidic nature represented by structure **8A**.

Scheme 4. Calculated Gibbs Free Energies for the Reaction of 8 with 10



In summary, we synthesized the first zwitterionic "half-parent" phosphasilene **8** featuring a highly polarized Si−P bond, which is capable of transferring the elusive :PH species to an unsaturated organic substrate. The behavior of **8** enables facile access to PH-functionalized organic molecules, which have been shown to be useful tools for ligand synthesis in coordination chemistry. Moreover, the strategy to liberate elusive low-valent species by facile homolytic bond cleavage of fragile Si═X compounds could be an attractive new method, for example, to generate the parent borylene (:BH)[28,29,8] using LSi═BH.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Details of single-crystal XRD analysis; selected NMR and HR-ESI-MS spectra of **6**−**11**; and Cartesian coordinates, NBO analysis, and optimized structures and additional MOs of **8**, **11**, and **TS**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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