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Si=P Double Bonds: Experimental and Theoretical Study of a NHC-Stabilized Phosphasilenylidene**

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Abstract: *An experimental and theoretical study of the first compound featuring a Si=P bond to a two-coordinate silicon atom is reported. The NHC-stabilized phosphasilenylidene (IDipp)Si=PMes* (IDipp = 1,3-bis(2,6-diisopropylphenyl)-imidazolin-2-ylidene, Mes* = 2,4,6-tBu$_3$C$_6$H$_2$) was prepared by SiMe$_3$Cl elimination from SiCl$_2$(IDipp) and LiP-(Mes*)SiMe$_3$ and characterized by X-ray crystallography, NMR spectroscopy, cyclic voltammetry, and UV/Vis spectroscopy. It has a planar trans-bent geometry with a short Si–P distance of 2.1188(7) Å and acute bonding angles at Si (96.90(6)°) and P (95.38(6)°). The bonding parameters indicate the presence of a Si=P bond with a lone electron pair of high s-character at Si and P, in agreement with natural bond orbital (NBO) analysis. Comparative cyclic voltammetric and UV/Vis spectroscopic experiments of this compound, the disilicon(0) compound (IDipp)Si=Si(IDipp), and the diphosphene Mes*P=PMes* reveal, in combination with quantum chemical calculations, the isolobal relationship of the three double-bond systems.*

Phosphaalkynes (**A**, Figure 1) are versatile building blocks in organoelement chemistry. Their chemistry evolved rapidly after the isolation of a derivative that is stable at room temperature (tBuC≡P) by Becker et al. in 1981.[1,2] In comparison, the valence isomers of phosphaalkynes, the isophosphaalkynes (**B**, Figure 1), are still elusive owing to their high thermodynamic and kinetic instability,[3,4] which can be rationalized with the reluctance of phosphorus and the other 3p-block elements towards isovalent s/p hybridization.[5] Consequently, the valence-isoelectronic silicon analogues of phosphaalkynes (**C** and **D** in Figure 1) are expected to be highly reactive species. In fact, attempts to generate phosphasilynes (silylidynephosphanes) **C** from suitable precursors failed so far.[6] Quantum chemical calculations revealed that the relative stability of phosphasilynes **C** versus their constitutional isomers **D** (phosphasilenylidenes) correlates with the electronegativity of the substituent R. Electronegative substituents, such as F, OH, OMe, NH$_2$, Me, Ph, stabilize the Si–P triple bond in the linear isomer **C**, whereas electropositive substituents, such as R = Li, BeH, BH$_2$, H, SiH$_3$, favor the bent isomer **D** featuring a Si–P double bond and a lone pair of electrons at silicon.[6,7] Remarkably, the parent compound SiPH was recently generated by electric discharge of SiH$_4$/PH$_3$ or SiH$_4$/P$_4$/H$_2$ mixtures and shown by FT microwave and millimeter wave absorption spectroscopy to have a bent structure (**D**, Figure 1) with a Si–P double bond, a P–H single bond and an acute Si-P-H angle of 60.5°, pointing to a significant interaction of the P–H bond with the Si center, as predicted previously by quantum chemical calculations.[8,9] However, attempts to prepare phosphasilenylidenes (:Si=PR), which are stable in solution or in the solid state have not been reported to date.

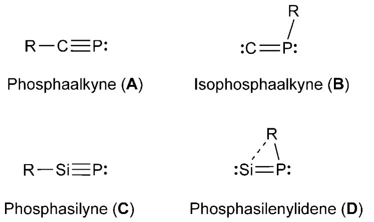

Figure 1. Constitutional isomers of REP (E = C, Si). The lone electron pairs are indicated by two dots.

Recently, N-heterocyclic carbenes (NHCs) have been shown to be particularly useful Lewis bases allowing the stabilization of highly reactive, unsaturated Si species such as Si$_2$,[10] SiX$_2$ (X = Cl,[11] Br,[12] I[13]), SiClR (R = 2,6-Ar$_2$C$_6$H$_3$ (Ar = 2,4,6-Me$_3$C$_6$H$_2$, 2,4,6-iPr$_3$C$_6$H$_2$), N(SiMe$_3$)(2,6-iPr$_2$C$_6$H$_3$)),[14,15] SiI$^+$,[13] a Si atom,[16] or R$_2$Si=Ge:, a heavier Group 14 homologue of a vinylidene.[17] Based on these results we envisaged that NHCs might be also suitable to trap phosphasilenylidenes (:Si=PR), and we thus decided to use the 1,2-elimination methodology of SiMe$_3$Cl, which proved to be particularly successful in the formation of C=P, C≡P, or P=P bonds.[2a,e,f] Herein, we present the successful implementation of this strategy into Si^{II} chemistry with the synthesis and full characterization of a room-temperature stable NHC-stabilized phosphasilenylidene.

SiCl$_2$(IDipp) (IDipp = 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene)[11] and LiP(Mes*)(TMS) (Mes* = 2,4,6-tBu$_3$C$_6$H$_2$; TMS = SiMe$_3$)[18] were chosen as promising starting materials to test the 1,2-elimination. Addition of one equivalent of LiP(Mes*)(TMS) to a yellow solution of SiCl$_2$(IDipp) in fluorobenzene at −30 °C (Scheme 1) was accompanied by a rapid color change to deep red. After warming to ambient

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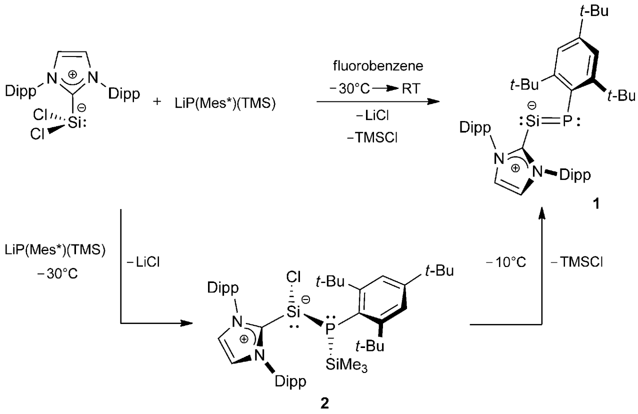

Scheme 1. Synthesis of (IDipp)Si=PMes* (**1**) via the assumed intermediate **2**. Lone pair of electrons are represented by two dots; formal charges are encircled.

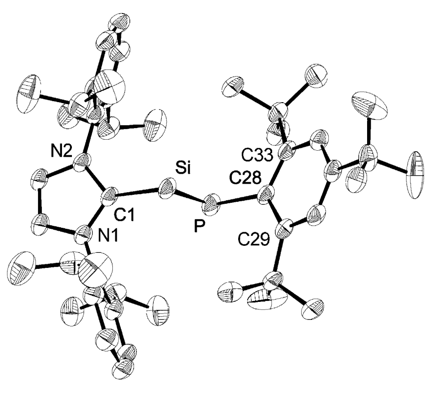

Figure 2. DIAMOND plot of the molecular structure of **1**·Et$_2$O at 123 K in the solid state.[42] Ellipsoids are set at 30% probability; hydrogen atoms and the solvent are omitted for clarity. Selected bond lengths [Å], angles [°], and torsion angles [°]: Si–P 2.1188(7), Si–C1 1.960(2), P–C28 1.877(2); P-Si-C1 96.90(6), Si-P-C28 95.38(6), C1-Si-P-C28 178.10(7), N1-C1-Si-P 92.7(2), N2-C1-Si-P −103.9(1), Si-P-C28-C29 81.4(1), Si-P-C28-C33 −91.7(1).

temperature, a second color change from deep red to brown–red was observed with concomitant precipitation of a white solid (LiCl). ^{31}P{^{1}H} NMR analysis of the resulting reaction solution revealed the formation of the NHC-stabilized phosphasilenylidene **1** along with PH(Mes*)(TMS)[19] and a small amount of P(Mes*)(TMS)$_2$.[20] Compound **1** was purified by fractional crystallization from *n*-hexane and isolated as a bright orange, very air-sensitive solid in 39% yield.[21] Compound **1** is stable at ambient temperature under exclusion of air and moisture for several months.

The course of the reaction leading to **1** was followed by ^{31}P{^{1}H} and ^{29}Si{^{1}H} NMR spectroscopy at low temperature. The ^{31}P{^{1}H} and ^{29}Si{^{1}H} spectra of the deep red fluorobenzene solution obtained at −30 °C revealed the formation of an intermediate displaying one ^{31}P singlet at $\delta = -117.3$ ppm flanked by two pairs of ^{29}Si satellite signals (^{1}J(P,Si) = 232 Hz and ^{1}J(P,Si) = 46 Hz), and two ^{29}Si doublets at $\delta = -9.8$ ppm (^{1}J(P,Si) = 232 Hz) and + 1.6 ppm (^{1}J(P,Si) = 46 Hz), respectively.[21] This intermediate is suggested to be the NHC-stabilized phosphinosilylene **2** based on a comparison of its NMR features with those of the base-stabilized silicon(II) phosphanides (phosphinosilylenes) (PhC(N*t*Bu)$_2$)SiP(TMS)$_2$ ($\delta_{SiP} = +44$ ppm (^{1}J(P,Si) = 194 Hz); δ_{Si}(TMS) = + 3.1 ppm (^{1}J(P,Si) = 22.9 Hz))[22] and Si[P(H)(R)][N(Dipp)(TMS)]-(I*i*Pr$_2$Me$_2$) (R = 2,6-(2,4,6-Me$_3$C$_6$H$_2$)$_2$C$_6$H$_3$, Dipp = 2,6-*i*Pr$_2$C$_6$H$_3$, I*i*Pr$_2$Me$_2$ = 1,3-diisopropyl-4,5-dimethylimidazolin-2-ylidene; $\delta_{Si} = -8.8$ ppm (^{1}J(P,Si) = 145.4 Hz)).[23] Compound **2** eliminates TMSCl upon warming to ambient temperature to give **1** (Scheme 1).

The molecular structure of **1**·Et$_2$O was determined by single-crystal X-ray diffraction (Figure 2). Compound **1** features as its isolobal congeners Si$_2$(IDipp)$_2$[10] and P$_2$Mes*$_2$[24] a *trans*-bent planar geometry with a torsion angle C1-Si-P-C28 of 178.10(7)°. The angles at the Si (P-Si-C1 96.90(6)°), and the P atom (Si-P-C28 95.38(6)°) resemble those of Si$_2$(IDipp)$_2$ (Si-Si-C 93.37(5)°)[10] and P$_2$Mes*$_2$ (P-P-C 102.8(1)°), respectively.[24] These angles indicate that silicon and phosphorus use predominantly p-orbitals for the Si=P bond in **1** and suggest furthermore the presence of a lone electron pair with high s character at each atom, in full agreement with the results of the natural bond orbital (NBO) analysis of **1** (see below). The Si=P bond length of **1** (2.1188(7) Å) compares well with the mean value (2.1315(1) Å) of the Si=Si bond length of Si$_2$(IDipp)$_2$ (2.229(1) Å)[10] and the P=P bond length of P$_2$Mes*$_2$ (2.034(2) Å),[24] and lies in the range of the Si=P bond lengths of phosphasilenes (silylidenephosphanes) (R$_2$Si=PR: *d*(Si=P) = 2.062(1)–2.172(1) Å).[25] Notably, the Mes* and the NHC substituents are oriented almost orthogonally to the central core, with dihedral angles of 92.7(2)° (N1-C1-Si-P) and 81.4(1)° (Si-P-C28-C29). The same conformation was observed in Si$_2$(Idipp)$_2$ (N-C-Si-Si# 90.8°), whereas in P$_2$Mes*$_2$ the Mes* substituents adopt a twisted conformation (C-C-P-P# 61.5°).[24,26]

Salient spectroscopic features of **1** are the very deshielded ^{29}Si and ^{31}P nuclei. In fact, the ^{29}Si{^{1}H} NMR spectrum of **1** in C$_6$D$_6$ displays a doublet signal at $\delta = 267.3$ ppm (^{1}J(P,Si) = 170.4 Hz), which appears at even lower field than that of Si$_2$(IDipp)$_2$ (δ(^{29}Si) = 224.5 ppm in C$_6$D$_6$)[10] or the most deshielded ^{29}Si NMR signal of a phosphasilene (δ(^{29}Si) of (*t*Bu$_3$Si)(Trip)Si=PH (*E* isomer) = 249.8 ppm).[27,28] The large ^{1}J(P,Si) coupling constant of 170.4 Hz is indicative of Si=P bonds[27,28] and considerably larger than those of silyl phosphanes.[29] Similarly, the ^{31}P{^{1}H} NMR spectrum of **1** in C$_6$D$_6$ shows a strongly deshielded singlet signal at $\delta = 402.4$ ppm with ^{29}Si satellites (^{1}J(P,Si) = 170.4 Hz, 4.9%). The ^{31}P NMR signal of **1** appears at even lower field than the most deshielded ^{31}P NMR signal observed so far for a phosphasilene (δ(^{31}P) of (*t*Bu$_2$MeSi)$_2$Si=PMes* in C$_6$D$_6$ = 389.3 ppm, ^{1}J(P,Si) = 171.3 Hz),[28j,30] but at higher field than that of the diphosphene P$_2$Mes*$_2$ (δ(^{31}P) in C$_6$D$_6$ = 494.2 ppm).[31]

The ^{31}P chemical shift of **1** in solution ($\delta_{\mathrm{soln}} = 402.4$ ppm) compares well with the isotropic value in the solid state (δ(^{31}P)$_{\mathrm{iso}}$ = 398.3 ppm), suggesting a minor influence of intermolecular or conformational effects on the chemical shift (Table 1).[21] The chemical shift tensor components δ_{ii} derived from the solid-state MAS ^{31}P{^{1}H} spectrum of **1** reveal a large chemical shift anisotropy with a span $\Delta\delta$ ($\delta_{11}-\delta_{33}$) of

Table 1: Experimental and calculated ^{31}P NMR spectroscopic data of **1**.[a]

Compound	Method	δ_{11}	δ_{22}	δ_{33}	δ_{iso}[d]	δ_{soln}[e]
(IDipp)Si=PMes* (**1**)	MAS-NMR	1252[b]	31.2[b]	−88.4[b]	398.3	402.4
	B3LYP/6-311G**	1357[c]	143.2[c]	−58.2[c]	480.7	
Mes*P=PMes*	MAS-NMR	1236	249	−3	494	494.2

[a] The experimental values of $P_2Mes^*_2$ are listed for comparison.[33b] Chemical shifts are given in ppm vs. 85 % aqueous H_3PO_4 solution ($\delta = 0$ ppm). [b] The principal components of the chemical shift tensor (δ_{11}, δ_{22}, and δ_{33}) were obtained by analysis of the side band intensities of the solid-state MAS ^{31}P NMR spectrum of **1**. [c] The chemical shielding tensor components σ_{11}, σ_{22}, and σ_{33} of **1** were calculated at the B3LYP/6-311G** level of theory and converted into the chemical shift tensor components δ_{11}, δ_{22}, and δ_{33} using the equations $\delta_{\parallel}(\mathbf{1}) = (\sigma_{ii}(PMe_3) - \sigma_{ii}(\mathbf{1})) + \delta(PMe_3)$, where $\sigma_{11}(PMe_3) = \sigma_{22}(PMe_3) = \sigma_{33}(PMe_3) = 357$ ppm calculated at the same level of theory, and $\delta(PMe_3)$ is the experimental ^{31}P chemical shift of PMe_3 in solution ($\delta(PMe_3)$ in C_6D_6 at 298 K = −61.9 ppm. [d] $\delta_{iso} = (\delta_{11} + \delta_{22} + \delta_{33})/3$. [e] ^{31}P NMR chemical shift in solution.

1340.4 ppm,[32] and compare acceptably well with the calculated values at the B3LYP/6-311G** level of theory (Table 1).[21] The large span value is a salient spectroscopic feature of compounds with E=E bonds.[33] A comparison of the experimental δ_{ii} values of **1** with those of $P_2Mes_2^*$[33b] suggests that the neighborhood to the more electropositive Si atom predominantly influences the in-plane tensor component δ_{22} along the Si=P bond axis, and the out-of-plane tensor component δ_{33} pointing in the direction of the Si−P π-bond.[34] The most significant contribution to the deshielding of the ^{31}P nucleus comes as in $P_2Mes^*_2$ from the in-plane tensor component δ_{11} pointing in the direction of the $P-C_{Mes^*}$ bond. Its large positive value can be attributed to the low HOMO(n_+)–LUMO(π^*) gap of **1** of 3.43 eV, which is similar with that for $P_2Mes^*_2$ ($\Delta E_{HOMO-LUMO} = 3.33$ eV; Figure 3).[21]

Comparative quantum chemical calculations of **1**, $Si_2(IDipp)_2$, and $P_2Mes^*_2$ reveal the same number, symmetry properties, shape, and approximate energy of the frontier orbitals (LUMO, HOMO, and HOMO−1), confirming the isolobal linkage between these three double-bond systems.[21,35] The HOMO is in all cases the symmetric combination of the lone-pair orbitals (n_+), the HOMO−1 is the E−E (E = Si, P) π bonding orbital, and the LUMO is the E−E π* orbital (Figure 3).

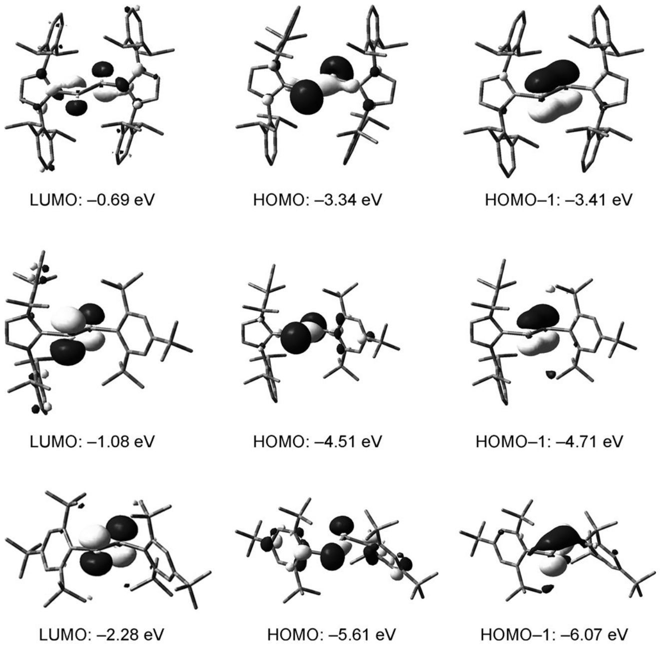

Figure 3. Selected frontier Kohn–Sham orbitals (B3LYP/6-311-G**/RIJ-COSX/COSMO(*n*-hexane)) of $Si_2(IDipp)_2$ (top), **1** (middle), and $P_2Mes^*_2$ (bottom) (isosurface value 0.05 e bohr^{-3}) and their respective energies in eV.

Comparison of the frontier orbitals reveals a shift of the HOMO to higher energy in the series Mes*P=PMes*→(IDipp)Si=PMes* (**1**)→(IDipp)Si=Si(IDipp), which can be rationalized by the successive replacement of the PMes* fragment by its electropositive pendant Si(IDipp).[36] Given the known relation between the HOMO energy and the redox potential for oxidation of isostructural compounds,[37] an increase of the HOMO energy in the series $P_2Mes^*_2$→(IDipp)Si=PMes*→$Si_2(IDipp)_2$ was expected to have a major impact on the oxidation potential of these compounds. This was confirmed by comparative cyclic voltammetric studies in 1,2-difluorobenzene at ambient temperature. In fact, the cyclic voltammogram of **1** displays a reversible wave for the oxidation of **1** (Figure 4).[21,38] Oxidation of **1** occurs at a half-wave potential $E_{1/2}$ of −53 mV, which lies in between that for the reversible one-electron oxidation of $Si_2(IDipp_2)$ ($E_{1/2}$ = −794 mV)[38] and the irreversible one-electron oxidation of $P_2Mes_2^*$ ($E_{1/2} = 1411$ mV; $v = 100$ mV s^{-1})[39] under the same conditions.[21,40] The large increase of the oxidation potential by 2.2 V upon moving from $Si_2(IDipp)_2$ to $P_2Mes^*_2$ reflects the large calculated difference of 2.27 eV between the HOMO energies of the two compounds.

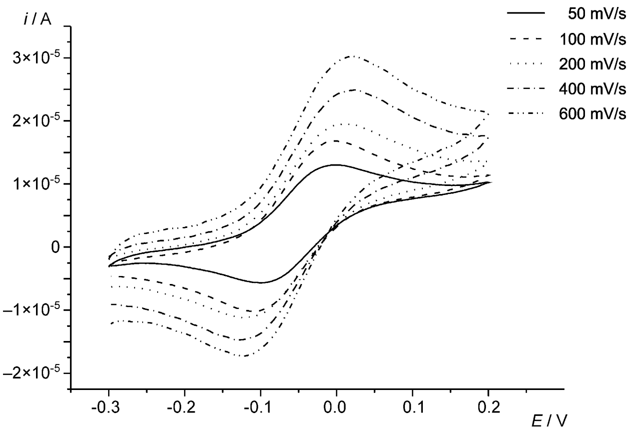

Figure 4. Single-scan cyclic voltammograms of **1** in 1,2-difluorobenzene at different scan rates in the potential range −350–250 mV; reference electrode: 0.4 M $[Fe(C_5Me_5)_2]^{+1/0}$/0.1 M $N(nBu)_4PF_6$/1,2-$C_6H_4F_2$.

Comparative UV/Vis studies of **1**, $Si_2(IDipp)_2$, and $P_2Mes^*_2$ provide additional evidence for the electronic analogy of the three double bond systems (Figure 5). In

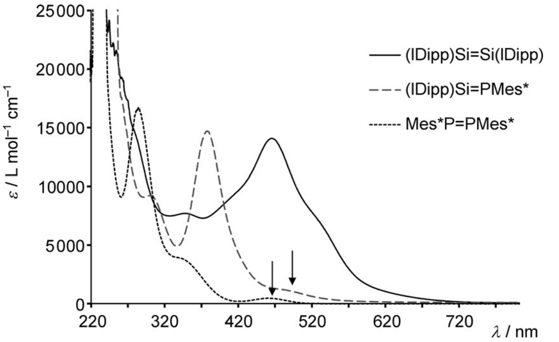

Figure 5. Electronic absorption spectra of $Si_2(IDipp)_2$, **1**, and $P_2Mes^*_2$ in *n*-hexane. The arrows indicate the positions of the HOMO (n_+)→ LUMO (π* (E=E)) bands.

general, a bathochromic shift of the absorption bands is observed in the direction $P_2Mes^*_2$→**1**→$Si_2(IDipp)_2$, providing a rational for the observed color change in solution from yellow ($P_2Mes^*_2$) over orange (**1**) to red ($Si_2(IDipp)_2$). The UV/Vis spectrum of **1** displays three absorption bands at $\lambda =$ 300, 378, and 480 nm (Table 2). Deconvolution of the observed bands, backed up by TDDFT calculations, allowed a full assignment of these bands. The weak band at $\lambda = 480$ nm stems from the symmetry forbidden HOMO(n_+)→ LUMO(π*(Si=P)) transition. The corresponding band of $P_2Mes^*_2$ appears at $\lambda = 460$ nm,[41] whereas that of $Si_2(IDipp)_2$ is not visible owing to its low oscillator strength, but is suggested by deconvolution of the experimental absorption bands to appear at $\lambda = 610$ nm, in good agreement with the results of the TDDFT calculations.[21] Remarkably, the bathochromic shift of this band in the series $P_2Mes^*_2$ (460 nm)→ (IDipp)Si=PMes* (**1**, 480 nm)→$Si_2(IDipp)_2$ (610 nm) correlates well with the decreasing HOMO–LUMO gap in the same direction.

Table 2: UV/Vis absorption bands of **1**, $Si_2(IDipp)_2$, and $P_2Mes^*_2$.[a]

	λ_1 (ε)	λ_2 (ε)	λ_3 (ε)
(IDipp)Si=Si(IDipp)	348 (1.26×10^4)	466 (1.43×10^4)	523[b]
(IDipp)Si=PMes* (**1**)	300 (9.37×10^3)	378 (1.49×10^4)	480[b]
Mes*P=PMes*	283 (1.66×10^4)	340 (3.93×10^3)	460 (4.63×10^2)

[a] λ [nm], ε [L mol⁻¹ cm⁻¹]. [b] No extinction coefficient could be determined for these shoulder absorption bands.

A further insight into the electronic structure of **1** was provided by a natural bond orbital (NBO) analysis of the wavefunction of **1**, which revealed a high localization of the molecular orbitals describing the Si=P double bond. Thus, the σ bond NBO features an occupation of 1.90 electrons, whereas the π bond NBO is filled with 1.92 electrons. Both orbitals are slightly polarized towards the P atom (62 % and 67 %, respectively) and are formed mainly from p-orbitals of the corresponding atoms. Both lone pair NBOs at P and Si have predominant s character and show an occupation of 1.95 electrons and 1.88 electrons, respectively. The moderate polarization of the Si=P bond and the high occupation numbers of its NBOs lead to a high Wiberg Bond Index of 1.68, indicating a strong covalent Si–P interaction. This was further confirmed by the Si=P bond cleavage energy (BCE) of 270 kJ mol⁻¹, which is reduced to a ZPVE corrected bond dissociation energy $D^0(0)$ of 222 kJ mol⁻¹ upon electronic and geometrical relaxation of the fragments Si(IDipp) and PMes* into their respective triplet ground states.[36] Interestingly, the energy required for the $Si-C_{NHC}$ bond dissociation ($D°(0) =$ 120 kJ mol⁻¹) to give IDipp and the phosphasilenylidene (Si=PMes*) (**D**, Figure 1) compares well with those of SiX_2(IDipp) (X = Cl, Br, I: $D°(0) = 121$–124 kJ mol⁻¹)[13] suggesting that **1** might act as a phosphasilenylidene transfer reagent in the presence of a suitable IDipp trapping agent. The phosphasilenylidene displays according to quantum theory a Si=P double bond (d(Si–P) = 2.157 Å), an acute angle at the P atom (Si-P-C_{Mes^*} 70.60°), and a short contact between the Si atom and a C_{ortho} atom of the Mes* substituent (d(Si···C) = 2.172 Å), leading to an electronic stabilization of the unsaturated silicon center.[21] It is less stable by 24.5 kJ mol⁻¹ than the silaphosphyne Mes*Si≡P (**C**, Figure 1), which features a linear-coordinated Si atom and a Si–P triple bond (d(Si–P) = 1.968 Å).[21]

In conclusion, the isolation and comprehensive characterization of the NHC-stabilized phosphasilenylidene **1** corroborates the ability of N-heterocyclic carbenes to stabilize unprecedented bonds between the heavier 3p block elements. Compound **1**, which is the first example of a compound featuring a Si=P bond to a two-coordinate silicon atom, contains with the Si=P bond and the Si and P lone pairs many potential reactive sites for further functionalization. Most inspiring is, however, the perspective to use **1** as transfer reagent of the elusive phosphasilenylidene :Si=PMes* taking advantage of the comparably low $Si-C_{NHC}$ bond dissociation energy. In fact, preliminary studies on the reactions of **1** with unsaturated metal complexes substantiate this perspective.

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[1] G. Becker, G. Gresser, W. Uhl, *Z. Naturforsch. B* **1981**, *36*, 16–19.

[2] Reviews: a) R. Appel, F. Knoll, I. Ruppert, *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 731–744; *Angew. Chem.* **1981**, *93*, 771–784; b) M. Regitz, P. Binger, *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1484–1508; *Angew. Chem.* **1988**, *100*, 1541–1565; c) J. F. Nixon, *Chem. Rev.* **1988**, *88*, 1327–1362; d) L. N. Markovski, V. D. Romanenko, *Tetrahedron* **1989**, *45*, 6019–6090; e) M. Regitz, *Chem. Rev.* **1990**, *90*, 191–213; f) *Multiple Bonds and Low Coordination in Phosphorus Chemistry* (Eds.: M. Regitz, O. J. Scherer), Georg Thieme, Stuttgart, **1990**; g) J. F. Nixon, *Chem. Soc. Rev.* **1995**, *24*, 319–328; h) M. Yoshifuji, *Pure Appl. Chem.* **2005**, *77*, 2011–2020; i) J. M. Lynam, *Organomet. Chem.* **2007**, *33*, 170–178.

[3] L. Weber, *Eur. J. Inorg. Chem.* **2003**, 1843 – 1856, and references therein.

[4] a) K. K. Lehmann, S. C. Ross, L. L. Lohr, *J. Chem. Phys.* **1985**, *10*, 4460 – 4469; b) M. T. Nguyen, T.-K. Ha, *J. Mol. Struct. (Theochem)* **1986**, *139*, 145 – 152; c) E. Goldstein, S. Jin, M. R. Carrillo, R. J. Cave, *J. Comput. Chem.* **1993**, *14*, 186 – 194; d) H. S. Hong, R. J. Cave, *J. Phys. Chem.* **1994**, *98*, 10036 – 10041; e) X. Cheng, Y. Zhao, L. Li, X. Tao, *J. Mol. Struct. (Theochem)* **2004**, *682*, 137 – 143; f) J. B. Ingels, J. M. Turney, N. A. Richardson, Y. Yamaguchi, H. F. Schaefer III, *J. Chem. Phys.* **2006**, *125*, 104306.

[5] a) W. Kutzelnigg, *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 272 – 295; *Angew. Chem.* **1984**, *96*, 262 – 286; b) W. Kutzelnigg, *J. Mol. Struct. (Theochem)* **1988**, *169*, 403 – 419; c) M. Kaupp, *J. Comput. Chem.* **2007**, *28*, 320 – 325.

[6] M. Driess, C. Monsé, D. Bläser, R. Boese, H. Bornemann, A. Kuhn, W. Sander, *J. Organomet. Chem.* **2003**, *686*, 294 – 305.

[7] C.-H. Lai, M.-D. Su, S.-Y. Chu, *Inorg. Chem.* **2002**, *41*, 1320 – 1322.

[8] V. Lattanzi, S. Thorwirth, D. T. Halfen, L. A. Mück, L. M. Ziurys, P. Thaddeus, J. Gauss, M. C. MacCarthy, *Angew. Chem. Int. Ed.* **2010**, *49*, 5661 – 5664; *Angew. Chem.* **2010**, *122*, 5795 – 5798.

[9] a) K. J. Dykema, T. N. Troung, M. S. Gordon, *J. Am. Chem. Soc.* **1985**, *107*, 4535 – 4541; b) A. G. Baboul, H. B. Schlegel, *J. Am. Chem. Soc.* **1996**, *118*, 8444 – 8451; c) D. B. Chesnut, *Chem. Phys.* **2005**, *315*, 59 – 64.

[10] Y. Wang, Y. Xie, P. Wei, R. B. King, H. F. Schaefer III, P. v. R. Schleyer, G. H. Robinson, *Science* **2008**, *321*, 1069 – 1071.

[11] R. S. Ghadwal, H. W. Roesky, S. Merkel, J. Henn, D. Stalke, *Angew. Chem. Int. Ed.* **2009**, *48*, 5683 – 5686; *Angew. Chem.* **2009**, *121*, 5793 – 5796.

[12] A. C. Filippou, O. Chernov, G. Schnakenburg, *Angew. Chem. Int. Ed.* **2009**, *48*, 5687 – 5690; *Angew. Chem.* **2009**, *121*, 5797 – 5800.

[13] A. C. Filippou, Y. N. Lebedev, O. Chernov, M. Straßmann, G. Schnakenburg, *Angew. Chem. Int. Ed.* **2013**, *52*, 6974 – 6978; *Angew. Chem.* **2013**, *125*, 7112 – 7116.

[14] A. C. Filippou, O. Chernov, B. Blom, K. Stumpf, G. Schnakenburg, *Chem. Eur. J.* **2010**, *16*, 2866 – 2872.

[15] H. Cui, C. Cui, *Dalton Trans.* **2011**, *40*, 11937 – 11940.

[16] Y. Xiong, S. Yao, S. Inoue, J. D. Epping, M. Driess, *Angew. Chem. Int. Ed.* **2013**, *52*, 7147 – 7150; *Angew. Chem.* **2013**, *125*, 7287 – 7291.

[17] a) A. Jana, V. Huch, D. Scheschkewitz, *Angew. Chem. Int. Ed.* **2013**, *52*, 12179 – 12182; *Angew. Chem.* **2013**, *125*, 12401 – 12404; b) A. Jana, M. Majumdar, V. Huch, M. Zimmer, D. Scheschkewitz, *Dalton Trans.* **2014**, *43*, 5175 – 5181.

[18] a) G. Märkl, K. M. Raab, *Tetrahedron Lett.* **1989**, *30*, 1077 – 1080; b) S. Sasaki, M. Yoshifuji, N. Inamoto, *Arcivoc* **2012**, *2*, 15 – 23.

[19] V. D. Romanenko, A. V. Ruban, S. V. Iksanova, L. K. Polyachenko, L. N. Markovski, *Phosphorus Sulfur Relat. Elem.* **1985**, *22*, 365 – 368.

[20] a) R. Appel, W. Paulen, *Angew. Chem. Int. Ed. Engl.* **1983**, *22*, 785 – 786; *Angew. Chem.* **1983**, *95*, 807 – 808; b) A. H. Cowley, M. Pakulski, N. C. Norman, *Polyhedron* **1987**, *6*, 915 – 919; c) M. Yoshifuji, K. Shimura, K. Toyota, *Bull. Chem. Soc. Jpn.* **1994**, *67*, 1980 – 1983.

[21] The synthesis and full characterization of **1**, including the solution and solid-state NMR spectra, cyclic voltammograms, results of the quantum chemical calculations, and comparisons of the experimental and the calculated UV/Vis spectra of **1**, $Si_2(IDipp)_2$, and $P_2Mes^*_2$ are given in the Supporting Information.

[22] S. Inoue, W. Wang, C. Präsang, M. Asay, E. Irran, M. Driess, *J. Am. Chem. Soc.* **2011**, *133*, 2868 – 2871.

[23] H. Cui, J. Zhang, C. Cui, *Organometallics* **2013**, *32*, 1 – 4.

[24] M. Yoshifuji, I. Shima, N. Inamoto, K. Hirotsu, T. Higuchi, *J. Am. Chem. Soc.* **1981**, *103*, 4587 – 4589.

[25] A CSD survey (21.11.2014) gave 15 compounds with Si=P double bonds, leading to a median and a mean Si=P bond length of 2.092 Å and 2.093 Å, respectively.

[26] H.-L. Peng, J. L. Payton, J. D. Protasiewicz, M. C. Simspon, *J. Phys. Chem. A* **2009**, *113*, 7054 – 7063.

[27] M. Driess, S. Block, M. Brym, T. M. Gamer, *Angew. Chem. Int. Ed.* **2006**, *45*, 2293 – 2296; *Angew. Chem.* **2006**, *118*, 2351 – 2354.

[28] a) C. N. Smith, F. Bickelhaupt, *Organometallics* **1987**, *6*, 1156 – 1163; b) E. Niecke, E. Klein, M. Nieger, *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 751 – 752; *Angew. Chem.* **1989**, *101*, 792 – 793; c) M. Driess, *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1022 – 1024; *Angew. Chem.* **1991**, *103*, 979 – 981; d) G. R. H. Bender, E. Niecke, M. Nieger, *J. Am. Chem. Soc.* **1993**, *115*, 3314 – 3315; e) M. Driess, S. Rell, H. Pritzkow, *J. Chem. Soc. Chem. Commun.* **1995**, 253 – 254; f) M. Driess, *Coord. Chem. Rev.* **1995**, *145*, 1 – 25; g) M. Driess, H. Pritzkow, S. Rell, U. Winker, *Organometallics* **1996**, *15*, 1845 – 1855; h) S. Yao, S. Block, M. Brym, M. Driess, *Chem. Commun.* **2007**, 3844 – 3846; i) M. Driess, S. Rell, H. Pritzkow, R. Janoschek, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1326 – 1329; *Angew. Chem.* **1997**, *109*, 1384 – 1387; j) V. Y. Lee, M. Kawai, A. Sekiguchi, H. Ranaivonjatovo, J. Escudié, *Organometallics* **2009**, *28*, 4262 – 4265; k) B. Li, T. Matsuo, D. Hashizume, H. Fueno, K. Tanaka, K. Tamao, *J. Am. Chem. Soc.* **2009**, *131*, 13222 – 13223; l) B. Li, T. Matsuo, T. Fukunaga, D. Hashizume, H. Fueno, K. Tanaka, K. Tamao, *Organometallics* **2011**, *30*, 3453 – 3456; m) K. Hansen, T. Szilvási, B. Blom, S. Inoue, J. Epping, M. Driess, *J. Am. Chem. Soc.* **2013**, *135*, 11795 – 11798; n) P. Willmes, M. J. Cowley, M. Hartmann, M. Zimmer, V. Huch, D. Scheschkewitz, *Angew. Chem. Int. Ed.* **2014**, *53*, 2216 – 2220; *Angew. Chem.* **2014**, *126*, 2248 – 2252.

[29] G. Fritz, P. Scheer, *Chem. Rev.* **2000**, *100*, 3341 – 3401.

[30] The ^{31}P NMR chemical shifts of phosphasilenes ($R_2Si{=}PR$) depend strongly on the P-substituent and range from −33 ppm (Ref. [28i]) to +389.3 ppm (Ref. [28j]). Interestingly, the ylidic phosphasilene LSi=PH ($L = CH(C{=}CH_2)CMe(NDipp)_2$) shows an exceptional shielded ^{31}P NMR signal at $\delta = -293.9$ ppm ($^{1}J(P,Si) = 186.4$ Hz) (Ref. [28m]).

[31] M. Schaffrath, A. Villinger, D. Michalik, U. Rosenthal, A. Schulz, *Organometallics* **2008**, *27*, 1393 – 1398.

[32] J. Mason, *Solid State Nucl. Magn. Reson.* **1993**, *2*, 285 – 288.

[33] Selected references: a) K. W. Zilm, G. A. Lawless, R. M. Merrill, J. M. Millar, G. G. Webb, *J. Am. Chem. Soc.* **1987**, *109*, 7236 – 7238; b) K. W. Zilm, G. G. Webb, A. H. Cowley, M. Pakulski, A. Orendt, *J. Am. Chem. Soc.* **1988**, *110*, 2032 – 2038; c) D. Gudat, W. Hoffbauer, E. Niecke, W. W. Schoeller, U. Fleischer, W. Kutzelnigg, *J. Am. Chem. Soc.* **1994**, *116*, 7325 – 7331; d) R. West, J. D. Cavalieri, J. J. Buffy, C. Fry, K. W. Zilm, J. C. Duchamp, M. Kira, T. Iwamoto, T. Müller, Y. Apeloig, *J. Am. Chem. Soc.* **1997**, *119*, 4972 – 4976; e) J. J. Buffy, R. West, M. Bendikov, Y. Apeloig, *J. Am. Chem. Soc.* **2001**, *123*, 978 – 979.

[34] The principal axis system of the ^{31}P magnetic shielding tensor in the molecular frame of **1** was calculated using EFGShield2.4 (S. Adiga, D. Aebi, D. L. Bryce, *Can. J. Chem.* **2007**, *85*, 496 – 505) and is depicted in the Supporting Information.

[35] The isolobal analogy between $Si_2(IDipp)_2$ and diphosphenes was mentioned recently without justification: D. Himmel, I. Krossing, A. Schnepf, *Angew. Chem. Int. Ed. Angew. Chem. Int. Ed.* **2014**, *53*, 370 – 374; *Angew. Chem.* **2014**, *126*, 378 – 382.

[36] Both fragments have a triplet ground state with a ZPVE corrected singlet–triplet gap of $-56.3\ kJ\,mol^{-1}$ (PMes*) and $-30.6\ kJ\,mol^{-1}$ (Si(IDipp)) calculated at the B3LYP/6-311G** level of theory.

[37] a) C.-G. Zhan, J. A. Nichols, D. A. Dixon, *J. Phys. Chem. A* **2003**, *107*, 4184 – 4195; b) I. Dance, *Inorg. Chem.* **2006**, *45*, 5084 – 5091.

[38] Oxidation of **1** by $[Fe(C_5Me_5)_2]B(Ar^F)_4$ ($Ar^F = 2,4,6\text{-}(CF_3)_3C_6H_2$) occurs rapidly in fluorobenzene at −40 °C. Attempts to isolate the radical salt $[(IDipp)Si{=}PMes^*]B(Ar^F)_4$ were unsuccessful owing to its thermolability. In comparison, the green radical salt $[Si_2(IDipp)_2]B(Ar^F)_4$ was isolated and fully characterized: "The Reactivity of Molecular Disilicon(0)": A. C. Filippou, O. Schiemann, M. Straßmann, A. Meyer, G. Schnakenburg, M. I. Arz, The 17th International Symposium on Silicon Chemistry (ISOS XVII), Berlin 3 – 8 August **2014**.

[39] $P_2Mes^*_2$ also undergoes a reversible one-electron reduction at $E_{1/2} = -1836$ mV, in full agreement with previous reports, which have shown that the radical anion $[P_2Mes^*_2]^-$ can be generated chemically and by bulk coulometry in THF solution: a) B. Cetinkaya, P. B. Hitchcock, M. F. Lappert, A. J. Thorne, H. Goldwhite, *J. Chem. Soc. Chem. Commun.* **1982**, 691 – 693; b) A. J. Bard, A. H. Cowley, J. E. Kilduff, J. K. Leland, N. C. Norman, M. Pakulski, G. A. Heath, *J. Chem. Soc. Dalton Trans.* **1987**, 249 – 251.

[40] The half-wave potentials are given versus the $[Fe(C_5Me_5)_2]^{+1/0}$ redox couple, which was shown to be a superior reference standard for potentials to the $[Fe(C_5H_5)_2]^{+1/0}$ redox couple: I. Noviandri, K. N. Brown, D. S. Fleming, P. T. Gulyas, P. A. Lay, A. F. Masters, L. Phillips, *J. Phys. Chem. B* **1999**, *103*, 6713 – 6722. For comparison reasons, the half-wave potential of the $[Fe(C_5H_5)_2]^{+1/0}$ redox couple was determined under the same conditions and found to be +562 mV vs. the $[Fe(C_5Me_5)_2]^{+1/0}$ redox couple.

[41] The UV/Vis spectrum of the diphosphene $P_2Mes^*_2$ was reported in CH_2Cl_2 and analyzed by quantum theory. The results compare well with those described herein: a) see Ref. [26]; b) D. V. Partyka, M. P. Washington, T. G. Gray, J. B. Updegraff III, J. F. Turner II, J. D. Protasiewicz, *J. Am. Chem. Soc.* **2009**, *131*, 10041 – 10048.

[42] CCDC 1037826 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.

Communications

Main-Group Multiple Bonds

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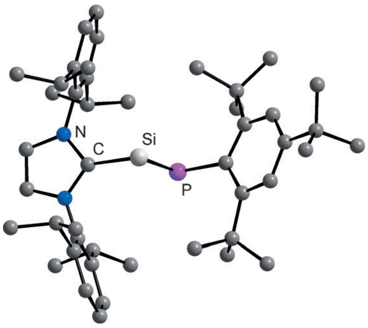
Si=P Double Bonds: Experimental and Theoretical Study of a NHC-Stabilized Phosphasilenylidene



An NHC-stabilized phosphasilenylidene was obtained from $SiCl_2$(IDipp) (IDipp = 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene) and LiP(Mes*)(TMS) (Mes* = 2,4,6-tBu$_3$C$_6$H$_2$). The compound was characterized by various experimental and theoretical methods and compared with those of the isolobal congeners (IDipp)Si=Si(IDipp) and Mes*P=PMes*.