

Si=P Double Bonds: Experimental and Theoretical Study of an NHC-Stabilized Phosphasilylenide**

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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 phosphasilylenide (IDipp)Si=PMes* (IDipp = 1,3-bis(2,6-diisopropylphenyl)-imidazolin-2-ylidene, Mes* = 2,4,6-*t*Bu₃C₆H₂) was prepared by SiMe₃Cl elimination from SiCl₂(IDipp) and LiP-(Mes*)SiMe₃ 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 (*t*BuC≡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 (silyldynephosphanes) **C** from suitable precursors failed so far.^[6] Quantum chemical calculations revealed that the relative stability of phosphasilynes **C** versus their constitutional isomers **D** (phosphasilylenides) correlates with the electronegativity of the substituent R. Electronegative substituents, such as F, OH, OMe, NH₂, Me, Ph, stabilize the Si–P triple bond in the linear isomer **C**, whereas electropositive substituents, such as R = Li, BeH, BH₂, H, SiH₃, 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 SiH₄/PH₃ or SiH₄/P₄/H₂ 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 phosphasilylenides (Si=PR), which are stable in solution or in the solid state have not been reported to date.

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 Si₂,^[10] SiX₂ (X = Cl,^[11] Br,^[12] I^[13]), SiCIR (R = 2,6-Ar₂C₆H₃ (Ar = 2,4,6-Me₃C₆H₂, 2,4,6-*i*Pr₃C₆H₂), N(SiMe₃)(2,6-*i*Pr₂C₆H₃)),^[14,15] SiH⁺,^[13] a Si atom,^[16] or R₂Si=Ge, a heavier Group 14 homologue of a vinylidene.^[17] Based on these results we envisaged that NHCs might be also suitable to trap phosphasilylenides (Si=PR), and we thus decided to use the 1,2-elimination methodology of SiMe₃Cl, 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 phosphasilylenide.

SiCl₂(IDipp) (IDipp = 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene)^[11] and LiP(Mes*)(TMS) (Mes* = 2,4,6-*t*Bu₃C₆H₂; TMS = SiMe₃)^[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 SiCl₂(IDipp) in fluorobenzene at –30 °C (Scheme 1) was accompanied by a rapid color change to deep red. After warming to ambient

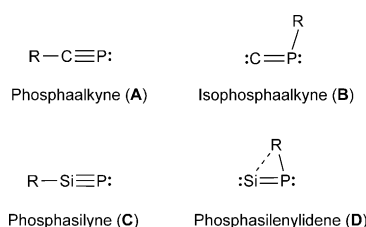
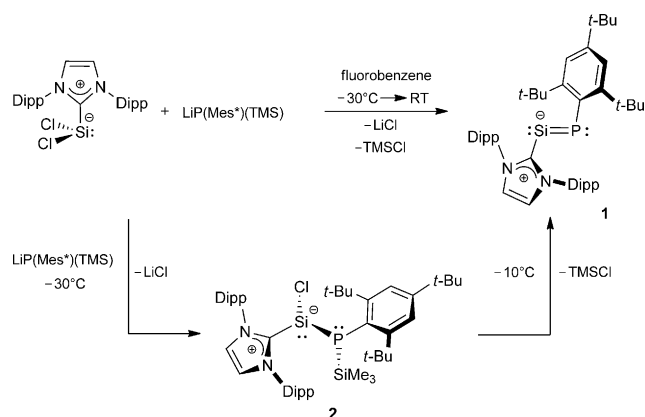


Figure 1. Constitutional isomers of REP (E = C, Si). The lone electron pairs are indicated by two dots.

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

temperature, a second color change from deep red to brown-red was observed with concomitant precipitation of a white solid (LiCl). $^{31}\text{P}\{^1\text{H}\}$ NMR analysis of the resulting reaction solution revealed the formation of the NHC-stabilized phosphasilenyliene **1** along with $\text{PH}(\text{Mes}^*)(\text{TMS})$ ^[19] and a small amount of $\text{P}(\text{Mes}^*)(\text{TMS})_2$.^[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 $^{31}\text{P}\{^1\text{H}\}$ and $^{29}\text{Si}\{^1\text{H}\}$ NMR spectroscopy at low temperature. The $^{31}\text{P}\{^1\text{H}\}$ and $^{29}\text{Si}\{^1\text{H}\}$ 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 ($^1J(\text{P},\text{Si}) = 232$ Hz and $^1J(\text{P},\text{Si}) = 46$ Hz), and two ^{29}Si doublets at $\delta = -9.8$ ppm ($^1J(\text{P},\text{Si}) = 232$ Hz) and $+1.6$ ppm ($^1J(\text{P},\text{Si}) = 46$ 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) $(\text{PhC}(\text{N}t\text{Bu})_2)\text{SiP}(\text{TMS})_2$ ($\delta_{\text{SiP}} = +44$ ppm ($^1J(\text{P},\text{Si}) = 194$ Hz); $\delta_{\text{Si}}(\text{TMS}) = +3.1$ ppm ($^1J(\text{P},\text{Si}) = 22.9$ Hz))^[22] and $\text{Si}[\text{P}(\text{H})(\text{R})][\text{N}(\text{Dipp})(\text{TMS})]_2$ (IPr_2Me_2) ($\text{R} = 2,6-(2,4,6-\text{Me}_3\text{C}_6\text{H}_2)_2\text{C}_6\text{H}_3$, $\text{Dipp} = 2,6-i\text{Pr}_2\text{C}_6\text{H}_3$, $\text{IPr}_2\text{Me}_2 = 1,3$ -diisopropyl-4,5-dimethylimidazolin-2-ylidene; $\delta_{\text{Si}} = -8.8$ ppm ($^1J(\text{P},\text{Si}) = 145.4$ Hz)).^[23] Compound **2** eliminates TMSCl upon warming to ambient temperature to give **1** (Scheme 1).

The molecular structure of **1**·Et₂O was determined by single-crystal X-ray diffraction (Figure 2). Compound **1** features as its isolobal congeners $\text{Si}_2(\text{IDipp})_2$ ^[10] and P_2Mes^*_2 ^[24] a *trans*-bent planar geometry with a torsion angle C1-Si-P-C28 of $178.10(7)^\circ$. The angles at the Si (P-Si-C1 $96.90(6)^\circ$), and the P atom (Si-P-C28 $95.38(6)^\circ$) resemble those of $\text{Si}_2(\text{IDipp})_2$ (Si-Si-C $93.37(5)^\circ$)^[10] and P_2Mes^*_2 (P-P-C $102.8(1)^\circ$), 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

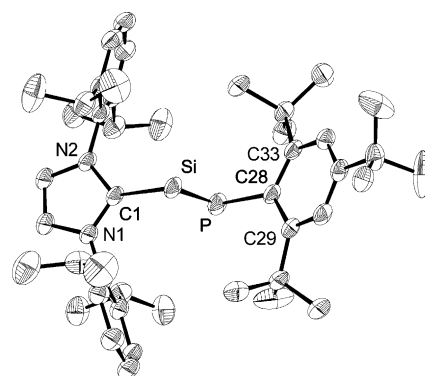


Figure 2. DIAMOND plot of the molecular structure of **1**·Et₂O at 123 K in the solid state.^[42] Ellipsoids are set at 30% probability; hydrogen atoms and the solvent are omitted for clarity. Selected bond lengths [Å], angles [°], and torsion angles [°]: Si–P 2.1188(7), Si–C1 1.960(2), P–C28 1.877(2); 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 $-91.7(1)$.

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 $\text{Si}_2(\text{IDipp})_2$ ($2.229(1)$ Å)^[10] and the P=P bond length of P_2Mes^*_2 ($2.034(2)$ Å),^[24] and lies in the range of the Si=P bond lengths of phosphasilenes (silylidenephosphanes) ($\text{R}_2\text{Si}=\text{PR}$: $d(\text{Si}=\text{P}) = 2.062(1)–2.172(1)$ Å).^[25] Notably, the Mes* and the NHC substituents are oriented almost orthogonally to the central core, with dihedral angles of $92.7(2)^\circ$ (N1–C1–Si–P) and $81.4(1)^\circ$ (Si–P–C28–C29). The same conformation was observed in $\text{Si}_2(\text{IDipp})_2$ (N–C–Si–Si# 90.8°), whereas in P_2Mes^*_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 $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of **1** in C_6D_6 displays a doublet signal at $\delta = 267.3$ ppm ($^1J(\text{P},\text{Si}) = 170.4$ Hz), which appears at even lower field than that of $\text{Si}_2(\text{IDipp})_2$ ($\delta(^{29}\text{Si}) = 224.5$ ppm in C_6D_6)^[10] or the most deshielded ^{29}Si NMR signal of a phosphasilene ($\delta(^{29}\text{Si})$ of $(t\text{Bu}_3\text{Si})(\text{Trip})\text{Si}=\text{PH}$ (*E* isomer) = 249.8 ppm).^[27,28] The large $^1J(\text{P},\text{Si})$ 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 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **1** in C_6D_6 shows a strongly deshielded singlet signal at $\delta = 402.4$ ppm with ^{29}Si satellites ($^1J(\text{P},\text{Si}) = 170.4$ 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 ($\delta(^{31}\text{P})$ of $(t\text{Bu}_2\text{MeSi})_2\text{Si}=\text{PMes}^*$ in $\text{C}_6\text{D}_6 = 389.3$ ppm, $^1J(\text{P},\text{Si}) = 171.3$ Hz),^[28j,30] but at higher field than that of the diphosphene P_2Mes^*_2 ($\delta(^{31}\text{P})$ in $\text{C}_6\text{D}_6 = 494.2$ ppm).^[31]

The ^{31}P chemical shift of **1** in solution ($\delta_{\text{soln}} = 402.4$ ppm) compares well with the isotropic value in the solid state ($\delta(^{31}\text{P})_{\text{iso}} = 398.3$ 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 $^{31}\text{P}\{^1\text{H}\}$ 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}	$\delta_{\text{iso}}^{[d]}$	$\delta_{\text{soln}}^{[e]}$
(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 $\delta_{ii}(\text{1}) = (\sigma_{ii}(\text{PMes}_3) - \sigma_{ii}(\text{1})) + \delta(\text{PMes}_3)$, where $\sigma_{11}(\text{PMes}_3) = \sigma_{22}(\text{PMes}_3) = \sigma_{33}(\text{PMes}_3) = 357$ ppm calculated at the same level of theory, and $\delta(\text{PMes}_3)$ is the experimental ^{31}P chemical shift of PMes_3 in solution ($\delta(\text{PMes}_3)$ in C_6D_6 at 298 K = −61.9 ppm). [d] $\delta_{\text{iso}} = (\delta_{11} + \delta_{22} + \delta_{33})/3$. [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^* ($\Delta E_{\text{HOMO-LUMO}} = 3.33$ eV; Figure 3).^[21]

Comparative quantum chemical calculations of **1**, $\text{Si}_2(\text{IDipp})_2$, 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).

Comparison of the frontier orbitals reveals a shift of the HOMO to higher energy in the series Mes*P=PMes* $\rightarrow$ (IDipp)Si=PMes* (**1**) $\rightarrow$

(IDipp)Si=Si(IDipp), which can be rationalized by the successive replacement of the PMes* fragment by its electro-positive 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 $\text{P}_2\text{Mes}_2^* \rightarrow (\text{IDipp})\text{Si}=\text{PMes}^* \rightarrow \text{Si}_2(\text{IDipp})_2$ 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

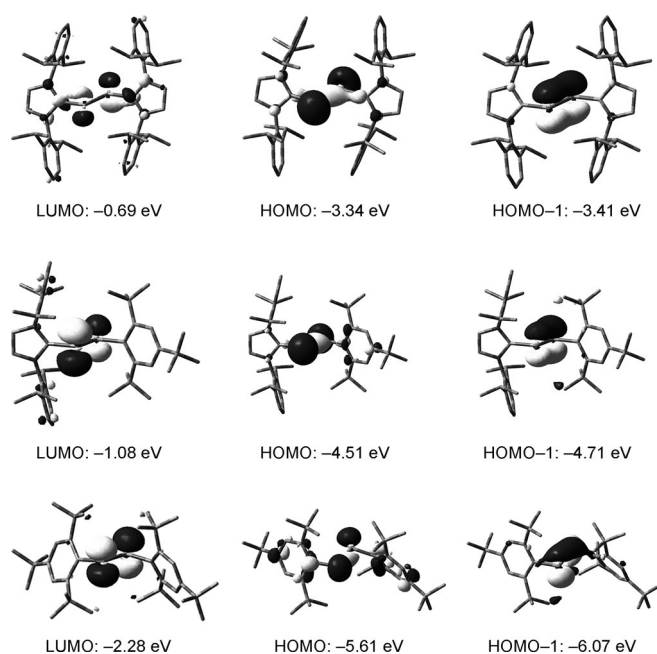


Figure 3. Selected frontier Kohn–Sham orbitals (B3LYP/6-311-G**/RI-COSX/COSMO(*n*-hexane)) of $\text{Si}_2(\text{IDipp})_2$ (top), **1** (middle), and P_2Mes_2^* (bottom) (isosurface value 0.05 ebohr^{−3}) and their respective energies in eV.

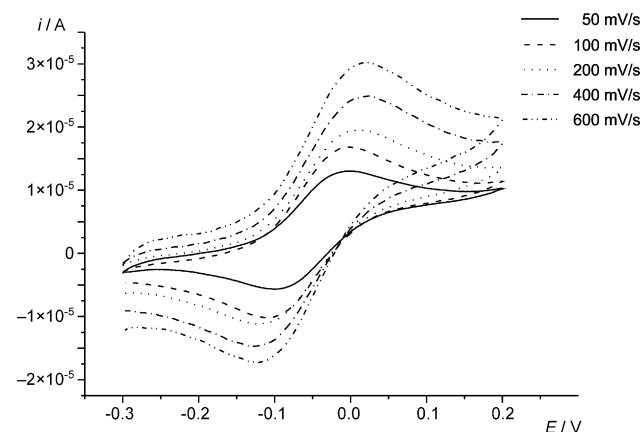


Figure 4. Single-scan cyclic voltammograms of **1** in 1,2-difluorobenzene at different scan rates in the potential range −350–250 mV; reference electrode: 0.4 M $[\text{Fe}(\text{C}_5\text{Me}_5)_2]^{+1}/0.1$ M $\text{N}(\text{nBu})_4\text{PF}_6/1,2\text{-C}_6\text{H}_4\text{F}_2$.

potential $E_{1/2}$ of −53 mV, which lies in between that for the reversible one-electron oxidation of $\text{Si}_2(\text{IDipp})_2$ ($E_{1/2} = -794$ mV)^[38] and the irreversible one-electron oxidation of P_2Mes_2^* ($E_{1/2} = 1411$ mV; $\nu = 100$ mV s^{−1})^[39] under the same conditions.^[21,40] The large increase of the oxidation potential by 2.2 V upon moving from $\text{Si}_2(\text{IDipp})_2$ to P_2Mes_2^* reflects the large calculated difference of 2.27 eV between the HOMO energies of the two compounds.

Comparative UV/Vis studies of **1**, $\text{Si}_2(\text{IDipp})_2$, and P_2Mes_2^* provide additional evidence for the electronic analogy of the three double bond systems (Figure 5). In

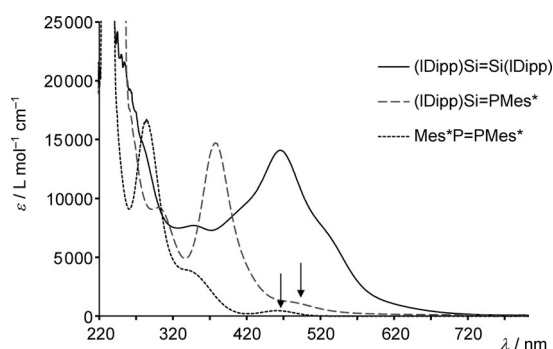


Figure 5. Electronic absorption spectra of $\text{Si}_2(\text{IDipp})_2$, **1**, and P_2Mes^*_2 in *n*-hexane. The arrows indicate the positions of the HOMO (n_+) → LUMO (π^* ($E=E$)) bands.

general, a bathochromic shift of the absorption bands is observed in the direction $\text{P}_2\text{Mes}^*_2 \rightarrow \mathbf{1} \rightarrow \text{Si}_2(\text{IDipp})_2$, providing a rationale for the observed color change in solution from yellow (P_2Mes^*_2) over orange (**1**) to red ($\text{Si}_2(\text{IDipp})_2$). 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

Table 2: UV/Vis absorption bands of **1**, $\text{Si}_2(\text{IDipp})_2$, 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 [$\text{L mol}^{-1} \text{cm}^{-1}$]. [b] No extinction coefficient could be determined for these shoulder absorption bands.

a full assignment of these bands. The weak band at $\lambda = 480$ nm stems from the symmetry forbidden HOMO(n_+) → LUMO($\pi^*(\text{Si}=\text{P})$) transition. The corresponding band of P_2Mes^*_2 appears at $\lambda = 460$ nm,^[41] whereas that of $\text{Si}_2(\text{IDipp})_2$ 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) → $\text{Si}_2(\text{IDipp})_2$ (610 nm) correlates well with the decreasing HOMO–LUMO gap in the same direction.

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 ($D^0(0) = 120 \text{ kJ mol}^{-1}$) to give IDipp and the phosphasilenylidene (Si=PMes*) (**D**, Figure 1) compares well with those of SiX₂–(IDipp) (X = Cl, Br, I: $D^0(0) = 121\text{--}124 \text{ kJ mol}^{-1}$)^[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 ($d(\text{Si}=\text{P}) = 2.157 \text{ \AA}$), 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 ($d(\text{Si} \cdots \text{C}) = 2.172 \text{ \AA}$), 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 ($d(\text{Si}=\text{P}) = 1.968 \text{ \AA}$).^[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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