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On the Electronic Structure of (Phosphino)(silyl)carbenes: Single-Crystal X-ray Diffraction and ELF Analyses

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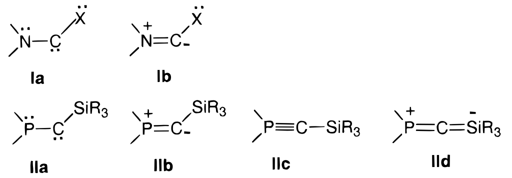
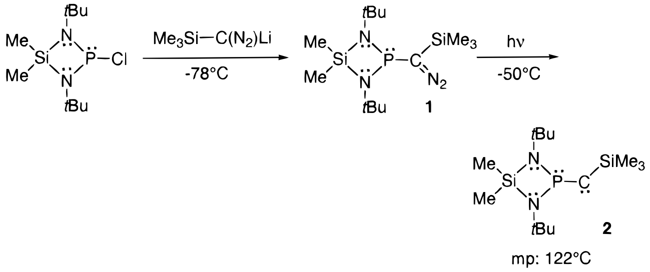
All known, stable singlet carbenes[1] feature at least one amino (type **I**) or phosphino substituent (type **II**) (Chart 1). It is now well-established that the unusual stability of these species is mainly due to electron donation from the heteroatom lone pair into the formally "empty" p_π orbital of the carbene center (ylide forms **Ib** and **IIb**).[2,3] However, for **II**, additional stabilization might result from the interaction of the carbene lone pair with the σ* orbitals of both the phosphino and silyl groups (negative hyperconjugation).[4] In such cases, **II** should best be regarded as a λ^5-phosphaacetylene **IIc** or a heterocumulene **IId.**[3] As far as chemical behavior is concerned, typical reactions for both the carbene **IIa** (CH-insertion,[5a] cyclopropanations,[5b]...), and phosphorus−carbon multiple-bonded forms **IIb** and **IIc** (dipolar cycloadditions)[5a] have been observed. Concerning the precise electronic structure of **II**, only spectroscopic data and contradictory ab initio calculations are available.[6] Herein we report the synthesis of a new, stable (phosphino)(silyl)carbene and the first single-crystal X-ray diffraction and electron localization function (ELF) analyses of such a species.

Chart 1



Scheme 1



Carbene **2** was generated by photolysis (−50 °C) of a pentane solution of the corresponding (phosphino)(silyl)diazomethane **1,**[7] which was prepared by addition of the corresponding chlorophosphine[8] to the lithium salt of trimethylsilyl diazomethane (Scheme 1). After evaporation of pentane, derivative **2** was obtained in nearly quantitative yield as a white solid. The spectroscopic data for **2** [^{31}P NMR δ −26.7; ^{29}Si NMR δ −17.8 (d, $^2J_{\mathrm{Si-P}} = 63.6$ Hz] compared well with those observed for the other known (phosphino)(silyl)carbenes.[1a] Note that even at −100 °C the two *tert*-butyl groups are magnetically equivalent (vide infra).

Colorless crystals of **2** (mp = 122 °C) suitable for an X-ray diffraction study[9] were obtained by cooling a saturated pentane solution to −50 °C. The molecular structure of **2** is shown in Figure 1 along with the pertinent metric parameters. The Si1N2C6N1C2P1C1Si2 skeleton is planar (maximum deviation from the best plane: 0.03 Å), and the P1C1 bond length [1.532(3) Å] is in the range expected for a PC triple bond.[10] These features are in agreement with both the ylide **IIb** and λ^5-phosphaacetylene forms **IIc**, and the presence of a strongly polarized $\mathrm{P}^{\delta+}\mathrm{C}^{\delta-}$ fragment is suggested by the short Si2C1 [1.795 Å compare to 1.86−1.88 Å for Si2−$\mathrm{CH_3}$] and PN bond distances [1.664(2) Å].[11] Last, as expected for the phosphorus vinyl ylide form **IIb**, the P1C1Si2 framework is bent [152.6(3)°].

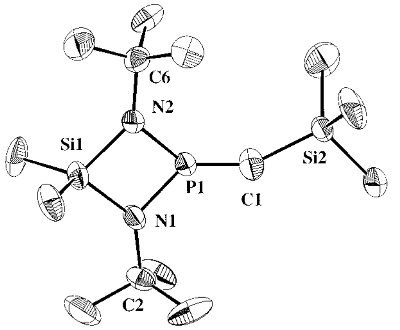


Figure 1. Molecular structure of **2**. Selected bond lengths [Å] and angles [deg]: Si(1)−N(1) 1.734(2), Si(1)−N(2) 1.745(2), P(1)−N(1) 1.664(2), P(1)−N(2) 1.665(2), P(1)−C(1) 1.532(3), C(1)−Si(2) 1.795(3), N(1)−P(1)−N(2) 87.01(11), N(1)−P(1)−C(1) 130.85(15), N(2)−P(1)−C(1) 142.12(14), P(1)−C(1)−Si(2) 152.6(3).

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(6) For the model derivative $[(\mathrm{H_2N})_2\mathrm{PCSiH_3}]$ **2′**, Dixon et al.[3b] concluded that it was best described as a quasi-linear λ^5-phosphaacetylene (P−C−Si angle: 175.9°), while Nyulaszi[3d] found that the bent structure (P−C−Si angle: 138.2°) was 0.83 kcal/mol lower in energy than the linear structure.

(7) **1**: ^{31}P NMR ($\mathrm{C_6D_6}$) δ 137.9; IR(THF) 2028 $\mathrm{cm^{-1}}$ ($\mathrm{CN_2}$). **2**: ^{31}P NMR ($\mathrm{C_6D_6}$) δ −26.7; ^{13}C NMR ($\mathrm{C_6D_6}$) δ 77.6 (d, $J_{\mathrm{P-C}} = 152.9$ Hz, P−C).

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(9) Crystal data for **2**: $\mathrm{C_{14}H_{33}N_2PSi_2}$, monoclinic, $P2_1$, $a = 9.641(1)$ Å, $b = 10.608(1)$ Å, $c = 10.587(1)$ Å, $\beta = 111.98(1)°$, $V = 1004.1(2)$ Å^3, $Z = 2$, $T = 173(2)$ K.; R1 [for $F > 2\sigma(F)$] = 0.035 and wR2 = 0.083.

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(11) The geometry of the $\mathrm{Me_2Si(\mathit{t}BuN)_2P}$ fragment is quite similar to that reported for the corresponding phosphenium ion.[8c]

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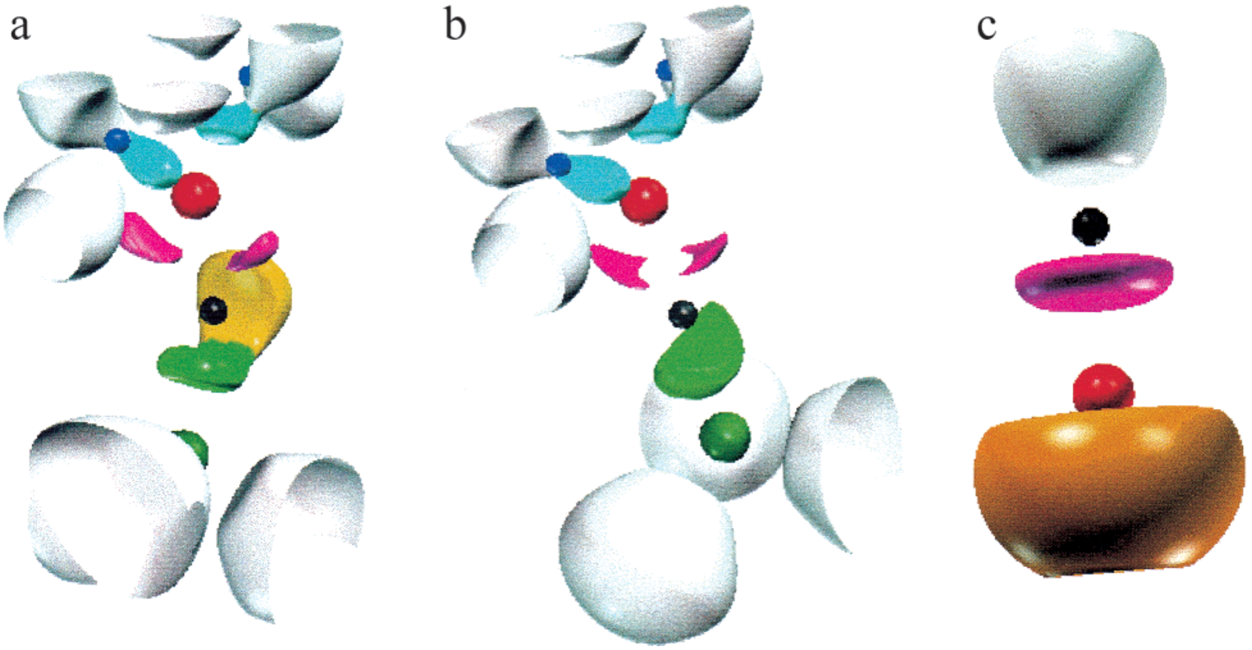

Figure 2. ELF plots, isosurfaces 0.85; color code: red = P core; black = C core; dark green = Si core; dark blue = N core; purple = PC bond; green = CSi bond; yellow = C lone pair; blue = PN bond; orange = P lone pair; white = all remaining electron pairs. (a) Bent form of **2′**, (b) linear form of **2′**, (c) PCH.

To have more of an insight into the electronic nature of (phosphino)(silyl)carbenes **II**, an ELF analysis[12] of the model compound **2′** [$(H_2N)_2PCSiH_3$] was carried out. First it should be noted that, in agreement with previous theoretical studies,[3a,d] this calculation[13] leads to a bent structure for the energy minimum of **2′**; however, the linear structure is only 1 kcal/mol higher in energy. The ELF plots of both the bent and linear forms of **2′** are depicted in Figure 2. The first important feature of the bent form of **2′** (Figure 2a) is the presence of a lone pair (yellow) on the carbon atom (core: black), which is directed away from both the phosphorus (core: red) and the silicon (core: dark green), indicating that neither the triple bond (**IIc**) nor the cumulene (**IId**) structure is the best formulation for **2′**. Since the PC double bond (purple) is clearly evident, **2′** has to be regarded as the phosphorus vinyl ylide **IIb**. Moreover, the isosurfaces representing the PC double bond are bent toward phosphorus, indicating that the phosphorus is reluctant to delocalize its lone pair into the formally vacant orbital of the carbene center. These observations as a whole rationalize the reactions of species **II** at the carbon atom with Lewis acids[14a] (presence of a lone pair) and with Lewis bases[14b] when the phosphorus lone pair "retracts" to the phosphorus. In addition, **II** can react with 1,3-dipoles because of the apparent PC double bond character.[5a] Interestingly, for the linear form of **2′** (Figure 2b), we again recognize the typical pattern for the presence of a double bond between phosphorus and carbon (purple) [for comparison, Figure 2c shows the ELF plot for HCP which possesses a genuine triple bond (purple)].[15] The stretched shape of the light green isosurface is an indication of SiC double bond character; moreover, since this isosurface is perpendicular to that attributed to the PC double bond, the linear form of **2′** is best described by the cumulenic structure **IId**.

In conclusion, (phosphino)(silyl)carbenes **II** are best described by a phosphorus vinyl ylide structure **IIb** with a lone pair at carbon, but because of the reluctance of phosphorus to participate in π-donation, which forces it to become planar,[16] the formally vacant orbital of the carbene center is easily available. Even the linear form, which is slightly higher in energy than the bent form, does not correspond to the phosphaacetylene structure **IIc** but rather to the cumulenic structure **IId**.

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Supporting Information Available: Experimental procedures and characterization data for **1** and **2**; X-ray structure determination and crystal data for **2** (PDF). An X-ray crystallographic file for **2** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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[15] See also the ELF plot for HCCH in Figure 2 of ref 13d.

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