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### Heavier Double Bonds

# From Disilene (Si=Si) to Phosphasilene (Si=P) and Phosphacumulene (P=C=N)\*\*

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Abstract: The generation of heavier double-bond systems without by- or side-product formation is of considerable importance for their application in synthesis. Peripheral functional groups in such alkene homologues are promising in this regard owing to their inherent mobility. Depending on the steric demand of the N-alkyl substituent R, the reaction of disilenide  $Ar_2Si=Si(Ar)Li$   $(Ar=2,4,6-iPr_3C_6H_2)$  with ClP- $(NR_2)_2$  either affords the phosphinodisilene  $Ar_2Si=Si(Ar)P$ - $(NR_2)_2$  (for R = iPr) or P-amino functionalized phosphasilenes  $Ar_2(R_2N)Si-Si(Ar)=P(NR_2)$  (for R = Et, Me) by 1,3-migration of one of the amino groups. In case of R = Me, upon addition of one equivalent of tert-butylisonitrile a second amino group shift occurs to yield the 1-aza-3-phosphaallene  $Ar_2(R_2N)Si$ - $Si(NR_2)(Ar) - P = C = NtBu$  with pronounced ylidic character. All new compounds were fully characterized by multinuclear NMR spectroscopy as well as single-crystal X-ray diffraction and DFT calculations in selected cases.

After the isolation of the first disilene,<sup>[1]</sup> heteronuclear double bonds with two heavier main-group elements soon moved into focus.<sup>[2]</sup> In particular, phosphasilenes allowed early on for the introduction of peripheral functionality,<sup>[3]</sup> while the emphasis in disilene chemistry was initially directed to reactivity studies of unfunctionalized Si=Si moieties.[4] For several years, functional disilenes have enjoyed increased attention,<sup>[5]</sup> which generates opportunities regarding the exploitation of the physical and chemical properties of the Si=Si bond. For example, the synthesis of  $\pi$ -conjugated systems lithium disilenides<sup>[6]</sup> results in better yields than the classical reductive coupling techniques, although the latter approach is still remarkably successful. Notably, it allowed Tamao et al. to obtain air-stable and luminescent disilenes<sup>[7]</sup> as well as  $\pi$ -conjugated systems with Si=P bonds.<sup>[8]</sup> Very recently, a proof-of-concept for organic light-emitting devices based on Tamao's disilenes was provided.<sup>[9]</sup> "Half-parent" phosphasilene HP=SiTip-Si(tBu)<sub>3</sub> (Tip = 2,4,6- $iPr_3C_6H_2$ ) has been employed for the grafting of a ZnMe<sup>[10]</sup> as well as

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a lead(II) moiety<sup>[11]</sup> to the Si=P unit, thus yielding P-metalated phosphasilenes.

For the prospect of the synthesis of novel polymeric materials, the interconversion of low-valent functionalities is crucial, preferably in reversible manner and free of byproducts.<sup>[12]</sup> While the transformation of an Si=Si moiety of anionic disilenides into heteronuclear silenes (Si=C) with concomitant LiCl elimination has been documented,<sup>[13]</sup> the addition of a disilenide to a bulky ketone followed by Peterson-type rearrangement to a silene remained the sole example of such reactivity without systematic by-product formation until very recently.<sup>[14]</sup> Earlier this year, we reported the complete cleavage of an Si=Si bond of unsymmetrically substituted disilenes by isonitriles to afford silenes with Si=C bond, a reaction that can be fully reversed by BEt3 as isonitrile scavenger.<sup>[15]</sup> Indications of reversibility were also found in case of the reaction of isonitriles with cyclotrisilenes vielding imino-functionalized cyclic disilenes.<sup>[16]</sup> The reversible formation of a base-stabilized arsasilene (Si=As) as reported by Driess et al. constitutes a remarkable milestone with heteronuclear double bond.<sup>[17]</sup> A related phosphasilene is capable of transferring the parent phosphinidene fragment to N-heterocyclic carbenes.<sup>[18]</sup>

We recently reported stable dialkylphosphino disilenes 1 (Scheme 1) and their use as ligands in palladium com-



**Scheme 1.** P-Diorganophosphino disilenes 1 (Tip = 2,4,6-iPr<sub>3</sub>C<sub>6</sub>H<sub>2</sub>; R=alkyl, aryl)<sup>[19]</sup> and degenerate rearrangement of P-fluorosilyl phosphasilene 2.<sup>[20]</sup>

plexes.<sup>[19]</sup> In consideration of the degenerate rearrangement of phosphasilene **2**, as described by Driess and co-workers,<sup>[20]</sup> we anticipated that the use of donor-substituted phosphino groups as substituent at the Si=Si moiety might result in the 1,3-migration of the functional donor-group to the  $\beta$ -silicon atom of the double bond and thus initiate the conversion of Si=Si into Si=P double bonds.

Indeed, the reactions of disilenide **3** with diamino-(chloro)phosphines depending on the bulkiness of the amino substituents either afford a P-diaminophosphinodisilene **4c** ( $\mathbf{R} = i\mathbf{Pr}$ ) or result in the isomeric phosphasilenes **5a**,**b** as E/Z-mixtures. Phosphasilenes **5a**,**b** are the formal products of 1,3-migration of one of the amino groups of the plausible but unobserved intermediates **[4a,b]**. The subsequent addi-



**Scheme 2.** Synthesis of *P*-diaminophosphino disilene **4c**, phosphasilenes E/Z-**5 a,b** and conversion of **5a** into 1-aza-3-phosphaallene **6a** (Tip = 2,4,6-iPr<sub>3</sub>C<sub>6</sub>H<sub>2</sub>; **a**: R=Me; **b**: R=Et; **c**: R=iPr).

tion of *tert*-butyl isocyanide to 5a yields the 1-aza-3-phosphaallene 6a, thus converting the Si=P to an Si=C bond (Scheme 2).

The diaminophosphino disilene 4c is isolated as orange crystals from pentane in 76% yield. The doublet resonances in the <sup>29</sup>Si NMR spectrum at  $\delta = 90.7$  and 71.1 ppm appear at characteristic chemical shifts for Tip<sub>2</sub>Si=SiTip moieties.<sup>[5,6,19]</sup> Curiously, the two P-Si coupling constants are almost identical ( ${}^{1}J_{PSi} = 115 \text{ Hz}$ ;  ${}^{2}J_{PSi} = 109 \text{ Hz}$ ), which suggests a certain through-space interaction between the phosphorus lone pair and the  $\beta$ -silicon atom. Indeed, the shape of the molecular orbitals as obtained by DFT calculations on a truncated model 4cPh (Ph groups instead of Tip; see Supporting Info for MOs) supports the presence of such an interaction. The HOMO-1, although in principle related to the lone pair at phosphorus, is extensively delocalized and shows a significant Si-Si σ-contribution. Furthermore, admixture of the non-bonding orbital at the phosphorus center is readily discerned in the predominantly Si-Si π-bonding HOMO (less so in the mostly phosphorus-centered HOMO-3). The fairly non-diagnostic  ${}^{31}P$  NMR signal of 4cat  $\delta = 58.4$  ppm is observed in the typical region for bis(diisopropylamino)-substituted phosphorus compounds between 30 and 100 ppm.<sup>[21]</sup> The longest wavelength absorption in the UV/Vis spectrum of **4c** at  $\lambda_{max} = 441$  nm is red-shifted by about 20 nm compared to dialkylphosphino disilenes.<sup>[19]</sup> Based on its intensity ( $\varepsilon = 23600 \text{ Lmol}^{-1} \text{ cm}^{-1}$ ), it is assigned to the  $\pi$ - $\pi$ \* transition.

An X-ray diffraction study on single crystals of 4c confirmed the constitution of a phosphino disilene (Figure 1)<sup>[22]</sup> even though the Si=Si and the Si-P bonds are significantly longer (Si1–Si2 2.1968(9), Si2–P1 2.3126(10) Å) than the corresponding bonds of the previously reported dicyclohexylphosphino disilene **1a** (Scheme 1, R = c-hexyl). This observation is, however, in line with the considerably more pronounced trans-bending of the Si=Si bond in 4c compared to the moderately *trans*-bent **1a** (**4c**:  $\theta^{\text{SiTip}} = 30.8^{\circ}$ ;  $\theta^{\text{SiTip}}_{2} = 19.2^{\circ}; \ \mathbf{1a}: \ \theta^{\text{SiTip}} = 7.7^{\circ}; \ \theta^{\text{SiTip}}_{2} = 8.9^{\circ}).$  The Carter-Goddard-Malrieu-Trinquier (CGMT) model predicts stronger trans-bending with more electronegative substituents (dialkylphosphino in 1a vs. diaminophosphino in 4c).<sup>[23]</sup> The phosphorus atom in 4c is significantly more pyramidal than that of the P-cyclohexyl-substituted counterpart 1a (sum of angles at P1: 320.91°). According to Bent's rule,<sup>[24]</sup> more



*Figure 1.* Molecular structure of **4c** in the solid state (ellipsoids set at 50% probability, H atoms and disordered *i*Pr groups omitted). Selected bond lengths [Å]: Si1–Si2 2.1968(9), Si2–P1 2.3126(10), P1–N1 1.699(2), P1–N2 1.714(2).

electronegative substituents induce a higher s-character of the lone pair at the phosphorus atom.

The phosphino disilene 4c melts at 163°C with almost complete decomposition to an intractable mixture of products (at least eight major <sup>31</sup>P NMR signals between  $\delta = +100$  and -300 ppm alongside more than 20 signals of minor intensity) with no indication of conversion into a hypothetical phosphasilene 5c. Conversely, in case of P-amino substituents with reduced steric requirements (R = Me, Et), the *E*/*Z*-isomeric mixtures of the phosphasilenes 5a,b are directly obtained from disilenide 3 and the appropriate chlorophosphine. Apparently, the formation of 5a,b results from the 1,3migration of one of the amino groups from phosphorus to silicon in the plausible but undetected intermediates [4a,b] (Scheme 2). DFT calculations on model systems 4a-cPh and 5a-cPh confirm, despite truncation (Ph instead of Tip), that the phosphasilene isomer is thermodynamically favored in the less-congested systems (*E*-**5 aPh** vs. **4aPh**:  $\Delta G_{298} = -28.8$  kcal  $mol^{-1}$ ; *E*-5 cPh vs. 4cPh:  $\Delta G_{298} = -18.1 \text{ kcal mol}^{-1}$ ; for details see Supporting Information). Both crude products are reasonably pure, but only 5a (R = Me) could be isolated as bright yellow crystals in an excellent yield (97%). The <sup>31</sup>P NMR spectra reveal chemical shifts at the downfield end of the spectrum for phosphasilenes at  $\delta^{31}P = 344.8$  and 336.2 ppm for the two isomers of **5a** and at  $\delta^{31}P = 344.8$  and 336.7 ppm for those of **5b** (*E*/*Z*-ratio **5a** 95:5, **5b** 70:30). More deshielded <sup>31</sup>P signals were only observed by Sekiguchi et al. in case of their "push-pull"-substituted phosphasilenes, for which a certain degree of inverse polarization<sup>[25]</sup> of the Si=P bond had been implied.<sup>[26]</sup> DFT calculation of the Mulliken charges of the model compound E-5 aPh shows a truly inverse polarization in this case (Si2: -0.095, P1: +0.169), which without doubt can be attributed to the electronegative,  $\pi$ donating amino group at the phosphorus end of the double bond.<sup>[27]</sup> In contrast to the phosphino disilene 4c, the magnitude of coupling within the typical range for phosphasilenes readily distinguishes the two different silicon nuclei in **5a** (*E*-**5a**  ${}^{1}J_{P-Si} = 186.5$  Hz,  ${}^{2}J_{P-Si} = 40.8$  Hz). For the NEt<sub>2</sub> derivative **5b**, the broad  ${}^{31}P$  signals at room temperature suggested that the interconversion of the two stereoisomers may be fast on the NMR timescale. Indeed, at 243 K the signals sharpened sufficiently for the determination of the  ${}^{2}J_{P-Si}$  coupling constants of both isomers (at 243 K : *E*-**5b**  ${}^{1}J_{P-Si} = 187.6$  Hz,  ${}^{2}J_{P-Si} = 44.3$  Hz; *Z*-**5b**  ${}^{1}J_{P-Si} = 188.3$  Hz,  ${}^{2}J_{P-Si} \approx 28$  Hz). The larger  ${}^{2}J_{P-Si}$  coupling that is due to the *cis*-relationship of the lone pair at phosphorus and the  $\beta$ -silicon atom allows for the unambiguous assignment of the major isomer *E*-**5b**.<sup>[28]</sup>

Although E/Z isomerism has been observed by Driess et al.<sup>[29]</sup> for unsymmetrically substituted phosphasilenes, the high barrier prevented the coalescence of signals in the observable temperature window.<sup>[30]</sup> This barrier is strongly correlated to the strength of the P–Si  $\pi$ -bond. In case of both 5a and 5b, the exchange is sufficiently fast at room temperature, but owing to the more favorable ratio of isomers we restricted a pulse-selective <sup>31</sup>P NMR study<sup>[31-33]</sup> to **5b** (see the Supporting Information for details). The free energy of activation for the conversion of E-5b into Z-5b was calculated using the DynaFit3 program<sup>[34]</sup> to  $\Delta G^{\#}_{300} = 59.5 \pm$  $0.8 \text{ kJmol}^{-1}$  and for the reverse reaction to  $\Delta G^{\#}_{300} = 55.5 \pm$ 2.1 kJ mol<sup>-1</sup>. The P–Si  $\pi$  bond energy of a phosphasilene can therefore be estimated for the first time on the basis of the experimental data. The value of  $\Delta G^{\#}_{347} \approx 64 \text{ kJ mol}^{-1}$ obtained from the coalescence of the  $^{31}$ P NMR signals of E/ Z-5b at 347 K roughly confirms these results and is only marginally larger than the calculated value for predominantly ylidic and therefore single-bonded phosphasilenes with nitrogen donors at the silicon end of the P=Si bond recently reported by the Driess group.<sup>[18]</sup>

Single crystals of *E*-**5a** were obtained from pentane. An X-ray diffraction study confirms the constitution of a phosphasilene with dimethylamino groups bonded to phosphorus and  $\beta$ -silicon, respectively (Figure 2).<sup>[22]</sup> The P1=Si2 bond distance of 2.1187(7) Å is fairly typical for phosphasilenes. The tricoordinate Si2 is slightly pyramidalized (sum of angles



*Figure 2.* Structure of *E*-**5a** in the solid state (ellipsoids set at 50% probability, H atoms, co-crystallized pentane and disordered *i*Pr groups omitted). Selected bond lengths [Å]: Si2–P1 2.1187(7), Si1–Si2 2.3895(7), P1–N1 1.6872(18), Si1–N2 1.7399(16).

Si2: 358.85°), thus further confirming the "inverse polarization" of the P1=Si2 bond. This is in line with the planarization of both NMe<sub>2</sub> groups by an apparent electron donation of the lone pairs to the adjacent phosphorus and silicon atoms (sum of angles: N1 359.5°, N2 359.5°).

The synthesis of stable 1-aza-3-phosphaallenes is usually achieved by either intra- or intermolecular elimination of disiloxanes or silanolates, respectively.<sup>[35]</sup> We reasoned that the presence of a potentially mobile amino functionality as the sole functionality at phosphorus might turn the phosphasilene 5a into a suitable phosphinidene equivalent (PR) that could be combined with isonitriles to afford a 1-aza-3phosphaallene without any systematically formed by-product. Indeed, treatment of 5a with one equivalent of tert-butyl isonitrile leads to full conversion into the 1-aza-3-phosphaallene 6a after heating to 55°C in toluene overnight, which was isolated a pale yellow crystals from toluene in 77 % yield. The constitution of 6a was deduced by multinuclear NMR analysis. Although 1-aza-3-phosphaallenes are typically observed between about -140 to -60 ppm<sup>[35]</sup> in <sup>31</sup>P NMR spectra, the resonance of **6a** at  $\delta = -214.5$  ppm is in line with a hitherto unknown P-silyl substituted derivative. Although the coupling constant of  ${}^{1}J_{PSi} = 91.2$  Hz to the  $\alpha$ -silicon atom suggests single bonding, the <sup>13</sup>C signal at  $\delta = 173.3$  ppm with  ${}^{1}J_{PC} = 87.0 \text{ Hz}$  is in a typical range for the fairly ylidic phosphaallene scaffold.

The molecular structure of 6a in the solid state confirmed the structural assignment (Figure 3).<sup>[22]</sup> Compared to the



*Figure 3.* Molecular structure of **6a** in the solid state (ellipsoids set at 50% probability, H atoms and disordered *i*Pr groups omitted). Selected bond lengths [Å]: N3–C51 1.471(2), N3–C50 1.195(3), P1–C50 1.6739(19), Si2–P1 2.2934(7), Si2–N2 1.7357(17), Si1–Si2 2.5011(6).

crystallographically characterized 1-aza-3-phosphaallene reported by Yoshifuji's group (Mes\*P=C=NPh (7); Mes\* =  $tBu_3C_6H_2$ ),<sup>[35d]</sup> the P1–C50 bond distance is slightly elongated (1.6739(19) for **6a** vs. 1.651 Å for **7**) and the angle at the phosphorus center significantly more acute (95.86(7)° for **6a** vs. 99.2° for **7**). In contrast, the C50–N3 bond is somewhat shorter (1.195(3) for **6a** vs. 1.209 Å for **7**) and the angle at the imino nitrogen atom closer to linearity (142.0(2)° for **6a** vs. 130.5° for **7**). These cumulative findings suggest a significant ylidic contribution to the ground state of **6a** along the lines of R–P–C=N+*t*Bu (R = disilanyl moiety).

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In conclusion, we have demonstrated that with sufficiently small amino substituents at phosphorus, phosphasilenes are favored over isomeric phosphino disilenes. The amino groups are rather mobile in this system and therefore addition of an isonitrile as relatively strong donor induces the shift of the second amino group from phosphorus (**5a**) to silicon (**6a**), affording a 1-aza-3-phosphaallene in a novel by-product free approach to a heterocumulene. Along with this kinetic argument, the gradual strengthening of the double bonds from Si=Si via Si=P to P=C is without doubt an important contributor to the increasing thermodynamic stability. Investigations concerning the scope of this reactivity as well as further manipulations of the residual functionality are currently in progress.

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