Main-Group Chemistry

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# A Compound with a Si–C Triple Bond**

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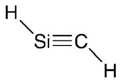
carbenes · main-group elements · multiple bonds · organosilicon compounds

Despite the impressive progress made in the last decade in the chemistry of multiple-bonded main-group compounds, triple bonds between carbon and its heavier homologues still have the touch of unattainability.[1] Efforts to synthesize stable or even only persistent compounds that feature an E–C triple bond (E = Si, Ge, Sn, Pb) face several principal obstacles. On the one hand, there is the essential reluctance of the heavier elements to engage in multiple bonds. As a result only relatively weak π bonds with small HOMO/LUMO energy differences are formed and consequently these compounds show extreme reactivity towards addition reactions and nucleophilic and electrophilic attack. This problem has been solved for compounds containing homonuclear E≡E bonds by using extremely bulky substituents. In addition, heteroleptic E≡E′ bonds are always polarized owing to the different electronegativity of the constituent atoms. Because of the relative high electronegativity of carbon, the polarization of the triple bond is extreme for carbynes, RE≡CR′. This further increases the reactivity of these compounds and severely complicates their synthesis and isolation.

All recent high-level calculations of the [CSiH$_2$] potential energy surface predict that the classical linear silyne **1**, the analogue of acetylene, is not at an energy minimum, but that a second-order Jahn–Teller distortion forces it into a *trans* bent structure **2**.[2] This parallels the situation found for disilynes, RSi≡SiR. The results of the calculations, however, reveal a second important aspect: Silyne **2** is thermodynamically and kinetically unstable, and undergoes unimolecular isomerization to silavinylidene **3**. Specifically, *trans* bent silyne **2** is less stable than monocoordinated silylene **3** by 143 kJ mol$^{-1}$ and the barrier for the 1,2-H shift which converts **2** into **3**, is rather small, merely 21 kJ mol$^{-1}$ (at CCSD(T)TZ2P(fd)//CCSD(T)/TZ2P + ZPVE).[3] These data for silyne **2** and similar results for substituted silynes suggest that compounds with the general topology XSiCY will not be isolable entities at ambient temperature. The equilibrium between silynes **4** and silavinylidenes **5** is, however, strongly dependent on the substituent X. For example, because of the strong SiF bond HC≡SiF (**4**(F)) is more stable than HFC=Si: (**5**(F)) by 44 kJ mol$^{-1}$ and the barrier separating the two isomers is 104 kJ mol$^{-1}$ (at QCISD(T)/6-31G(d,p)).

$H-Si\equiv C-H$

**1**



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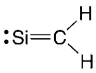

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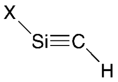

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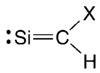
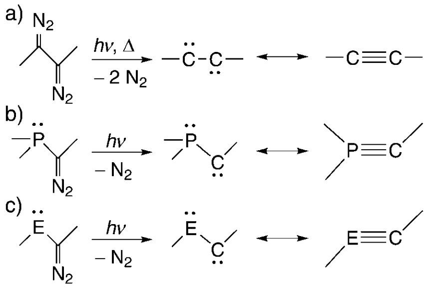


**5**

Based on these theoretical predictions Apeloig, Schwarz, and co-workers detected and identified the small silynes $HC\equiv SiX$ (X = Cl, F) in neutralization–reionization mass-spectrometric experiments, and demonstrated their existence as isolated molecules under high-vacuum conditions on a microsecond timescale.[4b] However, since then all attempts to synthesize silynes having larger substituents on a preparative scale, to isolate them, and to study their properties and their chemistry have failed. All the more important is the recent report from the team of Kato and Baceiredo from Toulouse University on the isolation and characterization of silyne **6**, which is stable up to temperatures of −30 °C.[5] The synthesis of silyne **6** followed the principle ideas that were already applied in the preparation of strained cycloalkynes and dates back to the finding by Curtius that alkynes are formed by photolysis of α-bisdiazoalkanes (Scheme 1 a).[6] This synthesis strategy was ingeniously transferred to main-group chemistry by Bertrand and co-workers in their landmark synthesis of λ$^3$-phosphinylcarbenes from α-diazophosphines.[7] The phosphinylcarbenes have substantial P–C multiple-bond character as expressed by the λ$^5$-phosphaalkyne representation (Scheme 1 b). The transfer of this reaction mode to heavy Group 14 elements (Scheme 1 c) seems to be straightforward, in partic-



*Scheme 1.* Photolysis of diazo compounds to give alkynes and heteroalkynes (E = Si, Ge, Sn, Pb).

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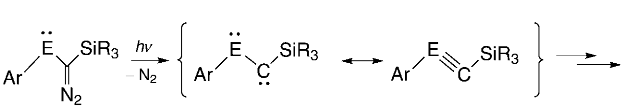
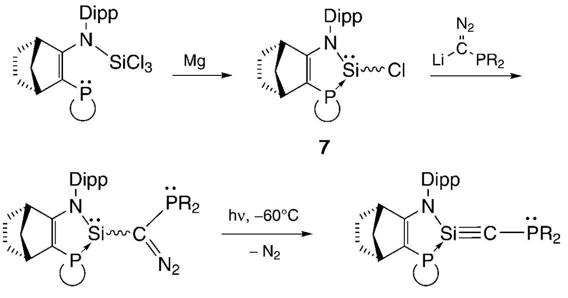
ular for germanium and tin: for these elements stable dicoordinated compounds REX (with X groups susceptible to substitution, for example in salt metathesis reactions) have been known for several years. Consequently, in 2001 the Couret group[8] and three years later Sakamoto, Kira, and coworkers[9] provided evidence for short-lived germynes and stannynes that form during photolysis of the corresponding methyldiazo compounds (Scheme 2). In both cases only



***Scheme 2.*** Synthesis of short-lived germyne (E = Ge) and stannyne (E = Sn) by photolysis of diazomethylgermylenes and -stannylenes (Ar = 2,6-bis-(dialkylamino)phenyl, 2,4,6-bis(triisopropylphenyl)phenyl; R = Me, *i*Pr).

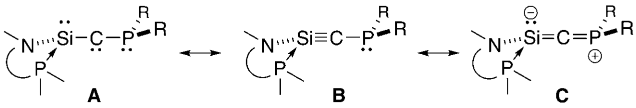
trapping products, either from intermolecular (E = Ge) or intramolecular follow-up reactions (E = Sn) were isolated. Photolysis experiments at 77 K in a methylpentane matrix indicated that the stannyne persists under these conditions and laser flash photolysis experiments suggested a lifetime of approximately 50 ms at room temperature.[9]

In the case of silicon the synthesis of the intramolecular phosphanyl-stabilized chlorosilylene **7** paved the way for the preparation of silyne **6** (Scheme 3).[5] Further functionalization of silylene **7** to give diazomethylsilylene **8** and its photolysis at −60 °C gave the dark red silyne **6** in 68 % yield. Is compound **6** a genuine silyne or are the canonical representations **A** and **C** (Scheme 4) of importance? At temperatures higher than −30 °C the compound is unstable; that is, the diisopropylamino group migrates from the phosphorus to the carbon atom. It reacts with *tert*-butylisocyanide to form a ketenimine. These are typical reactions for singlet carbenes; however, no information about the characteristic reactivity of compounds with a Si–C triple bond is available. In addition, the reaction of a disilyne with isocyanide to give a silaketimine was also reported.[10] More revealing is certainly the molecular structure of compound **6** as obtained by X-ray diffraction analysis. The most remarkable feature is the very short Si–C bond of 166.7 pm, which is somewhat shorter than the Si=C double bond in silene $H_2Si{=}CH_2$ (170.4 pm)[2b] and similar to the value predicted by ab initio calculations for silyne **2** (166.5 pm)[3] and suggested from a recent compilation of self-consistent covalent radii for a Si–C triple bond (162 pm).[11]



***Scheme 3.*** Synthesis of silyne **6** (Dipp = 2,6-diisopropylphenyl, P⊃: P(N*t*Bu)$_2$SiMe$_2$), R = N*i*Pr$_2$).

The strongly bent NSiC group (α(NSiC) = 128.5° vs. 123.9° calculated for α(HSiC) in **2**) is also predicted by theory. The coordination around the central carbon atom is almost linear (α(SiCP) = 178.2°), as would commonly be expected for an alkyne analogue. However, this linearity around the carbon atom is rather unusual considering the theoretical reference structure (α(SiCH) = 149.5° predicted for **2**). In addition the small C–P distance (168.2 pm) indicates multiple-bond character for this bond as well. While the molecular structure of compound **6** does not support the carbene Lewis structure **A**, it is consistent with contributions from the silyne-like representation **B** (Scheme 4) and the cumulenic structure **C**. The latter indicates electron donation from the lone pair at the phosphorus atom to the π* orbital of the Si–C bond. A complete description of the bonding in this intriguing compound clearly requires further theoretical investigation. In particular an evaluation of the effects of the P and N substituents on the structure of the Si–C linkage and on its energy relative to the isomeric silavinylidene is needed.



***Scheme 4.*** Possible canonical representations for silyne **6**.

Even if future investigations reveal that silyne **6** is a special case owing to its particular substitution pattern, its synthesis, isolation, and structural characterization are a milestone in organosilicon chemistry. Several research teams reported recently the synthesis of isolable and storable silicon(II) compounds with the potential for further functionalization.[12] If the synthetic approach to silynes established by the Toulouse group proves to be general and can be applied to other stable silicon(II) compounds, the synthesis of silyne **6** will certainly mark the opening of a new chapter in the book of organosilicon chemistry.

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[1] Recent review: R. C. Fischer, P. P. Power, *Chem. Rev.* **2010**, *110*, 3877.

[2] a) M. Karni, Y. Apeloig in *The Chemistry of Organosilicon Compounds*, *Vol. 3* (Eds.: Z. Rappoport, Y. Apeloig), Wiley, Chichester, **2001**, p. 1; b) S. Bailleux, M. Bogey, J. Breidung, H. Bürger, R. Fajgar, Y. Liu, J. Pola, M. Senzlober, W. Thiel, *Angew. Chem.* **1996**, *108*, 2683; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2513.

[3] R. Stegmann, G. Frenking, *J. Comput. Chem.* **1996**, *17*, 781.

[4] a) Y. Apeloig, M. Karni, *Organometallics* **1997**, *16*, 310; b) M. Karni, Y. Apeloig, D. Schröder, W. Zummack, R. Rabezzana, H.

Schwarz, *Angew. Chem.* **1999**, *111*, 343–347; *Angew. Chem. Int. Ed. Engl.* **1999**, *38*, 331–335.

[5] D. Gau, T. Kato, N. Saffon-Merceron, A. De Cózar, F. P. Cossío, A. Baceiredo, *Angew. Chem.* **2010**, 122, 6735–6738; *Angew. Chem. Int. Ed.* **2010**, 49, 6585–6588.

[6] a) G. Wittig, *Angew. Chem.* **1962**, *74*, 479; *Angew. Chem. Int. Ed.* **1962**, *1*, 415; b) A. Krebs, H. Kimling, *Angew. Chem.* **1971**, *83*, 540; *Angew. Chem. Int. Ed. Engl.* **1971**, *10*, 509; c) T. Curtius, R. J. Kastner, *J. Prakt. Chem.* **1911**, *83*, 215.

[7] J. Vignolle, X. Cattoën, D. Bourissou, *Chem. Rev.* **2009**, *109*, 3333.

[8] C. Bibal, S. Mazières, H. Gornitzka, C. Couret, *Angew. Chem.* **2001**, *113*, 978; *Angew. Chem. Int. Ed.* **2001**, *40*, 952.

[9] W. Setaka, K. Hirai, H. Tomioka, K. Sakamoto, M. Kira, *J. Am. Chem. Soc.* **2004**, *126*, 2696.

[10] K. Takeuchi, M. Ichinohe, A. Sekiguchi, *J. Am. Chem. Soc.* **2008**, *130*, 16848.

[11] P. Pyykkö, M. Atsumi, *Chem. Eur. J.* **2009**, *15*, 12770.

[12] a) R. S. Ghadwal, H. W. Roesky, S. Merkel, J. Henn, D. Stalke, *Angew. Chem.* **2009**, *121*, 5793–5796; *Angew. Chem. Int. Ed.* **2009**, *48*, 5683–5686; b) A. C. Filippou, O. Chernov, G. Schnakenburg, *Angew. Chem.* **2009**, *121*, 5797–5800; *Angew. Chem. Int. Ed.* **2009**, *48*, 5687–5690; c) A. C. Filippou, B. Blom, O. Chernov, K. W. Stumpf, G. Schnakenburg, *Chem. Eur. J.* **2010**, *16*, 2866; d) C. Gerdes, T. Müller, *Angew. Chem.* **2010**, *122*, 4978–4981; *Angew. Chem. Int. Ed.* **2010**, *49*, 4860–4862.