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Si=Si Double Bonds

Reversible Base Coordination to a Disilene**

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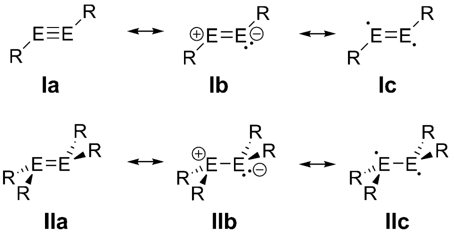
Dedicated to Prof. Theophil Eicher on occasion of his 80th birthday

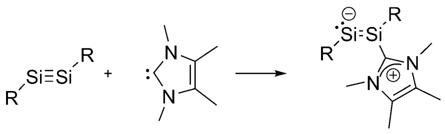
During the last few decades, alkene and alkyne analogues of the heavier Group 14 elements have attracted considerable interest. Their isolation as stable derivatives has become possible by the use of carefully designed bulky substituents that provide kinetic (and to some extent thermodynamic) stabilization. The considerable differences in structure, bonding, and reactivity of such compounds in comparison to the carbon-based species have prompted various experimental and theoretical studies.[1–4] By and large, the lower electronegativity of heavier elements and the increasing spatial extension of their valence electron shells are responsible for many of these differences.[5] One of several rationalizations for structure and reactivity of such doubly and triply bonded species is based on zwitterionic (**Ib** and **IIb** in Scheme 1) and diradical contributions (**Ic** and **IIc** in Scheme 1) to the ground state structures, which illustrate both the weakness and the *trans*-bent structure of heavier multiple bonds. Such contributions are, however, more prominent in compounds of germanium, tin, and lead, and less pronounced in compounds of silicon.[1–4]



Scheme 1. Zwitterionic and diradical contributions to RE≡ER and $R_2E{=}ER_2$ (E = Si, Ge, Sn, Pb; R = sterically demanding substituent).

Conversely, heteronuclear silicon multiple bonds, in particular those involving chalcogen atoms, are inherently polar owing to the differences in electronegativity. The strong ylidic contribution to the ground-state structure becomes apparent by facile base coordination to the positively polarized silicon atom.[6] Similarly, silylenes as the formal constituents of the Si=Si bond are readily coordinated by various bases owing to their vacant p orbital.[7]

In marked contrast, the first experimentally observed example showing the importance of polar contributions (**Ib** in Scheme 1) in species with a homonuclear Si≡Si triple bond was reported only very recently.[8] Reaction of the disilyne **1** with the N-heterocyclic carbene (NHC) 1,3,4,5-tetramethylimidazol-2-ylidene irreversibly afforded the corresponding polar disilyne–NHC complex **2** with *trans* geometry of the remaining Si=Si moiety and a lone pair of electrons residing on the dicoordinate silicon atom (Scheme 2).



1 **2**

Scheme 2. R = Si*i*Pr[CH(SiMe$_3$)$_2$]$_2$.

Despite a plethora of fully characterized disilenes,[9] no disilene–NHC adduct analogous to **2** has been reported to date. Herein, we describe the reversible formation and isolation of a Lewis acid–base adduct between a disilene and an NHC and thus demonstrate experimentally the importance of polar contributions to the electronic structure of Si=Si double bonds (**IIb** in Scheme 1). Reaction of cyclotrisilene **3** with 1,3-di(isopropyl)-4,5-dimethylimidazol-2-ylidene leads to the formation of the cyclotrisilene–NHC complex **4** by nucleophilic attack of the carbene carbon atom at the Cp*-substituted silicon atom of the Si=Si bond. (Scheme 3).

Previously, only cyclotrisilenes with silyl groups, *cyclo*-$Si_3(SiR_3)_4$, have been reported, by the groups of Kira and Sekiguchi.[10–12] For the synthesis of **3**,[13] the first cyclotrisilene with carbon-based substituents (Cp* = C_5Me_5; Tip = 2,4,6-$iPr_3C_6H_2$), we developed a novel synthetic strategy. Reaction of the silicon(II) tetrakis(pentafluorophenyl)borate **5**[14] with the lithium disilenide **6**[15] in DME at −65 °C visibly resulted in

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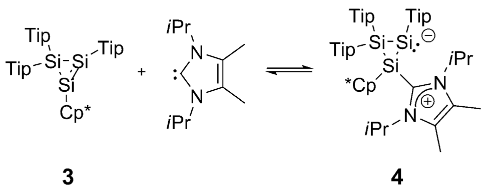
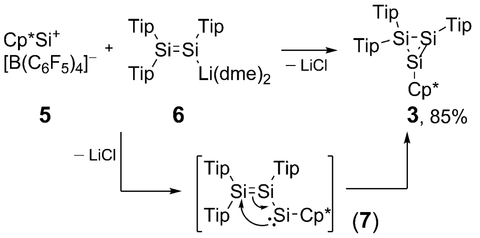


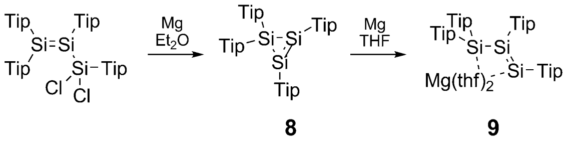
Scheme 3. Tip = 2,4,6-$iPr_3C_6H_2$.



Scheme 4. Tip = 2,4,6-$iPr_3C_6H_2$; DME = 1,2-dimethoxyethane.

salt elimination to produce a mixture containing 85 % of **3** (Scheme 4). Formation of **3** is readily explained by intramolecular attack of the Si^{II} center of a transient silylene species **7** at the β-silicon atom of the double bond. This step is followed by the cyclic rearrangement of the electrons in the Si_3 fragment and the change of the coordination mode of the Cp* system. To a small extent, the tetrasilabutadiene Si_4Tip_6,[16] decamethyl silicocene,[17] and elemental silicon were detected as byproducts. Apparently, competing electron transfer processes generate radical fragments that subsequently homocouple. The latter two products would thus be produced by disproportionation of transient $Cp^*_2Si_2$.[18] Si_4Tip_6 and Cp^*_2Si were separated for the most part by crystallization from hexane solution. The cyclotrisilene was finally obtained as an orange-brown oil, still containing some residual contamination (see the Supporting Information). Compound **3** was characterized by ^{29}Si, ^{1}H, and ^{13}C NMR spectroscopy and derivatization to NHC complex **4**.

To validate the general applicability of the new synthetic procedure and for corroboration of the structural assignment of cyclotrisilene **3** by means of comparison, we have also prepared the first fully aryl-substituted cyclotrisilene **8**. On the basis of the successful synthesis of **3**, we concluded that **8** might occur as an intermediate of the previously reported synthesis of the magnesium salt of a trisilendiide **9**.[19] Indeed, the use of Et_2O as a solvent instead of THF during the reduction of the dichlorosilyl disilene precursor with magnesium powder halts the reaction at the stage of neutral species **8** (Scheme 5). Cyclotrisilene **8** was isolated as orange crystals from a concentrated pentane solution in 51 % yield (mp. 150–151 °C) and characterized by multinuclear NMR spectroscopy.



Scheme 5. Tip = 2,4,6-$iPr_3C_6H_2$; THF = tetrahydrofuran.

The molecular structure of **8** based on X-ray crystal structure analysis confirmed the constitution of a cyclotrisilene (Figure 1, Table 1).[13] An apparent disorder of the central Si_3 ring was ignored owing to the relatively low intensity of residual electron density peaks. Despite the resulting less-than-ideal refinement, an acceptable bond precision allows a cautious discussion of bond parameters. The Si1=Si2 bond (2.1182(12) Å) is at the short end of Si=Si double bonds. The deviation of the Tip substituents from the Si_3 plane is small, as illustrated by the sums of angles about Si1 (359.45°) and Si2 (359.98°).

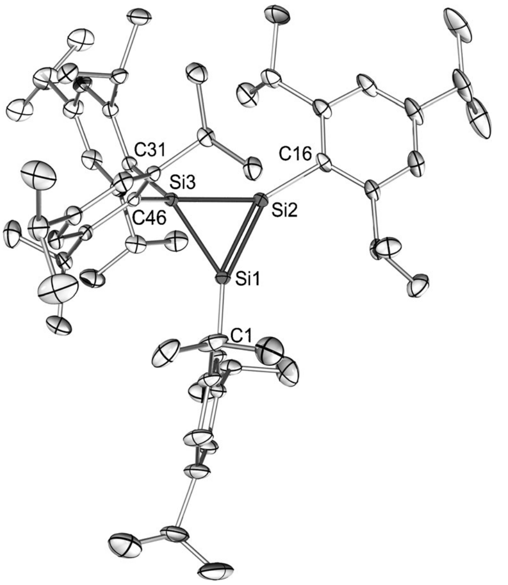


Figure 1. Molecular structure of **8** in the solid state. Ellipsoids are set at 30 % probability; hydrogen atoms are omitted for clarity.[13]

Table 1: Comparison of structural parameters for **4** and **8** (X-ray data) and **3 Dip** and **4 Dip** (B3LYP/6-31G(d)).[20]

	3 Dip	**8**	**4**	**4 Dip**
Si1−Si2 [Å]	2.1336	2.118(1)	2.2700(5)	2.2839
Si1−Si3 [Å]	2.3370	2.289(1)	2.4332(5)	2.4882
Si2−Si3 [Å]	2.3539	2.289(1)	2.3389(5)	2.3504
Si1−$C_{\alpha/ipso}$ [Å]	1.9619	1.880(3)	1.992(1)	2.0425
Si1−C_β	2.7264/ 2.7792	n/a	2.857(1)/ 2.906(1)	2.9224/ 2.9804
C-Si1-Si2-C [°]	−12.37	9.07	−86.54(7)	−83.97
Σ angles Si1 [°]	358.91	359.46	317.0	314.5
Σ angles Si2 [°]	360.00	359.98	340.2	345.4

Compared to the silyl-substituted cyclotrisilenes,[10–12] the ^{29}Si NMR signals of the unsaturated silicon atoms of **3** and **8** are observed significantly upfield (Table 2), which is in line with the general observations for open-chained disilenes.[9] Unlike most unsymmetrically substituted Si=Si double bonds,[21,22] however, the downfield resonance of **3** is observed for the silicon atom with the less electronegative substituent (Cp*). From the NMR spectra of **3**, it is concluded that the

Table 2: Comparison of the NMR data of **3**, **8**, and **4** with the data calculated for **3 Dip**.[a]

$\delta^{29}Si/^{13}C$	3	3 Dip	4	8
$SiAr_2$	−15.3	3.3	−85.9	−23.2
SiAr	37.1	51.8	−61.5	42.5
SiCp* or SiAr	57.7	92.6	−85.6	42.5
NCN	–	–	161.4	–

[a] NMR spectroscopy for **3** ([D_{10}]-1,2-dimethoxyethane, 298 K, Ar = Tip), **8** ([D_6]benzene, 293 K, Ar = Tip), and **4** ([D_8]toluene, 298 K, Ar = Tip); calculations for **3 Dip** with Ar = Dip = 2,6-iPr$_2$C$_6$H$_3$ (B3LYP/6-311 + G-(2df) on Si, 6-31G(d) on C,H).[20]

Cp* substituent shows fast exchange processes at ambient temperature. Such sigmatropic rearrangements of cyclopentadienyl silanes have been investigated in detail previously.[23]

With the purpose of clarifying the influence of the Cp* ligand on the Si=Si double bond in the absence of an experimental solid-state structure, calculations of the model system **3 Dip** (Dip = 2,6-iPr$_2$C$_6$H$_3$ instead of Tip) were performed at the B3LYP/6-31G(d) level of theory (Figure 2, Table 2).[20] The trends in the ^{29}Si NMR shifts of **3** are well-reproduced in the calculated data for **3 Dip** (B3LYP/6-311 + G(2df) on Si; 6-31G(d) on C,H), lending support to the validity of the model. Similarly to **8** and the persilyl-substituted cyclotrisilenes,[10–12] the Si1=Si2 bond (2.1336 Å) in the fully optimized structure of **3 Dip** is relatively short. The sums of the bond angles at the respective silicon atoms indicate slight pyramidalization of the Cp*-substituted Si1 atom (358.91), while the coordination environment of Si2 with the Dip group is perfectly planar (360.00°). In general, unsymmetrical substitution patterns in open-chained disilenes lead to a more pronounced pyramidalization of the silicon atom with the more electropositive substituents and thus a partial negative charge at this atom (resonance structure **3′** in Scheme 6).[22] In the case of **3** and **3 Dip**, however, despite the slightly pyramidal Si1 atom, the Mullikan atomic charges (Si1 +0.227, Si2 −0.012) in concert with the ^{29}Si NMR data suggest the reverse polarization of the Si=Si double bond according to resonance structure **3″**.

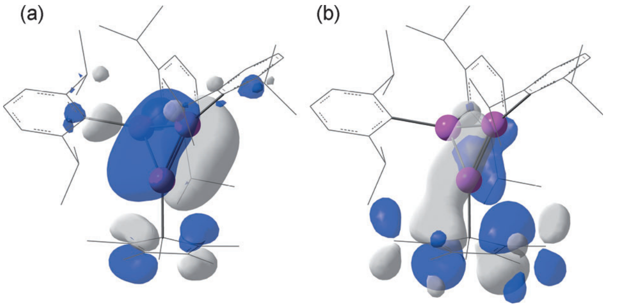
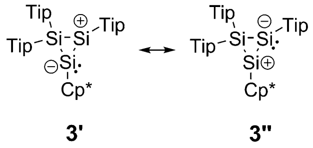


Figure 2. Contour plots of a) HOMO and b) HOMO−1 of **3 Dip** at an isovalue of 0.03.[20]

Closer analysis of the distances between the Cp* carbon atoms and Si1 in **3 Dip** reveals weak contacts to the β-carbon atoms (2.7264 and 2.7792 Å). Indeed, the topologies of the HOMO (Figure 2a) and HOMO−1 (Figure 2b) formally result from the antibonding and bonding linear combination of the Si=Si π orbital with a π orbital of the Cp* ligand. The resulting weak π donation approximates a η^3 coordination mode and apparently stabilizes a partial positive charge at Si1.



Scheme 6. Tip = 2,4,6-iPr$_3$C$_6$H$_2$.

To further probe the polarization of the Si=Si bond experimentally, we treated **3** with an N-heterocyclic carbene as a strong σ donor. Addition of a hexane solution of the NHC 1,3-di(isopropyl)-4,5-dimethylimidazol-2-ylidene to a hexane solution of **3** at −20 °C resulted in an immediate color change to deep red caused by the formation of the 1:1 adduct **4** (Scheme 3), which was isolated as red crystals in 48 % yield and characterized by elemental analysis, X-ray crystallography, and multinuclear NMR spectroscopy (see the Supporting Information).

The molecular structure of **4** in the solid state as determined by X-ray diffraction on single crystals (Figure 3, Table 1)[13] reveals NHC coordination by the carbenic carbon atom to the Si=Si bond of **3**. The coordination site is the Cp*-substituted silicon atom, which is in line with reversed polarity discussed above. The NHC ligand and the Tip substituent are positioned at the same side of the Si$_3$ ring plane. The newly formed donor–acceptor bond, however, appears to be relatively weak: the Si−C(NHC) bond distance (1.9843(14) Å) is significantly longer than the corresponding one in the adduct **2** (1.9221(16) Å)[8] and in the formal Si(0) compound NHC−Si=Si−NHC (1.9271(15) Å).[24] The Si1−Si2 bond (2.2700(5) Å) is longer than the Si=Si double bond in **3**

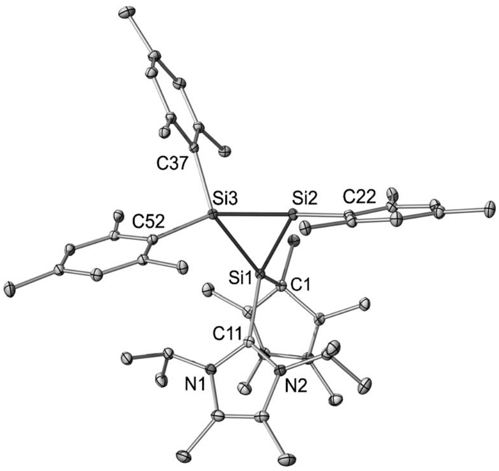


Figure 3. Molecular structure of **4** in the solid state. Ellipsoids are set at 30% probability; hydrogen atoms and methyl groups of the Tip substituents are omitted for clarity.[13]

(calc. 2.13362 Å), as expected, but remains shorter than Si–Si bonds in Tip substituted cyclotrisilanes.[25] Coordination of the carbene results in strong pyramidalization of both silicon atoms, Si1 and Si2, as seen by the sum of angles (ignoring the Si–C bond between cyclotrisilene and NHC): 317° at Si1 and 340° at Si2. As a consequence, the electron pair at Si2 acquires a strongly non-bonding character. Furthermore, the weak η^3-like interaction of the Cp* ligand with the adjacent silicon atom is cancelled upon NHC-coordination, as shown by the increased distances between silicon and the Cp* β-carbon atoms. For adequate comparison with **3Dip**, the structure of **4Dip** was fully optimized, and it shows elongation of the distances in question by approximately 0.2 Å (Table 1).[20]

The coordination of the NHC to the cyclotrisilene **3** causes an upfield shift for all of the ^{29}Si signals of **4**, which were unambiguously assigned by ^{1}H/^{29}Si 2D NMR spectroscopy (Table 2). The ^{13}C chemical shift of the carbene center of **4** at $\delta = 161.4$ ppm is shifted by $\Delta\delta = 44.5$ ppm with respect to the free NHC ($\delta^{13}\text{C} = 205.7$ ppm[26]). A similar upfield ^{13}C shift had been observed by Sekiguchi et al. for the coordinated NHC in **2**.[8] Unlike in the case of **2**, however, complex formation is reversible, as VT-NMR studies show that **4** dissociates in solution (Scheme 3). Although **3** and **4** thus coexist at room temperature in comparable concentrations, only signals for the adduct **4** are observed at 223 K. The enthalpy of the dissociation process at 298 K is estimated at $\Delta G \approx 9\ \text{kJ}\,\text{mol}^{-1}$ (see the Supporting Information).

Reversibility of individual reaction steps is a prerequisite for the experimental realization of catalytic cycles, for example in small-molecule activation. Heavier main-group systems are attracting increasing interest as potential replacement for transition-metal systems.[3] Herein, we have shown that a strong base, namely an N-heterocyclic carbene, reversibly coordinates the Si=Si double bond of a cyclotrisilene. We are currently exploring how the formation of such donor–acceptor complexes influences the reactivity of cyclotrisilenes, and disilenes in general, in this regard.

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Keywords: donor–acceptor interactions · multiple bonds · reversibility · silicon · small rings

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[13] An Experimental Section, including crystallographic details, is supplied in the Supporting Information. CCDC 869292 (**4**) and 872266 (**8**) contain 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.
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[20] Theoretical calculations were carried out with the Gaussian 09, Revision A.02. Geometry optimization and IR frequencies were at the B3LYP/6-31G(d) level of theory. NMR spectroscopy shifts were obtained using a polarizable continuum model for benzene and with an expanded basis set (6-311+G(2df) for Si, 6-31G(d) for C and H). Details have been deposited and can be retrieved free of charge at http://dx.doi.org/ under the following identifiers: 10042/to-8287 (frequencies, **3Dip**); 10042/to-8286 (NMR, **3Dip**); 10042/to-8290 (frequencies, **4Dip**).
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