Angewandte Communications

Silicon Double Bonds

DOI: 10.1002/anie.201209281

Reversible, Complete Cleavage of Si=Si Double Bonds by Isocyanide Insertion**

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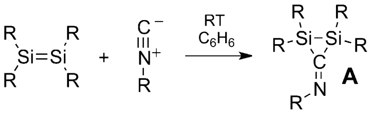
Since the discovery of the first stable compound with Si=Si double bond, tetramesityldisilene ($Mes_2Si=SiMes_2$, Mes = 2,4,6-trimethylphenyl) by West, Michl, and Fink,[1] numerous disilenes have been reported and their reactivity studied.[2] For instance, even in the absence of catalysts the Si=Si bond of disilenes readily adds various reagents, such as alcohols, alkenes, alkynes, carbonyl compounds, and dienes.[2,3]

Isocyanides ($R-N\equiv C$) serve as versatile building blocks in organic synthesis and as ligands in metal complex chemistry.[4] They undergo facile [2+1] cycloadditions with different dipolarophiles.[5] In view of the inherently dipolar nature of the Si=Si bond,[6] the reaction of disilenes with isocyanides appears to be particularly promising for the preparation of extended systems incorporating unsaturated or cyclic silicon-based repeat units. To date, however, only two reports of such reactivity are available: West et al. reported the reaction of tetra(2,6-dimethylphenyl)disilene with 2,6-dimethylphenylisocyanide at room temperature to form disilacyclopropanimine **A** (Scheme 1).[7] A similar [2+1] cycloaddition of isocyanide with R*PhSi=SiPhR* (R* = SitBu$_3$) was reported by Wiberg et al.[3b]

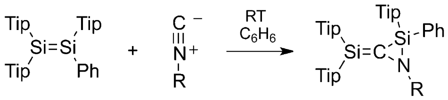


Scheme 1. The disilacyclopropanamine **A** from West et al. ($R = 2,6\text{-}Me_2C_6H_3$).

In the case of silicon–silicon triple-bonded systems, Sekiguchi et al. recently reported the reaction of a disilyne with *tert*-butylisocyanide or 1,1,3,3-tetramethylbutylisocyanide to produce disilyne–isocyanide adducts $[(R'NC)_2RSiSiR]$ ($R = Si\textit{i}Pr[CH(SiMe_3)_2]_2$, $R' = t$Bu or CMe_2CH_2tBu) that are stable at −30 °C but decompose to the corresponding 1,2-dicyano disilenes at room temperature.[8] The heavier Group 14 element homologues, digermyne Ar′GeGeAr′ and distannyne Ar′SnSnAr′ ($Ar' = 2,6\text{-}(2,6\text{-}iPr_2C_6H_3)_2C_6H_3$), exhibited similar reactivity with *tert*-butyl or mesityl isocyanide to afford the mono or bis adducts,[9] in the case of distannyne in a reversible fashion.[10] Isocyanide complexes of silylenes display two bonding extremes. They form silylene–isocyanide Lewis adducts with very bulky substituents;[11] however, a heterocumulene structure has been reported with less-bulky substituents.[12]

Notably, up to now all reactivity studies of the multiply bonded heavier Group 14 elements with isocyanides have revolved around symmetrically substituted double or triple bonds, which is presumably due to the synthetically more challenging access to unsymmetrical substitution patterns.[13] Earlier, we established a facile method for the multiple transfer of Si=Si moieties to aromatic substrates and thus the synthesis of unsymmetrical disilenes, including phenyl disilene **1** as well as phenylene-bridged tetrasiladienes.[14]

Herein, we report the surprising reactivity of isocyanides towards unsymmetrically substituted (and thus somewhat polar) disilenes to yield silaaziridines **2a–c** with exocyclic Si=C double bonds (Scheme 2; Tip = 2,4,6-isopropylphenyl). The reaction is akin to the formation of silaaziridines with exocyclic C=C bond from isocyanides and inherently polar silenes,[15] but in marked contrast to the previously reported reactivity of symmetrical disilenes.[3b,7] Notably, the process of complete cleavage of the Si=Si bond to form **2a–c** is reversible inasmuch as the disilene starting material **1** is regenerated upon addition of large excess of BEt_3 as isocyanide scavenging reagent. Compounds **2a–c** were characterized by multinuclear NMR spectroscopy and, in the case of **2a**, also by X-ray crystallography.



1 **2a-c**

Scheme 2. Reaction of **1** with isocyanides, yielding silenes **2a–c** ($Tip = 2,4,6\text{-}iPr_3C_6H_2$; R = tBu (**a**), CMe_2CH_2tBu (**b**), $2,6\text{-}Me_2C_6H_3$ (**c**)).

Reaction of the unsymmetrical phenyl disilene **1** with *tert*-butyl isocyanide in 1:1 ratio in benzene at room temperature yields compound **2a** almost quantitatively,[16] which was crystallized from pentane as bright orange crystals in 85% yield (m.p. 65–67 °C). The ^{29}Si NMR spectrum has two peaks at $\delta = -4.4$ and -80.2 ppm. The peak at $\delta = -4.4$ ppm is attributed to the Si = C silicon atom, at much higher field than in case of most previously reported silenes, suggesting an inversely polarized Si=C bond.[17] The ^{13}C NMR signal of the Si=C moiety, however, is observed at relatively high field as

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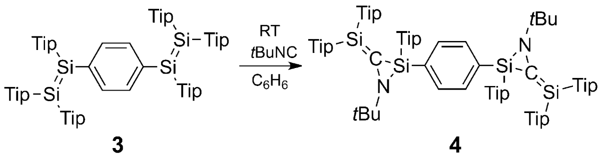
[**] Funding by the EPSRC (EP/H048804/1) and the Alfried Krupp Foundation is gratefully acknowledged.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201209281.

well ($\delta = 144.15$ ppm), which is a likely consequence of the incorporation into the three-membered ring. Significantly high-field shifted signals for both atoms of the Si=C unit had also been observed in case of a stable 4-silatriafulvene.[18] UV/Vis spectroscopy of **2a** in hexane revealed the longest wavelength absorption at $\lambda_{max} = 397$ nm ($\varepsilon = 9620\ \mathrm{L\,mol^{-1}\,cm^{-1}}$).

In analogous fashion, reaction with *tert*-octyl isocyanide gives **2b**, which was characterized by NMR spectroscopy, in quantitative yield. Conversely, according to the ^{29}Si NMR spectrum, reaction of **1** with the aromatic xylyl isocyanide yields **2c** ($\delta = 2.5$ and -75.7 ppm) only as part of a mixture with unidentified byproducts (see the Supporting Information).[16] In an effort to shed light on the diverging reactivity of isocyanides towards symmetrically substituted disilenes,[7] we treated $Tip_2Si{=}SiTip_2$[19] with one equivalent of *t*BuNC in [D$_6$]benzene. No reaction was observed by NMR spectroscopy even after heating to 75 °C for 16 h. Apparently, the steric congestion in the homoleptic disilene with four Tip substituents is too high to allow for the attack of the isocyanide. In view of the aforementioned results of West et al. regarding tetra(2,6-dimethylphenyl)disilene,[7] however, it is reasonable to assume that the steric discrimination in phenyl disilene **1** is in part responsible for the observed rearranged isocyanide addition product **2a**.

To check the suitability of this new reaction mode for the preparation of extended conjugated systems containing more than one Si=C unit, we treated *para*-phenylene-bridged **3** with two equivalents of *t*BuNC. As anticipated, we obtained **4** with two silaaziridine units comprising exocyclic Si=C bonds (Scheme 3).[16] The ^{29}Si NMR signals of the reaction mixture at $\delta = -1.3$, -6.9, -80.3, and -80.6 ppm suggest the formation of a pair of diastereomers in an approximate 1.2:1 ratio. The ^{13}C NMR signals of the two Si=C units appears at $\delta = 144.27$ and 143.78 ppm at very similar field as in the case of **2a** confirming the expected formation of **4**. Crystallization at room temperature from benzene led to the isolation of the racemic mixture with *R*,*R*- and *S*,*S*-configuration in 56 % yield (δ^{29}Si NMR -6.9 and -80.3 ppm; δ^{13}C = 144.27 ppm (Si=C)). UV/Vis spectra in hexane shows an absorption at $\lambda_{max} = 398$ nm ($\varepsilon = 15{,}700\ \mathrm{L\,mol^{-1}\,cm^{-1}}$) and a shoulder at 477 nm ($\varepsilon = 5410\ \mathrm{L\,mol^{-1}\,cm^{-1}}$).



Scheme 3. Reaction of *para*-phenylene-bridged tetrasiladiene **3** with *tert*-butylisocyanide.

The structure of **2a** in the solid state was determined by X-ray diffraction on single crystal obtained from pentane at room temperature (Figure 1).[16] The exocyclic silicon atom, Si2, is substituted with two Tip groups, while the silicon atom of the silaaziridine ring, Si1, features one phenyl and one Tip group as substituents. The endocyclic ring angles at Si1, C01, and N1 are 47.48(9), 62.61(12), and 69.91(11)°, respectively, reflecting the larger covalent radius of silicon. The Si2=C01 bond distance is 1.735(2) Å, which is at the short end of values found for donor-substituted silenes.[20] Although the presence of π-donating nitrogen atom at the carbon center is predicted to elongate the Si=C bond,[21] the electronegative aryl groups at Si can be expected to overcompensate for this effect.[22] Nonetheless, the sum of bond angles ΣSi2 = 355.85(18)° is indicative of slight pyramidalization, as had previously only been demonstrated in case of a cyclic Brook-type silene.[23] The twist angle around Si2=C01 with $\tau = 14.61(12)$° confirms the distortion from the classical double-bond geometry.

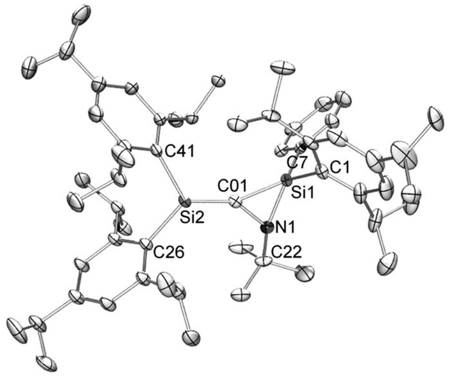


Figure 1. Structure of **2a** in the solid state (ellipsoids set at 30% probability). Hydrogen atoms, solvent molecules, and disorder in isopropyl groups omitted for clarity. Selected bond lengths [Å]: Si2–C01 1.735(2), Si1–C01 1.835(2), Si1–N1 1.735(2), C01–N1 1.440(3).

Despite repeated efforts, only relatively poor quality crystals of one diastereomer of **4** could be obtained by crystallization from benzene solution at room temperature. Although the X-ray diffraction study leaves no doubt about the constitution as the *R*,*R*- and *S*,*S*-racemic mixture (Figure 2),[16] the bond precision is limited. The Si2−C50 and Si4−C103 distances of the two Si=C bonds are 1.743(4) and 1.726(4) Å, respectively, as obtained after the less-than-ideal final refinement, and hence similar to the bond parameters found in **2a**.

Silenes **2a–c** are stable at room temperature in the absence of air and moisture. Heating of **2a** in C_6D_6 for 12 hours in a sealed NMR tube at 65 °C, however, led to the

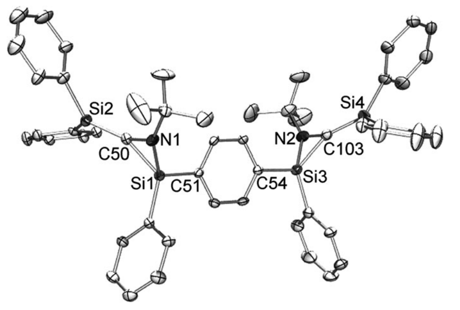


Figure 2. Structure of **4** in the solid state (ellipsoids set at 30% probability). Hydrogen atoms, solvent molecules, and isopropyl groups of the Tip substituents omitted for clarity. Selected bond lengths [Å]: Si2–C50 1.743(4), Si1–C50 1.820(4), N1–C50 1.419(5), Si1–N1 1.707(3), Si1–C51 1.839(4), Si4–C103 1.726(4), Si3–C103 1.808(4), N2–C103 1.425(5), Si3–N2 1.705(4), Si3–C54 1.856(4).

regeneration of phenyl disilene **1** in low yield (18 %), along with the formation of unidentified products. The principal reversibility of the reaction thus demonstrated, we speculated that the side-products arise from the reaction of liberated isocyanide with remaining **2a** under these conditions. This prompted us to investigate whether Lewis acids could trap isocyanide and thus shift the equilibrium to the disilene side at lower temperatures. Indeed, addition of excess triethylborane as Lewis acid to **2a** at room temperature leads to slow conversion to phenyl disilene **1** in 91 % NMR yield in 10 days. The regeneration is accelerated upon heating overnight at 65 °C and hence phenyl disilene was cleanly obtained in 96 % yield (according to NMR spectroscopy). Appearance of peaks at $\delta = 7.51$ and 13.27 ppm in the ^{11}B NMR spectrum strongly suggests the formation of $Et_3B{-}CN$*t*Bu and its decomposition products.[24] Among silenes **2a–c**, compound **2c** is more prone to the elimination of isocyanide. When **2c** is heated overnight at 65 °C, free phenyl disilene **1** is formed in 30 % yield (NMR spectroscopy; **2a**: 18 %; see the Supporting Information).[16] The aniline-like conjugation of the nitrogen lone pair with the aromatic xylyl substituent might be responsible for this increased reversibility.

To elucidate the potential of silenes of type **2** to engage in extended conjugation, DFT calculations were performed on a truncated model system **2aDip** (Dip = 2,6-iPr$_2$C$_6$H$_3$ instead of Tip in **2a**) at the B3LYP/6-31G(d,p) level of theory.[25] Figure 3 shows the optimized geometry, which reproduces the experimental data of **2a** reasonably well. Mulliken charge distribution analysis of **2aDip** shows charges of +0.28 at the silicon and −0.10 at the carbon of the Si=C moiety, indicating slight reverse polarization as asserted on the basis of the solid-state structure of **2a**. The experimental ^{29}Si NMR shifts of **2a** agree satisfactorily with those calculated for the model compound **2aDip** (exp. $\delta = -4.4$ and −80.2 ppm; $\delta = 18.1$ and −76.8 ppm at GIAO/6-311+G(2df) for Si and 6-31G-(d,p) for C, N and H). The calculated ^{13}C NMR chemical shift value of Si=C at $\delta = 158.8$ ppm is, however, only a qualitative match with the experimental value of $\delta = 144.15$ ppm.

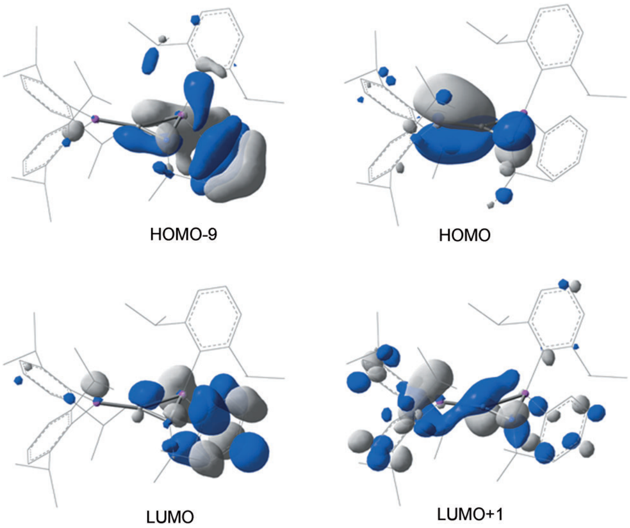


Figure 3. Relevant contour plots of **2aDip** at an isovalue of 0.04 au.

The UV/Vis spectrum of **2aDip** simulated by TD-DFT shows the most intense absorption peak at $\lambda = 422$ nm (HOMO→LUMO+1, $f = 0.1086$) to correspond to the $\pi_{Si=C}$ to $\pi^*_{Si=C}$ transition, which is reasonably close to the experimental value of 397 nm. The pronounced red-shift in comparison to most silenes[20] is attributed to the antibonding interaction of the Si=C π-bond with the nitrogen p-type lone pair, which appears to be more prominent in the HOMO than in the LUMO+1 and therefore accounts for the decreased energy gap between these orbitals (Figure 3). In marked contrast to previously reported silenes,[20] TD-DFT reveals an additional transition at longer wavelength (486 nm, HOMO→LUMO, $f = 0.0477$). The LUMO is related to LUMO+1 inasmuch that it also features a certain $\pi^*_{Si=C}$ character, but is mainly located on the phenyl group. Furthermore, it shows a significant stabilizing contribution by antibonding Walsh-type orbitals at the silaaziridine moiety (Figure 4), suggesting an unusual case of the conjugative interaction that is common in cyclopropane chemistry.[26]

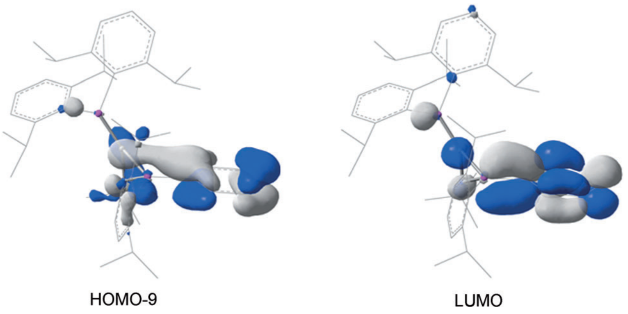


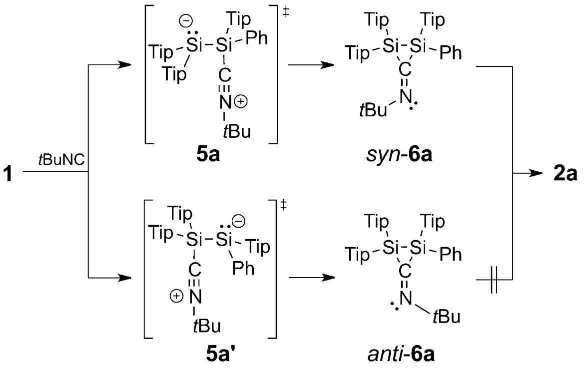
Figure 4. Contour plots of the HOMO−9 and the LUMO of **2aDip** in an orientation showing interaction of Walsh-type with p-type orbitals (isovalue 0.04 au).

The shape of HOMO−9 demonstrates that this interaction is not restricted to the frontier orbitals. In the experimental absorption spectrum, the peak corresponding to the HOMO→LUMO transition apparently merges with the more intense band at $\lambda_{max} = 397$ nm, but at lower concentrations of **2a** it can be perceived as a barely discernible shoulder at $\lambda \approx 450$ nm.

TD-DFT calculations on **4Ph** (a truncated version of the experimental structure of **4** with Ph instead of Tip) yield numerous states with absorption wavelengths between $\lambda =$ 425 and 386 nm that comprise contributions from the $\pi_{Si=C} \rightarrow \pi^*_{Si=C}$ transitions. More importantly, longer wavelength absorptions at $\lambda = 557$ and 538 nm (HOMO→LUMO and HOMO−1→LUMO, $f = 0.1065$ and 0.0266) are predicted that correspond to transitions from the $\pi_{Si=C}$ bonds to the LUMO, which is almost exclusively formed from quinoid π-orbitals of the phenylene bridge and Walsh-type orbitals at the silicon atoms of the silaaziridine rings (see the Supporting Information). Compared to **2aDip**, this constitutes a red-shift of at least $\Delta\lambda = 52$ nm and as such provides an illustrative example of the conjugative interaction of Walsh-type orbitals via a bridging π-system. In the experimental case, the red-shift of the longest-wavelength transition is slightly less pronounced: phenylene-bridged **4** features a prominent shoulder at $\lambda \approx 477$ nm in accordance with the frequently observed underestimation[14a,27] of the HOMO–LUMO gap in conjugated systems of silicon by the B3LYP functional.

In view of the fundamentally different behavior of **1** compared with the simple [2+1] cycloaddition of an isocyanide to a disilene,[7] we attempted to detect possible primary addition products at low temperature. The ^{13}C NMR spectrum of a 1:1 mixture of phenyl disilene **1** and *t*BuNC in [D$_8$]toluene at 213 K shows the appearance of at least three distinct peaks around $\delta = 200$ ppm and thus much closer to that reported for **A** than to the corresponding signal of **2a** (**A**: $\delta = 214.0$ ppm;[7] **2a**: $\delta = 144.15$ ppm; see the Supporting Information). These low-field signals suggested the initial formation of isomers of disilaaziridines akin to **A**. Accordingly, in the ^{29}Si NMR, three pairs of signals appear that show some further splitting, which is presumably due to the presence of a large number of discernible rotamers at 213 K. Upon warming to 243 K, the ^{29}Si spectrum simplifies to one major product with sharp signals at $\delta = -53.9$ and -79.9 ppm, and two minor products in an approximate 2:1 ratio at $\delta = -54.6$ and -61.9 ppm as well as $\delta = -57.9$ and -62.8 ppm, respectively. The major product is the least stable in view of the complete disappearance of the signals at the low- and high-field ends of the ^{29}Si NMR spectrum upon an increase in the temperature to 273 K.

In accordance with theoretical predictions,[28,29] we assume that a donor–acceptor complex such as **5a** (or the related **5a′**) is probably not a detectable intermediate in the reaction of **2a** with *t*BuNC, but rather a transition state (Scheme 4). This is in contrast to the recently reported case of the reversible adduct formation between a cyclotrisilene and an *N*-heterocyclic carbene.[6] A donor–acceptor type complex analogous to **5a** had also been suggested as a transition state of the reaction of Brook's silene with isocyanides.[15,29] Indeed, the optimizations of the model systems **5aDip** and **5aDip′** at the B3LYP/6-31G(d,p) level of theory converge to the two conceivable stereoisomers of a West-type isocyanide adduct, *syn*- and *anti*-**6aDip** (see the Supporting Info). For the assignment of the experimentally observed species, we calculated the ^{29}Si NMR shifts of both isomers (*syn*-**6aDip**: $\delta = -41.4$ and -56.6 ppm; *anti*-**6aDip** $\delta = -46.4$ and -81.76 ppm at GIAO/6-311+G(2df) for Si and 6-31G(d,p) for C, N and H). On this basis, the thermally least stable signals at -53.9 and -79.9 ppm could be assigned to *anti*-**6a**, featuring a stereochemistry that is unsuitable for isomerization to **2a**. The two pairs of signals at $\delta = -54.6$ and -61.9 ppm, -57.9 and -62.8 ppm are tentatively attributed to two unspecified rotational isomers of *syn*-**6a** due to the similarity of chemical shifts with the computed values for *syn*-**6aDip**. Finally, as the interconversion between rotational isomers becomes fast on the NMR timescale at 273 K, the aforementioned two pairs of signals collapse and isomerization sets in to **2a** as the only detectable product at room temperature.



Scheme 4. Proposed reaction mechanism for the formation of silenes of type **2**.

The formation of cyclic silenes from the reaction of disilenides with vinyl bromides or carboxylic acid chlorides was previously reported by us and Sekiguchi's group in a collaborative effort.[23,30] Independently, Sekiguchi et al. have demonstrated the formation of silenes from a disilenide and ketones in a Brook-type rearrangement.[31] In this work, we presented the formation of an Si=C moiety from a neutral disilene by reaction with isocyanides. The complete, reversible rupture of the Si=Si moiety is instructive for the development of new synthetic strategies towards double bonds between heavier elements in general and Si=Si bonds in particular. The analogous clean conversion of conjugated phenylene-bridged tetrasiladienes with *tert*-butyl isocyanide reveals significant potential in polymer chemistry concerning the use of silaaziridine repeat units with pronounced conjugative interactions of Walsh-type orbitals.

Received: November 20, 2012

Keywords: disilenes · insertion reactions · isocyanides · reversibility · silenes

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[16] Experimental details and NMR spectra are supplied in the Supporting Information. CCDC 907680 (**2a**) and 907681 (**4**) 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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