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Reaction of a Base-Stabilized Bis(silylene) [PhC(N*t*Bu)$_2$Si]$_2$ with Cyclooctatetraene without Cleavage of the Si–Si Bond

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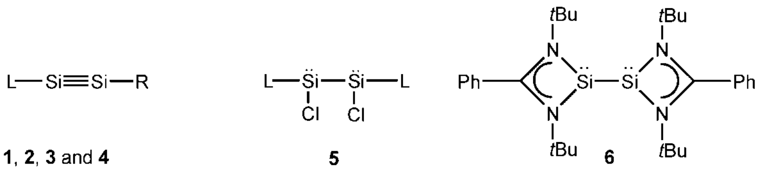
The reaction of the benzamidinato-stabilized bis(silylene) [PhC(N*t*Bu)$_2$Si]$_2$ with cyclooctatetraene resulted in the formation of a colorless compound **7** whithout cleavage of the Si–Si bond of the bis(silylene), whereas one of each Si–N(ligand) bond is opened. Compound **7** was characterized by single-crystal X-ray diffraction, NMR spectroscopy, EI mass spectrometry, and elemental analysis. Investigation of the molecular structure shows that the Si–Si bond length in **7** is 2.4150(7) Å and is comparable to that of **6** [2.413(2) Å].

Introduction

Recently, numerous species with multiple bonds containing heavier group 14 elements have been isolated and characterized.[1] In particular, considerable interest has been focused on the nature of the alkyne analogues of silicon owing to their unusual structures and bonding since the isolation of stable disilyne [LSi≡SiL; L = Si(*i*Pr){CH(SiMe$_3$)$_2$}$_2$ (**1**), SiMe(Si*t*Bu$_3$)$_2$ (**2**)] by Sekiguchi et al. and Wiberg et al., respectively.[2] Later, Tokitoh's group reported an aryl-substituted disilyne supported by the bulky Bbt ligand {Bbt = 2,6-[CH(SiMe$_3$)$_2$]$_2$-4-C(SiMe$_3$)$_3$-C$_6$H$_2$} (**3**),[3] and very recently Sekiguchi et al. published the first unsymmetrically substituted disilyne LSi≡SiR (**4**) [L = Si(*i*Pr){CH(SiMe$_3$)$_2$}$_2$, R = (CH$_2$*t*Bu){CH(SiMe$_3$)$_2$}$_2$].[4] Parallel to this, Robinson et al. and our group independently reported two compounds LSi(Cl)Si(Cl)L (**5**) [L = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene][5a] and LSi–SiL (**6**) [L = PhC(N*t*Bu)$_2$][5b] with an Si–Si covalent single bond and a lone pair of electrons on each silicon atom. These two compounds can be termed as bis(silylene) and are valence isomers of disilyne. Therefore, a comparison of the chemical behavior of disilyne and bis(silylene) is of special interest (Scheme 1).

In contrast to the versatile reactivities of disilynes,[6] the chemistry of bis(silylenes) is at its infancy. The nature of the Si–Si bond has been theoretically investigated,[7a] which indicates that bis(silylenes) are very reactive due to the presence of two lone pairs and one reactive Si–Si bond. Recently, we examined the reactions of **6** with benzophenone, benzil, and N$_2$O, which afforded the formation of interesting silicon-containing heterocycles.[7b,7c] These reactions are thermodynamically favorable due to the oxidation of Si from the monovalent to the tetravalent state. Another interesting observation was the cleavage of the central Si–Si bond in almost every reaction, except in the reaction with benzil. Moreover, the reaction of **6** with phenylethyne yielded 1,4-bis(silylene),[8a] whereas the reaction with diphenylethyne led to the formation of the hitherto unknown 1,4-disilabenzene.[8b] As usual, in these two reactions the Si–Si bond was also cleaved. From these observations, reac-



1, **2**, **3** and **4** **5** **6**

1: L = R = Si(*i*Pr){CH(SiMe$_3$)$_2$}$_2$ L = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene
2: L = R = SiMe(Si*t*Bu$_3$)$_2$
3: L = R = 2,6-[CH(SiMe$_3$)$_2$]$_2$-4-C(SiMe$_3$)$_3$-C$_6$H$_2$
4: L = Si(*i*Pr){CH(SiMe$_3$)$_2$}$_2$
R = Si(CH$_2$*t*Bu){CH(SiMe$_3$)$_2$}$_2$

Scheme 1. Structures of compounds **1**–**6**.

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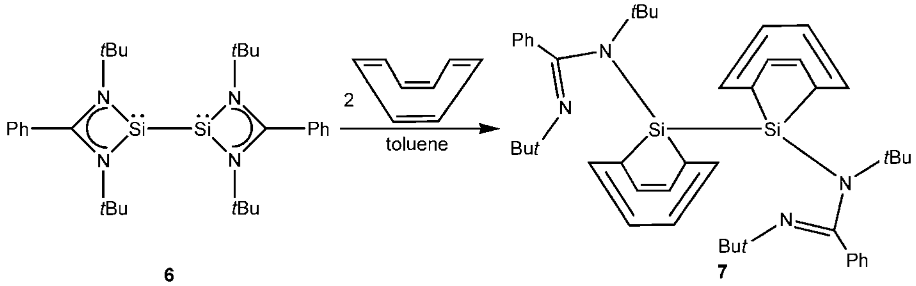
tions without cleavage of the Si–Si bond appeared to be less plausible. Anyhow, all these results indicate that compound **6** is a new and promising building block for silicon chemistry. So it is of interest to study its chemistry with some cyclic polyolefinic molecules. Among these cyclic polyolefins cyclooctatetraene (COT) has emerged as a potential functional group, and COT-bridged molecules are known for f- and s-block elements, whereas transition-metal analogues isolated to date display olefinic or "semi-aromatic" COT character.[9] Very recently, Power et al. reported the formation of the inverse π-bound sandwich complex $[(Ar'Sn)_2(\mu\text{-}\eta^2{:}\eta^3\text{-COT})]$ $[Ar' = C_6H_3\text{-}2,6\text{-}(C_6H_3\text{-}2,6\text{-}iPr_2)_2]$ by treating Ar′SnSnAr′ with COT at ambient temperature.[10a] Following this, the same group has described the reaction of digermyne with COT, which afforded two isomeric products: (a) Ge^{II} inverse sandwich complex as a kinetic product and (b) a tetracyclic dienedigermane as a thermodynamic product.[10b] All these results prompted us to study the reaction of COT with **6**. The question arises whether it will give a [1+2] or [1+4] cycloaddition product and whether the central Si–Si bond will remain unchanged during the reaction.

Result and Discussion

Addition of COT to **6** in a 2:1 ratio in toluene at room temperature resulted in an immediate color change from dark red to pale yellow. The reaction mixture was stirred for 10 min, and the solvent was removed under vacuum. The residue was recrystallized from toluene in 57% yield (**7**, Scheme 2) as a [1+4] cycloaddition product.[11] Formation of the same product was observed irrespective of the molar ratio of the reaction partners. Compound **7** is soluble in diethyl ether, toluene, and THF.

The composition and constitution of **7** were confirmed by single-crystal X-ray diffraction studies. Compound **7** crystallizes in the monoclinic space group $P2_1/c$,[12] with a center of symmetry passing through the center of the Si–Si bond. Selected bond lengths and angles are provided in the caption of Figure 1. The most apparent feature of the structure is the stable Si–Si bond during the reaction, whereas one of the Si–N bonds from each ligand fragment is opened. Evidence for this behavior comes from the Si(1)–N(1) interatomic separation (2.695 Å) which conclusively indicates that there is not even a weak interaction between Si(1) and N(1). This observation was further supported by different C–N bonds [C(1)–N(1) 1.2835(17) Å, vs. C(1)–N(2) 1.4049(16) Å] in the benzamidinato fragments in **7**. The cleavage of Si–N bonds was also observed when monochlorosilylene was treated with COT.[13] The length of the new Si–Si bond [2.4150(7) Å] is almost the same as that of **6** [2.413(2) Å],[5b] although there is a shortening of the Si–Si bond [2.3628(7) Å] in bis(siladioxolene).[7c] Here it must be noted that the geometries of N(1) and N(2) are also different. N(2) displays a distorted tetrahedral geometry, whereas N(1) adopts a distorted trigonal-planar geometry



Scheme 2. Preparation of **7**.

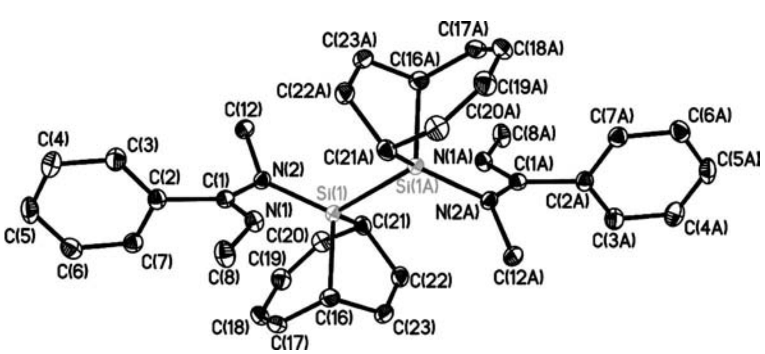


Figure 1. Molecular structure of **7**. Hydrogen atoms and *t*Bu groups are omitted for clarity. Selected bond lengths [Å] and angles [°]: N(1)–C(1) 1.2835(17), N(2)–C(1) 1.4049(16), N(2)–Si(1) 1.7835(11), Si(1)–C(16) 1.9097(13), Si(1)–C(21) 1.9148(13), Si(1)–Si(1A) 2.4150(7), C(16)–C(17) 1.5076(19), C(16)–C(23) 1.5113(18), C(17)–C(18) 1.343(2), C(18)–C(19) 1.455(2), C(19)–C(20) 1.3437(19), C(20)–C(21) 1.5077(18), C(21)–C(22) 1.5146(18), C(22)–C(23) 1.327(2); C(1)–N(2)–Si(1) 111.34(8), C(12)–N(2)–Si(1) 126.27(8), N(2)–Si(1)–C(16) 112.07(5), N(2)–Si(1)–C(21) 113.51(5), C(16)–Si(1)–C(21) 89.43(6), N(2)–Si(1)–Si(1)#1 119.32(4), C(16)–Si(1)–Si(1)#1 113.09(4), C(21)–Si(1)–Si(1)#1 105.28(4).

considering the lone pair of electrons. Both COT rings have lost their planar geometry exhibiting different C–C and C=C bonds. In the crystalline state the five-membered moieties of the Si–COT units of **7** are facing each other. Both silicon atoms are four-coordinate and adopt a distorted tetrahedral geometry. Two of the four sites of the silicon atom are occupied by two carbon atoms C(16) and C(21) of the COT ring. The two other sites are connected with nitrogen atom N(2) of the amidinato ligand and the second Si atom. The Si–C(COT) bond lengths are similar [1.9097(13), 1.9148(13) Å] and match well the Si–C single bond lengths reported in the literature.[7b,14] The Si(1)–N(2) bond length is 1.7835(11) Å, which is quite longer than those in Me_2N-$SiCl_3$ [1.665(3) Å] and Me_2NSiMe_3 [1.719(1) Å].[15] This demonstrates its dependence on the nature of the substituents at the silicon atom but unequivocally indicates that the Si–N bonds are single bonds. So, the reaction of **6** with COT is distinct from previous studies with unsaturated systems due to the unchanged central Si–Si bond and the formation of the acyclic benzamidinato ligands.

The composition and constitution of **7** derived from X-ray crystallography is further confirmed by multinuclear NMR spectroscopy, EI mass spectrometry, and elemental analysis. The ^1H NMR spectrum exhibits two sharp singlets for the *t*Bu protons (δ = 1.14 and 1.21 ppm). This is due to the presence of the two chemically different *t*Bu groups. The resonances at δ = 3.15 and 5.45–5.90 ppm correspond to four C*H* and twelve C*H*=C protons, respectively. In the ^{29}Si NMR spectrum a sharp resonance at δ = 3.57 ppm is in accordance with a four-coordinate silicon atom.[8b] A similar resonance in the ^{29}Si NMR spectrum was observed (δ = –9.49 ppm) when chlorosilylene was treated with COT.[13] The low-field shift is due to the replacement of the Cl atom by the LSi unit. In the EI mass spectrum the molecular ion peak was observed at *m*/*z* (%) = 726 (100) [M^+]. All these data are in accordance with the proposed formulation of **7**.

Conclusions

We have demonstrated the reaction of base-stabilized bis(silylene) with COT. The unique feature of this reaction is the unchanged Si–Si bond of **7** compared to that of **6**. Product **7** was characterized by ^1H, ^{13}C, and ^{29}Si NMR spectroscopy, EI mass spectrometry, elemental analysis, and single-crystal X-ray diffraction studies. The driving force of this unique reaction is likely the enthalpy change during the oxidation of Si^I in **6** to Si^{III} in **7**. We are currently exploring other reactivities of **6**, and the results will be published in due course.

Experimental Section

General: All manipulations were carried out under dinitrogen by using standard Schlenk techniques and in a dinitrogen-filled glove box. The solvents used were purified by a MBRAUN solvent purification system MB SPS-800. Compound **6** was prepared according to a literature method.[5b] All chemicals purchased from Aldrich were used without further purification. ^1H, ^{13}C, and ^{29}Si NMR spectra were recorded in [D_8]toluene with a Bruker Avance DPX 200 or a Bruker Avance DRX 500 spectrometer. The chemical shifts δ are reported in ppm relative to $SiMe_4$ as external standard. EI mass spectra were obtained with a Finnigan MAT 8230 instrument. Elemental analyses were performed by the Institut für Anorganische Chemie, Universität Göttingen. The melting point was measured in a sealed glass tube with a Büchi B-540 melting point apparatus.

Preparation of 7: To a solution of **6** (0.10 g, 0.19 mmol) in toluene (25 mL) cyclooctatetraene (0.04 g, 0.38 mmol) was added through a syringe, resulting in an immediate color change from deep red to pale yellow. The solution was stirred for 10 min, reduced to ca. 5 mL under reduced pressure, and stored at room temperature for 2 d to afford colorless crystals of **7** (0.08 g, 57%). M.p. 120–125 °C. $C_{46}H_{62}N_4Si_2$ (726.45): calcd. C 75.98, H 8.59, N 7.70; found C 75.75, H 8.50, N 7.43. ^1H NMR (200 MHz, [D_8]toluene, 25 °C): δ = 1.14 (br., 18 H, *t*Bu), 1.21 (br., 18 H, *t*Bu), 3.15 (br., 4 H, C*H*), 5.45–5.90 (m, 12 H, C*H*=C), 6.88–7.04 (m, 10 H, Ph) ppm. ^{13}C NMR (125.75 MHz, [D_8]toluene, 25 °C): δ = 29.3 (C*Me*$_3$), 36.6 (*C*H), 54.5 (*C*Me$_3$), 125.8, 127.5, 128.0, 128.5, 128.9, 129.3, 135.9 (*Ph*), 164.6 (N*C*N) ppm. $^{29}Si\{^1H\}$ NMR (99.36 MHz, C_6D_6, 25 °C): δ = 3.57 ppm. EI-MS: *m*/*z*: 726 [M^+] (100%).

X-ray Crystallography: Data was collected from shock-cooled crystals, which were selected and mounted under nitrogen by using the X-TEMP2 device.[12a,12b] The data of **7** was measured by using a Bruker TXS-Mo rotating anode equipped with an APEX II detector on a D8 goniometer. The diffractometer was equipped with a low-temperature device and used Mo-K_α radiation (λ = 0.71073 Å). The data set was integrated with SAINT,[12c] and an empirical absorption with SADABS[12d] was applied. The structure was solved by direct methods (SHELXS) and refined against F^2 by using full-matrix least-squares methods of SHELXL.[12e] Crystallographic data for **7**: M_r = 727.18, monoclinic, space group $P2_1/c$, a = 10.6464(15), b = 14.560(2), c = 13.6522(19) Å, β = 105.197(2)°, V = 2042.2(5) Å^3, Z = 2, $\rho_{calcd.}$ = 1.183 g/cm^3, μ (Mo-K_α) = 0.124 mm^{-1}, θ = 1.98–26.53°, T = 100(2) K, $R1$ = 0.0331 [$I > 2\sigma(I)$], $wR2$ = 0.0882, data/restaints/parameter 4223/0/241. CCDC-807092 (**7**) contains 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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