Reaction of a Sterically Hindered Silylene with Isocyanides: The First Stable Silylene−Lewis Base Complexes

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Although there has been much interest recently in the Lewis acid behavior of diorganosilylenes and many silylene complexes with Lewis bases have been reported, they are too unstable to exist at ambient temperature and can be observed spectroscopically only in low-temperature matrices.[1-3] We now report the first isolation of stable silylene−Lewis base complexes by the reaction of a silylene with isocyanides.

We recently synthesized an extremely hindered disilene (**1**) bearing an efficient steric protection group, 2,4,6-tris[bis-(trimethylsilyl)methyl]phenyl (denoted as Tbt hereafter) and found that **1** is kinetically very stable but thermally labile to give the corresponding silylene **2** bearing bulky substituents under very mild conditions (Scheme 1).[4] This prompted us to examine the reaction of silylene **2** with bulky isocyanides which might lead to the isolation of stable products.[5]

When a THF or C_6D_6 solution of disilene **1** and an isocyanide substituted by 2,4,6-triisopropylphenyl (Tip) (**3a**), Tbt (**3b**), or 2,4,6-tri-*tert*-butylphenyl (Mes*) (**3c**),[6] was heated in a sealed tube at 60 °C for several minutes, the original orange solution turned blue-green (for **3a**), green-blue (for **3b**), or deep blue (for **3c**). After further heating at the same temperature for 2 h (for **3a**) or for 6 h (for **3b** and **3c**), the almost quantitative

Scheme 1

a: R = Tip; **b**: R = Tbt; **c**: R = Mes*
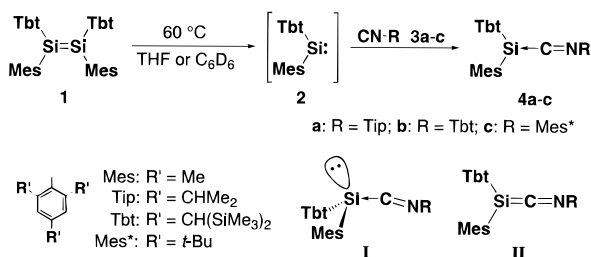
formation of the corresponding silylene−isocyanide adducts **4a**−**c** was confirmed by UV−vis and ^{1}H, ^{13}C, and ^{29}Si NMR spectra (Scheme 1 and Table 1).[9] The slow evaporation of the solvent from the reaction solution gave blue-green (for **4a**), green-blue (for **4b**), or deep blue (for **4c**) powder, but crystals of **4a**−**c** suitable for X-ray crystallographic analysis have not been obtained so far. The adducts **4a**−**c** are stable in solution at 60 °C for several hours, although they are highly sensitive to the air and moisture. The ^{29}Si NMR spectra of **4a**−**c** showed peaks at much higher field than those of a silaallene ($\delta = 48.4$)[10] and silenes ($\delta = 41$−144) bearing sp^2 silicon,[11] indicating that the Si−C bonds of the SiCN unit in **4a**−**c** were not doubly bonded. Almost the same [29]Si chemical shifts in THF as those in C_6D_6 (Table 1) suggest the absence of any interaction between **4a**−**c** and THF. The coupling constants in the Si−C bonds of the SiCN unit, $^1J_{SiC}$, were determined by ^{29}Si NMR spectra of the ^{13}C-labeled silylene−isocyanide adducts [^{13}C]**4a**−**c** which were prepared by the reaction of **2** with ^{13}C-labeled isocyanides, R−N[13]C, [^{13}C]**3a**−**c**, in C_6D_6.[12] The $^1J_{SiC}$ values for **4a**−**c** (Table 1) with the order of **4a** > **4b** > **4c** are smaller than the coupling constants for Si−C single bonds (50 Hz for Me$_4$Si)[13] and double bonds (83−85 Hz),[14] indicating that the Si−C bonds of the SiCN unit are considerably weak and their strength decreases in the order of **4a** > **4b** > **4c** with increasing bulkiness of the substituents. These spectroscopic results have revealed that **4a**−**c** is better described as a Lewis acid−base complex (**I**), not a cumulene (**II**).[15] The adducts **4a**−**c** represent the first examples of stable silylene−Lewis base complexes.

The experimental results were supported by the B3LYP/6-31G(d) calculations[17a] of Ph$_2$SiCNPh (Figure 1) which show clearly a silylene−Lewis base complex with a bent Si−C−N bond (163.4°), a long Si−C distance (1.882 Å) which is comparable with a Si−C single bond length (the average value of Si−C$_{sp}$, Si−C$_{ar}$, and Si−C$_{sp3}$ distances, 1.837, 1.868, and 1.863 Å),[18] a weak binding energy (25.1 kcal/mol),[19] and an sp^3-like hybridization at Si. The calculated chemical shifts of the Si and C atoms in the SiCN unit were −38.9 and 178.0

(1) (a) Ando, W.; Hagiwara, K.; Sekiguchi, A. *Organometallics* **1987**, *6*, 2270. (b) Gillette, G. R.; Noren, G. H.; West, R. *Organometallics* **1987**, *6*, 2617. (c) Ando, W.; Sekiguchi, A.; Hagiwara, K.; Sakakibara, A.; Yoshida, H. *Organometallics* **1988**, *7*, 558. (d) Gillette, G. R.; Noren, G. H.; West, R. *Organometallics* **1989**, *8*, 487. (e) Levin, G.; Das, P. K.; Bilgrien, C.; Lee, C. L. *Organometallics* **1989**, *8*, 1206. See also references cited in these papers.

(2) (a) Arrington, C. A.; Petty, T. J.; Payne, S. E.; Haskins, W. C. K. *J. Am. Chem. Soc.* **1988**, *110*, 6240. (b) Pearsall, M.-A.; West, R. *J. Am. Chem. Soc.* **1988**, *110*, 7228. (c) Tacke, M.; Klein, C.; Stufkens, D. J.; Oskam, A.; Jutzi, P.; Bunte, E. A. *Z. Anorg. Chem.* **1993**, *619*, 865.

(3) It has been reported that Me$_5$CpSiCO[2c] and Mes(*t*-Bu)Si−2-MeTHF[1b] adduct have a short lifetime in solution at −30 and −135 °C, respectively.

(4) (a) Tokitoh, N.; Suzuki, H.; Okazaki, R.; Ogawa, K. *J. Am. Chem. Soc.* **1993**, *115*, 10428. (b) Suzuki, H.; Tokitoh, N.; Okazaki, R.; Harada, J.; Ogawa, K.; Tomoda, S.; Goto, M. *Organometallics* **1995**, *14*, 1016. (c) Suzuki, H.; Tokitoh, N.; Okazaki, R. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 2471.

(5) Weidenbruch et al. have proposed the formation of silylene−isocyanide adducts as a transient intermediate in the reaction of di-*tert*-butylsilylene with some isocyanides, but no spectroscopic evidence was obtained. (a) Weidenbruch, M.; Brand-Roth, B.; Pohl, S.; Saak, W. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 90. (b) Weidenbruch, M.; Brand-Roth, B.; Pohl, S.; Saak, W. *Polyhedron* **1991**, *10*, 1147.
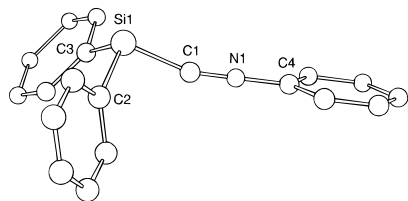
(6) Isocyanides **3a** and **3c** were prepared from the reported methods,[7] and Tbt−NC (**3b**) was synthesized by the reaction of Tbt−NHCHO with P(O)Cl$_3$ and *i*-Pr$_2$NH in CH$_2$Cl$_2$. The formamides, R−NHCHO (R = Tip, Tbt, Mes*), were synthesized by treatment of R−NH$_2$[8] with HCO$_2$COMe prepared from HCO$_2$H and (MeCO)$_2$O. For the details in the synthesis of formamides, see: Burgers, J.; Hoefnagel, M. A.; Verkade, P. E.; Visser, H.; Wepster, B. M. *Recl. Trav. Chim. Pays-Bas* **1958**, *77*, 491.

(7) (a) Obrecht, R.; Herrmann, R.; Ugi, I. *Synthesis* **1985**, 400. (b) Yamamoto, Y.; Aoki, K.; Yamazaki, H. *Inorg. Chem.* **1979**, *18*, 1681.

(8) Nishiyama, K.; Tanaka, N. *J. Chem. Soc., Chem. Commun.* **1983**, 1322.

(9) The spectral data for **4a**−**c** are detailed in the Supporting Information.

(10) Miracle, G. E.; Ball, J. L.; Powell, D. R.; West, R. *J. Am. Chem. Soc.* **1993**, *115*, 11598.

(11) Brook, A. G.; Brook, M. A. *Adv. Organomet. Chem.* **1996**, *39*, 71.

(12) A ^{13}C nuclide was introduced by the use of H[13]CO$_2$H in the synthesis of the corresponding formamides.

(13) Levy, G. C.; White, D. M.; Cargioli, J. D. *J. Magn. Reson.* **1972**, *8*, 290.

(14) Brook, A. G.; Abdesaken, F.; Gutekunst, G.; Plavac, N. *Organometallics* **1982**, *1*, 994.

(15) The reaction product of a silylene with carbon monoxide, which is isoelectronic to an isocyanide, has been proposed to be also a silylene−Lewis base adduct of type **I** by experiments[2b] and theoretical calculations.[16]

(16) (a) Hamilton, T. P.; Schaefer, H. F., III. *J. Chem. Phys.* **1989**, *90*, 1031. (b) Trinquier, G.; Malrieu, J.-P. *J. Am. Chem. Soc.* **1987**, *109*, 5303.

(17) (a) For the nonlocal hybrid density functional method, see: Beck, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) For a recent calibration of GIAO-B3LYP chemical shifts, see: Cheeseseman, J. R.; Trucks, G. W.; Keith, T. A.; Frisch, M. J. *J. Chem. Phys.* **1996**, *104*, 5497. All calculations were carried out using the Gaussian 94 program.

(18) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1.

(19) It is smaller than the value of 39.1 kcal/mol calculated for H$_2$SiCNH.[17a]

Table 1. Spectroscopic Data of Silylene−Isocyanide Complexes **4a**, **4b**, and **4c**

	$\delta_{Si}(SiCN)$			$\delta_C(SiCN)$ rt (C₆D₆)	$^1J_{SiC}(SiCN)$/Hz rt (C₆D₆)	λ(UV−vis)/nm rt (THF)
	rt (C₆D₆)	rt (THF)	60 °C (C₆D₆)			
4a, R = Tip	−53.6	−55.7	−53.2	209.2	38.6	596 (ϵ 400)
4b, R = Tbt	−57.4	−57.9	−56.5	196.6	22.1	397 (ϵ 3000)
						632 (ϵ 100)
4c, R = Mes*	−48.6	−48.9	−47.9	178.5	1.0	390 (ϵ 2000)
						671 (ϵ 200)

Figure 1. Optimized structure of Ph₂SiCNPh at the B3LYP/6-31G(d) level. Selective bond lengths (Å) and bond angles (deg): Si1−C1 1.882, Si1−C2 1.917, Si1−C3 1.920, C1−N1 1.180, N1−C4 1.372; C1−Si1−C2 99.7, C1−Si1−C3 99.1, C2−Si1−C3 108.0, Si1−C1−N1 163.4, C1−N1−C4 180.0.

Scheme 2
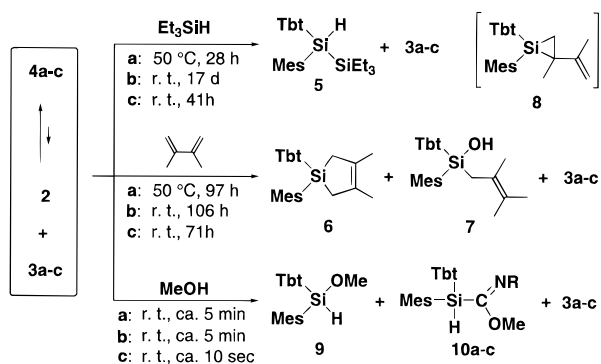
ppm, respectively, at the GIAO-B3LYP level (6-311G(3d) for Si and 6-311G(d) for C, N, and H).[17b] These are in good agreement with the experimental data.

The silylene−isocyanide complexes **4a−c** were stable for a long time in solution, but in the presence of triethylsilane, a silylene adduct (**5**) was obtained in the yields of 66, 86, and 69%, respectively, along with the corresponding isocyanides **3** (**a**, 42%; **b**, 94%; **c**, 98%) (Scheme 2). Reaction with 2,3-dimethyl-1,3-butadiene gave the corresponding isocyanides **3** (**a**, 58%; **b**, 92%; **c**, 100%), [1+4] adduct **6** with silylene **2** (**a**, 49%; **b**, 33%; **c**, 34%), and compound **7** (**a**, 15%; **b**, 39%; **c**, 47%), the formation of which was explained by hydrolysis of a [1+2] adduct (**8**) during separation. These results clearly indicate that **4a−c** dissociate into **2** and **3a−c** in solution and there exists an equilibrium among them. Grützmacher et al. have reported[20] that a stannaketenimine dissociates into the corresponding stannylene and isocyanide and that the variable-

(20) Grützmacher, H.; Freitag, S.; Herbst-Irmer, R.; Sheldrick, G. S. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 437.

temperature ¹¹⁷Sn NMR experiments show a low-field shift with increasing temperature owing to an increase of the ratio of the stannylene in the equilibrium mixture. In contrast, the ²⁹Si chemical shifts of **4a−c** at 60 °C were almost the same as those at room temperature. Moreover, the reaction of **2** with a small excess of **3a−c** resulted in the observation of separate signals of **3a−c** and **4a−c** in the ¹H and ¹³C NMR at room temperature. These findings indicate that the rate of the interconversion between **4a−c** and **2** plus **3a−c** is very slow and that the ratio of **2** in the equilibrium mixture is too small to be observed by NMR spectroscopy. In the above trapping reactions, the reaction rates became larger in the order of **4a** < **4b** < **4c** with increasing bulkiness of the substituents. This tendency can be explained by the fact that the larger the substituents, the larger the steric repulsion between the substituents and Tbt group, thus increasing the rate of the dissociation of **4a−c** into silylene **2**.

When the silylene−isocyanide complex **4a** was allowed to react with MeOH at room temperature in THF, the blue-green color of the solution disappeared immediately to give **9** (70%) and **10a** (7%) along with **3a** (54%). The extremely rapid formation of **9** and **10a** compared with the reactions with triethylsilane and 2,3-dimethyl-1,3-butadiene can be interpreted by the initial protonation by methanol to the silicon atom of **4a** followed by an attack of MeO⁻ (or MeOH) on the carbon or silicon in the SiCN unit. The former leads to the production of **10a**, while the latter results in the formation of **9**, which is likely to be partially formed also by the reaction of MeOH with silylene **2** generated by dissociation of **4a**. In the reaction of **4b** or **4c** with MeOH, **9** was obtained in the yield of 86 or 75%, respectively, together with **3** (**b**, 91%; **c**, 98%) without production of **10b** or **10c**. The sole formation of **9** is most likely due to the higher congestion of Tbt and Mes* groups than Tip group attached to the nitrogen atom which disturbs the attack of MeO⁻ (or MeOH) to the carbon atom in the SiCN unit.

Further investigations on the silylene−isocyanide complexes **4a−c** are in progress.

Supporting Information Available: Physical properties of the silylene−isocyanide complexes **4a−c** and MeOH adduct **10a** (2 pages). See any current masthead page for ordering and Internet access instructions.

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