6066 *Organometallics* **2004,** *23,* 6066−6069

Notes

Activation of a Si−Si Bond by Hypercoordination: Cleavage of a Disilane and Formation of a Si−C Bond

Jörg Wagler, Uwe Böhme, and Gerhard Roewer*

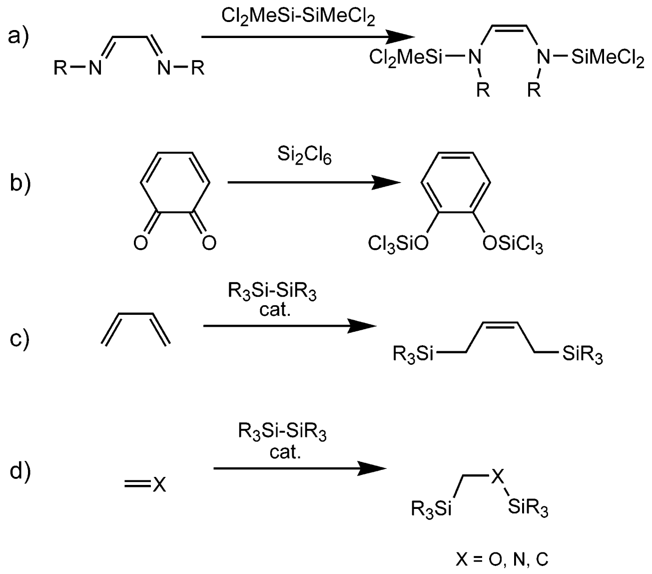
Institut für Anorganische Chemie, Technische Universität Bergakademie Freiberg,
Leipziger Strasse 29, D-09596 Freiberg, Germany

Received July 7, 2004

Summary: The disilane derivative 2-(dichloromethylsilyl)-2-methyl-1,3-diphenyl-1,3,2-diazasilolidine was reacted with a salen-type tetradentate ligand to yield a pentacoordinate methylsilane with a silylated ligand. This surprising rearrangement reaction—with Si−Si bond cleavage and Si−C bond formation at 0 °C without a catalyst and without special external energy input such as irradiation—is confirmed by X-ray structure analysis as well as ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopic data of this novel hypercoordinate silicon complex.

Chlorodisilanes, usually byproducts of the Mueller−Rochow Process, are interesting starting materials for various approaches in preparative organosilicon chemistry. The thermodynamically weak Si−Si bond of the disilanes is quite inert toward Lewis acids. In the presence of donor atoms (e.g. imine nitrogen atoms) the Si−Si bond of many disilanes with π-donor substituents (e.g. −Cl, −F, −OMe) is easily broken under extrusion of a donor-stabilized silylene, which undergoes subsequent reactions such as polymerization and typical silylene trapping reactions.[1] Disilanes can be reacted with 1,2-diimines to give N,N′-silylated enediamines (Scheme 1a).[2] An analogous approach for the preparation of *O*,*O*′-bis(trichlorosilyl)hydroquinones from quinones and hexachlorodisilane[3] was also reported (Scheme 1b). The 1,4-addition of disilanes to 1,3-dienes under Si−C bond formation (Scheme 1c) can be catalyzed by fluoride ions or transition-metal complexes.[4] The 1,2-addition reactions of disilanes to aldehydes (Scheme 1d)[4a,d] as well as to CC multiple bonds[5] also require the use of catalysts. In 2003, the palladium-catalyzed 1,2-addition reaction of disilanes with imines to form one Si−C and one Si−N bond (Scheme 1d) was published by Tanaka et al.[6]

Scheme 1. Silylation Reactions via Disilanes



A novel approach of Si−C bond activation by hexacoordination of organosilanes with salen-type ligands (Scheme 2) has been recently published.[7] Irradiation of such hexacoordinate diorganosilanes with UV light gives rise to the breaking of a Si−C bond, resulting in the formation of a covalent Si−N bond and rearrangement of one organic substituent. The current objective was to explore the possibility of cleaving the Si−Si bond of a disilane in a similar manner.

2-(Dichloromethylsilyl)-2-methyl-1,3-diphenyl-1,3,2-diazasilolidine (**2**), a disilane with a bulky substituent, was selected as a suitable educt for the investigation. It is easily available by reacting 1,1,2,2-tetrachloro-1,2-dimethyldisilane with *N*,*N*′-diphenylethylenediamine/triethylamine in toluene, similar to the published

---

* To whom correspondence should be addressed. Tel.: (+49) 3731 39 3174. Fax: (+49) 3731 39 4058. E-mail: gerhard.roewer@chemie.tu-freiberg.de.

(1) (a) Herzog, U.; Schulze, N.; Trommer, K.; Roewer, G. *Main Group Met. Chem.* **1999**, *22*, 19−33. (b) Knopf, C.; Herzog, U.; Roewer, G.; Brendler, E.; Rheinwald, G.; Lang, H. *J. Organomet. Chem.* **2002**, *662*, 14−22.

(2) Herzog, U.; Roewer, G.; Ziemer, B.; Herrschaft, B. *J. Organomet. Chem.* **1997**, *533*, 73−77.

(3) Yang, J.; Verkade, J. G. *J. Organomet. Chem.* **2002**, *651*, 15−21.

(4) For 1,4-addition reactions of disilanes to 1,3-dienes see e.g.: (a) Mori, A.; Fujita, A.; Ikegashira, K.; Nishihara, Y.; Hijama, T. *Synlett* **1997**, 693−694. (b) Tsuji, Y.; Lago, R. M.; Tomohiro, S. *Organometallics* **1992**, *11*, 2353−2355. (c) Ishikawa, M.; Nishimura, Y.; Sakamoto, H.; Ono, T.; Ohshita, J. *Organometallics* **1992**, *11*, 483−484. (d) Hiyama, T.; Obayashi, M.; Mori, I.; Nozaki, H. *J. Org. Chem.* **1983**, *48*, 912−914.

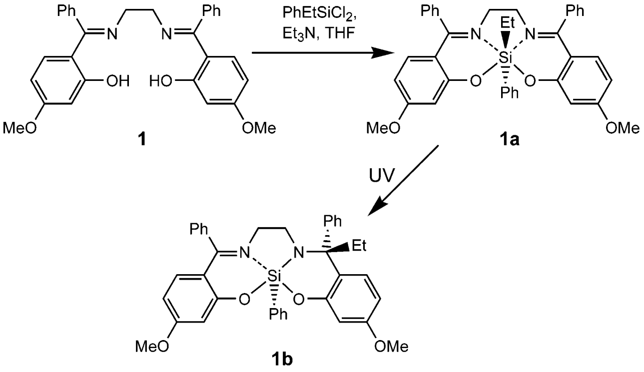
(5) (a) Naka, A.; Lee, K. K.; Yoshizawa, K.; Yamabe, T.; Ishikawa, M. *Organometallics* **1999**, *18*, 4524−4529. (b) Naka, A.; Yoshizawa, K.; Kang, S.; Yamabe, T.; Ishikawa, M. *Organometallics* **1998**, *17*, 5830−5835. (c) Chen, Y.-C.; Lin, C.-H.; Lee, C.-Y.; Liu, C.-S. *Organometallics* **1987**, *6*, 1882−1886.

(6) Williams, N. A.; Uchimaru, Y.; Tanaka, M. *Dalton* **2003**, 236−243.

(7) Wagler, J.; Doert, Th.; Roewer, G. *Angew. Chem., Int. Ed.* **2004**, *43*, 2441−2444.

10.1021/om040096w CCC: $27.50 © 2004 American Chemical Society
Publication on Web 11/04/2004

Scheme 2. Si−C Bond Activation by Hexacoordination and UV Irradiation



method by Schmidbaur et al.[8] Crystals for X-ray structure analysis were grown from *n*-hexane/toluene. The molecular structure of **2** is presented in Figure 1.

The bond length Si1−Si2 (2.358 Å) is within the usual range of Si−Si single bonds. The Cl_2MeSi group has a staggered conformation to the substituents at Si1, as can be seen from the torsion angle C1−Si1−Si2−Cl21 with 161.1°. Both silicon atoms are tetrahedrally surrounded by their substituents. The angle N1−Si1−N2 is diminished to 93.5°, due to formation of the five-membered diazasilolidine ring. Despite the Si atom's position in a five-membered cycle, the bond distances Si1−N1, Si1−N2, and Si1−C1 are comparable with those of similarly substituted noncyclic silanes.[10] The five-membered silaheterocycle has the envelope conformation. The carbon atom C10 is situated 0.450 Å above the plane N1−Si1−N2, while atom C9 is far less displaced in the opposite direction (0.033 Å). The nitrogen atoms have slightly pyramidalized coordination spheres (sum of angles 356.6° at N1 and 354.5° at N2). Owing to the only restrained refinement of the rotationally disordered $-SiMeCl_2$ group, its Si−C and Si−Cl bond distances cannot be compared with those of other disilanes.

2 was reacted with the tetradentate salen-type ligand **1** in the presence of triethylamine. Surprisingly, the product of this reaction was not the disilane **3** with a hexacoordinate Si atom but rather complex **4**, which was isolated in large quantities (Scheme 3). Even the ^{29}Si NMR spectrum of the crude product solution did not provide any evidence for Si-containing byproducts. Single crystals of **4** were grown from 1,2-dichloroethane. Figure 2 shows the molecular structure of this novel complex.

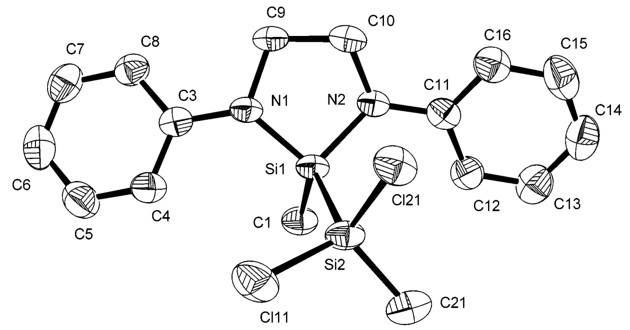


Figure 1. Molecular structure of **2** in the crystal state[9] (ORTEP plot with 50% probability ellipsoids; hydrogen atoms and less occupied (40%) part of the rotationally disordered $-SiMeCl_2$ group omitted).

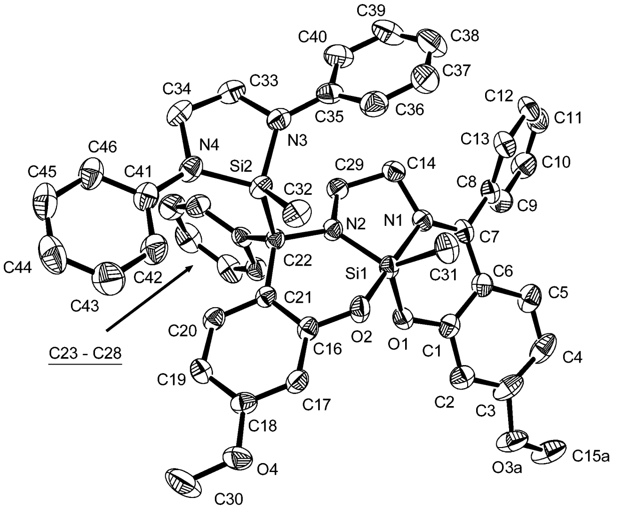
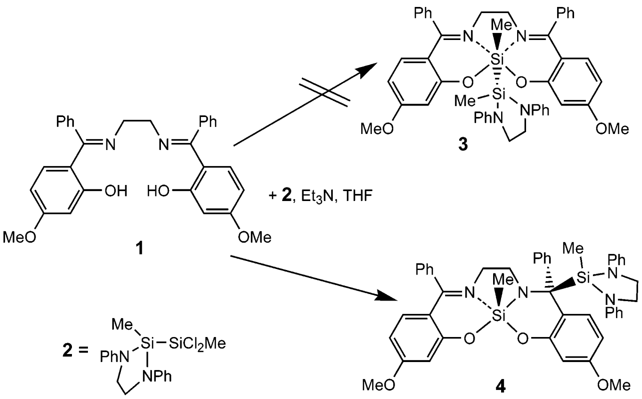


Figure 2. Molecular structure of **4** in the crystal state[11] (ORTEP plot with 50% probability ellipsoids; hydrogen atoms and less occupied (30%) part of the disordered −OMe group O3−C15 omitted).

Scheme 3. Si-Si Bond Cleavage and Si−C Bond Formation



The molecular structure of **4** reveals the formation of the product where the Si−Si bond was cleaved. One silicon atom (Si1) is coordinated by the tetradentate salen-type ligand, thus forming a pentacoordinate silicon complex. The diazasilolidine group containing Si2 is attached to one of the previous imine carbon atoms (C32). This new Si−C bond has transformed the salen-type ligand into an amine−imine−bis(oxo) chelate ligand. As in other pentacoordinate silicon complexes with salen-type ligands,[7,12] the coordination sphere of

---

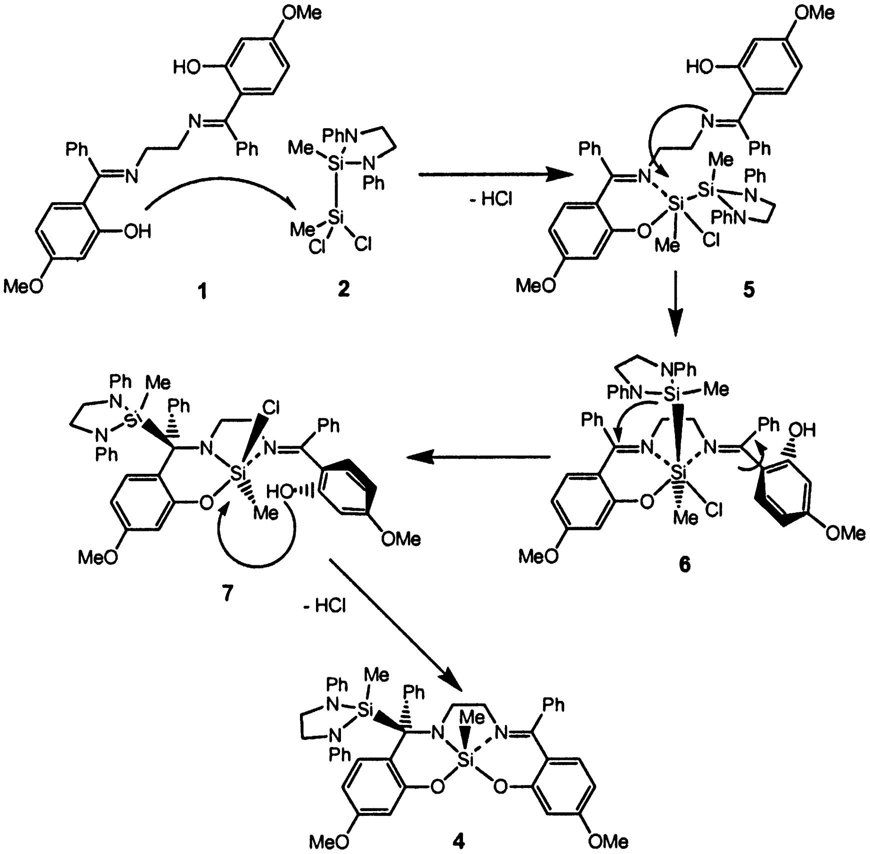
[8] Schlosser, Th.; Sladek, A.; Hiller, W.; Schmidbaur, H. *Z. Naturforsch.* **1994**, *49B*, 1247−1255.

[9] Crystal structure of **2**: formula $C_{16}H_{20}Cl_2N_2Si_2$; monoclinic, space group $P2_1/c$; unit cell $a = 9.949(2)$ Å, $b = 24.138(5)$ Å, $c = 8.1414(16)$ Å, $\beta = 108.54(3)°$; determined at 213(2) K; R1 (wR2) = 0.0796 (0.1077) for all data. Selected bond distances (Å), bond angles (deg), and torsion angles (deg): Si1−N1 = 1.733(2), Si1−N2 = 1.748(2), Si1−C1 = 1.860(3), Si1−Si2 = 2.358(1); N1−Si1−N2 = 93.5(1), C1−Si1−Si2 = 110.8(1); Si1−N1−C3−C4 = 26.9(4), Si1−N2−C11−C12 = 30.2(4).

[10] Böhme, U.; Günther, B.; Rittmeister, B. *Eur. J. Inorg. Chem.* **2003**, 751−758.

[11] Crystal structure of **4**: formula $C_{46}H_{46}N_4O_4Si_2$; monoclinic, space group $P2_1/c$; unit cell $a = 10.522(3)$ Å, $b = 17.006(4)$ Å, $c = 22.655(6)$ Å, $\beta = 101.420(4)°$; determined at 213(2) K; R1 (wR2) = 0.0759 (0.1198) for all data. Selected bond distances (Å) and angles (deg): Si1−N1 = 1.992(2), Si1−N2 = 1.740(2), Si1−O1 = 1.708(2), Si1−O2 = 1.709(2), Si1−C31 = 1.876(3), Si2−C22 = 1.947(3), Si2−C32 = 1.859(3), N1−C7 = 1.295(3), N2−C22 = 1.511(3); N1−Si1−O2 = 179.2(1), O1−Si1−N2 = 116.8(1), C31−Si1−N2 = 127.2(1), O1−Si1−C31 = 114.5(1).

Scheme 4. Suggested Mechanism 1 for the Formation of 4



the silicon atom is distorted trigonal bipyramidal, involving the axial angle O2−Si1−N1 of 179.16°. This value significantly differs from the axial angle in complex **1b** (171.49°). As reported also in other cases, the dative Si−N bond is situated in an axial position. The bond length of Si1−N1 (1.992 Å) is significantly shorter than the analogous one in complex **1b** (2.036 Å), which has a comparable coordination sphere of the silicon atom. The other four bonds to the Si atom, Si1−N2, Si1−O1, Si1−O2, and Si1−C31 in **4**, do not differ much from those of **1b**. According to "Gutmann's Rules"[13] a lengthening of the axial bonds along with an increasing axial angle up to 180° had to be expected. In contrast with this, the nearly ideal axially situated bond Si1−N1 of **4** is much shorter than the bond in **1b**, where the axial angle is much smaller than 180°. Thus, it must be assumed that remarkable covalent bonding interactions along the axes of these trigonal-bipyramidal complexes occur by means of a 4e−3c bond. In this case, an intense orbital overlap must be expected in the case of an axial angle of 180°. However, the shortening of the dative Si−N bond does not influence the imine bond length N1=C7 in **4** (1.295 Å), which is still in the range of a common C=N double bond as it is in **1b** (1.299 Å). Owing to the bulky silyl substituent at atom C22, the C22−N2 bond of **4** (1.511 Å) is significantly longer than the analogous bond in **1b** (1.492 Å). The C22−C bonds (C22−C21, C22−C23) are less affected by the bulky silyl group. The bond Si2−C22 is also surprisingly longer (1.947 Å) than the bond Si2−C32 (1.859 Å). This difference in Si−C bond length is expected to originate from the repulsive interaction between the diazasilolidine group and the other bulky substituents at the carbon atom C22. Further examples of such long or even longer Si−C bonds caused by repulsion between bulky substituents have been published already.[14]

Surprisingly, the rearranged silyl group (Si2), as well as the methyl group C31 of the pentacoordinate silicon atom Si1, are situated on the same side of the tetradentate ligand. As proven by the ^{29}Si NMR spectrum of the crude product solution, this is the only diastereomer formed. Thus, an intermediate hexacoordinate disilane with axially situated substituents Si2 and C31, such as **3** in Scheme 3, should not play a role in the formation process of complex **4** by means of a (1,3)-sigmatropic rearrangement. The fact that the Si−Si bond cleavage occurred thermochemically—unlike the photochemically driven formation of **1b** from **1a**—also indicates a different kind of rearrangement mechanism. Due to the less stable Si−Si bond, compared with Si−C, two reaction pathways can be discussed.

(1) Assuming a single substitution of an Si-linked Cl atom for an O atom of the tetradentate ligand followed by stepwise chelation of the Si atom, hexacoordination of the chelated Si atom is realized in the intermediate complex **6** for the first time (Scheme 4). With increasing

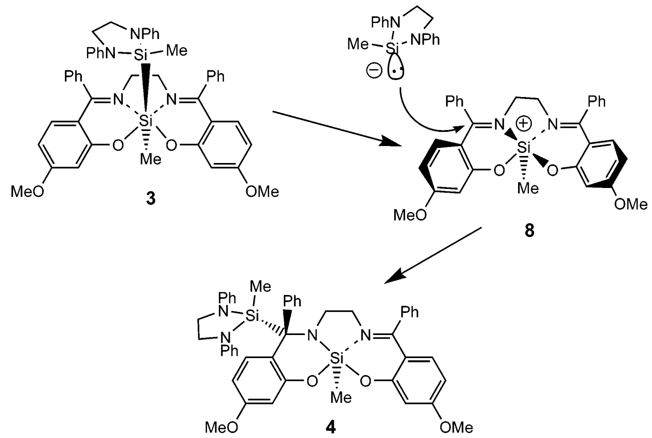
---

[12] Wagler, J.; Böhme, U.; Roewer, G. *Angew. Chem., Int. Ed.* **2002**, *41*, 1732−1734.

[13] (a) Gutmann, V. *Coord. Chem. Rev.* **1975**, *15*, 207. (b) Gutmann, V. *Coord. Chem. Rev.* **1976**, *18*, 225. (c) Gutmann, V. *The Donor-Acceptor Approach to Molecular Interactions*; Plenum Press: New York, 1978; pp 4−16.

[14] For examples of long Si−C bonds, see: (a) Kabeta, K.; Powell, D. R.; Hanson, J.; West, R. *Organometallics* **1991**, *10*, 827. (b) Rengstl, A.; Schubert, U. *Chem. Ber.* **1980**, *113*, 278. (c) Dakternieks, D.; Jurkschat, K.; Tozer, R.; Hook, J.; Tiekink, E. R. T. *Organometallics* **1997**, *16*, 3696.

Scheme 5. Suggested Mechanism 2 for the Formation of 4



coordination number, the bonds between the silicon atom and its substituents are becoming increasingly activated. In this system of Si−O, Si−N, Si−Cl, Si−C, and Si−Si bonds, the last represents the thermodynamically weakest bond. Neglecting kinetic barriers, dissociation of the thermodynamically weaker Si−Si bond should be preferred. After the rearrangement of **6** into **7**, **4** is produced diastereoselectively by the S_N2 substitution of the second chlorine atom for the tetradentate ligand's second oxygen atom.

The configuration of the monodentate ligands assumed in the case of the intermediate complex **6** is supported by the results of other research groups: the Si−N dative bonds are preferably situated trans to halide atoms if no trans configuration of two Si−N bonds can be formed.[15]

(2) The primarily formed complex **3** is assumed to dissociate into the pentacoordinate siliconium cation **8** with a trigonal-bipyramidal Si atom and a free silyl anion (Scheme 5). Attack of the silyl anion at the open side of the C=N plane affords **4**.

This rearrangement reaction represents a novel kind of Si−C bond formation. It occurs at 0 °C without catalyst and without special external energy input such as irradiation. Further investigation of its mechanism is currently under way.

Experimental Section

Syntheses were carried out under an inert atmosphere of dry argon using standard Schlenk techniques. ^{1}H, ^{13}C, and ^{29}Si NMR spectra (solution) were recorded on a Bruker DPX 400 spectrometer using TMS as an internal standard. Melting points were determined in sealed capillaries and not corrected. Single-crystal X-ray structure analyses were carried out on a Siemens SMART CCD diffractometer using Mo Kα radiation (λ = 0.710 73 Å). Detailed data for the crystal structures of **2** and **4** can be found in the Supporting Information.

2 was prepared from 1,1,2,2-tetrachloro-1,2-dimethyldisilane, *N*,*N*′-diphenylethylenediamine, and triethylamine in toluene according to a published method.[8] The product was purified by extraction with *n*-hexane. Yield: 70%. Mp: 107 °C. ^{1}H NMR ($CDCl_3$): δ 0.59 (s, 3H, $SiSiN_2CH_3$), 0.89 (s, 3H, $SiSiCl_2CH_3$), 3.64 (m, 4H, NCH_2CH_2N), 6.85 (m, 6H, Ar), 7.27 (m, 4H, Ar). ^{13}C NMR ($CDCl_3$): δ 0.3 ($SiSiN_2CH_3$), 8.4 ($SiSiCl_2CH_3$), 45.4 (NCH_2CH_2N), 115.5, 119.2, 129.4, 146.4 (Ar). ^{29}Si NMR ($CDCl_3$): δ 22.0 ($Si\mathit{Si}MeCl_2$), −5.0 ($Si\mathit{Si}MeN_2$). Anal. Calcd for $C_{16}H_{20}N_2Si_2Cl_2$: C, 52.30; H, 5.49; N, 7.62. Found: C, 51.90; H, 6.00; N, 7.42.

To prepare **4**, a Schlenk flask was charged with 4.0 g (8.3 mmol) of **1**,[16] 2.7 g (26.7 mmol) of triethylamine, and 80 mL of THF. The mixture was stirred at 0 °C, and a solution of 3.15 g (8.6 mmol) of **2** in 40 mL of THF was added dropwise within 30 min. After the mixture was stirred for 1 h at 0 °C, the precipitated triethylamine hydrochloride was removed by filtration and washed with THF. The volume of the filtrate was reduced under vacuum to 70 mL, and the clear solution was stored at 8 °C. After 3 days, the crystallized product **4** was filtered off, washed with THF, and dried under vacuum. The volume of the filtrate was reduced to 25 mL and stored at 8 °C. After 4 days, a second fraction of **4** was filtered off, washed with THF, and dried under vacuum. Yield: 3.45 g (5.74 mmol, 69%). Mp: 275 °C. ^{1}H NMR ($CDCl_3$): δ 0.41 (s, 3H, $Si_{tetracoordinate}CH_3$), 1.10 (s, 3H, $Si_{pentacoordinate}CH_3$), 1.95−2.05, 2.20−2.30, 2.70−2.80, 2.90−3.00 (m, 4H, $C{=}NCH_2CH_2N$), 3.59, 3.89 (m, 4H, $PhNCH_2CH_2NPh$), 3.75, 3.81 (s, 6H, OCH_3), 5.85−7.50 (m, 26H, Ar). ^{13}C NMR ($CDCl_3$, selected peaks): δ 1.0, 3.7 ($SiCH_3$), 46.7, 47.1, 47.2, 47.9 (NCH_2CH_2N), 55.1, 55.6 (OCH_3), 67.0 ($C_{N,C,C,Si}$), 157.6, 159.5, 161.8, 165.0 (Ar, O−C), 166.3 (C=N). ^{29}Si NMR ($CDCl_3$): δ −10.0, −106.3. Anal. Calcd for $C_{46}H_{46}N_4O_4Si_2$: C, 71.29; H, 5.98; N, 7.23. Found: C, 70.84; H, 5.99; N, 7.11.

Acknowledgment. This work was financially supported by The German Science Foundation (DFG) and the German Chemical Industry Fund. Prof. Dr. Joachim Sieler, Institut für Anorganische Chemie, Universität Leipzig, Johannisallee 29, D-04103 Leipzig, Germany, is kindly acknowledged for the single-crystal structure analyses of **2** and **4**.

Supporting Information Available: Crystallographic data for **2** and **4** and complete ^{13}C NMR data of **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM040096W

---

(15) (a) van den Ancker, T. R.; Raston, C. L.; Skelton, B. W.; White, A. H. *Organometallics* **2000**, *19*, 4437−4444. (b) Nakash, M.; Goldvaser, M. *J. Am. Chem. Soc.* **2004**, *126*, 3436−3437. (c) Anglada, J. M.; Bo, C.; Bofill, J. M.; Crehuet, R.; Poblet, J. M. *Organometallics* **1999**, *18*, 5584−5593. (d) Kim, B. K.; Choi, S.-B.; Kloos, S. D.; Boudjouk, P. *Inorg. Chem.* **2000**, *39*, 728−731. (e) Kalikhman, I.; Krivonos, S.; Ellern, A.; Kost, D. *Organometallics* **1996**, *24*, 5073−5076.

(16) Dinjus, U.; Stahl, H.; Uhlig, E. *Z. Anorg. Allg. Chem.* **1980**, *464*, 37−44.