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Synthesis of a Stable Four-Membered Si_2O_2 Ring and a Dimer with Two Four-Membered Si_2O_2 Rings Bridged by Two Oxygen Atoms, with Five-Coordinate Silicon Atoms in Both Ring Systems

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The base-stabilized bis-silylene (LSi−SiL, L = PhC(N*t*Bu)$_2$) was reacted with benzophenone in a 1:2 ratio in THF, which afforded a Si_2O_2 four-membered ring, stabilized by bulky amidinato ligands. The most striking phenomenon is the abstraction of oxygen from benzophenone and the simultaneous formation of a silicon carbon bond. The four-membered Si_2O_2 ring is planar, and both the silicon atoms are five-coordinate. The two silicon atoms are arranged opposite each other in the four-membered Si_2O_2 ring. Moreover LSi−SiL was treated with N_2O to afford two four-membered Si_2O_2 rings connected with two oxygen atoms. In this structure also the silicon atoms are five-coordinate.

Introduction

Interest has increased over the last decades in the chemistry of strained ring systems containing silicon atoms. While many routes to silacyclopropanes and silacyclopropene have been investigated,[1] there are only a few reports on the synthesis of small ring compounds containing silicon and oxygen.[2] Although the four-membered ring structure has previously been suggested for a few silicon−oxygen containing compounds,[3] definite evidence for its existence was obtained when West et al. reported the four-membered cyclodisiloxane.[4] It was prepared by the reaction of disilene ($R_2Si{=}SiR_2$, R = $Me_3C_6H_2$) with triplet oxygen and also by the reaction of disilaoxirane with *m*-CPBA (*meta*-chloroperoxybenzoic acid). After that a series of *ab initio* calculations have been done on the four-membered cyclodisiloxane, and to date most of the theoretical studies conclude that there is no Si−Si bond.[5] The resulting close proximity between the tetravalent silicon atoms in the Si_2O_2 ring is due to strong repulsion between the two highly negatively charged oxygen atoms and geometric constraint by the four-membered ring.[5] Taking this into account, it is quite interesting to synthesize a compound where two O atoms are connected with two Si atoms with the support of bulky ligands. It can also be argued that the fragment of such a cyclic compound (R_2SiO) would be a key monomer in silicon chemistry and one step toward the isolation of room-temperature stable silanone ($R_2Si{=}O$) (Kipping's dream),[6] which is still elusive. Moreover the cyclic siloxanes $(R_2SiO)_n$ have great commercial importance as precursors for high molecular weight silicones.[7]

Now it is frequently experienced that the utilization of compounds with low valent silicon is always an alternative strategy to prepare silicon containing ring compounds.[8] Recently we were successful in isolating a compound consisting of a Si−Si

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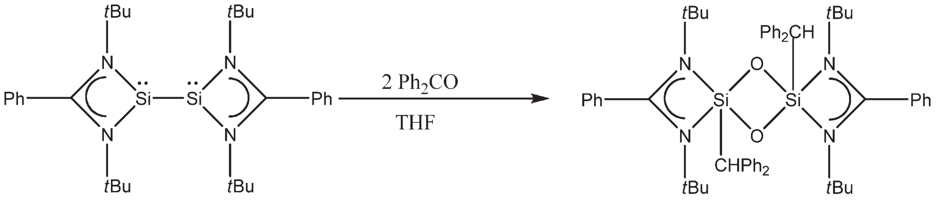
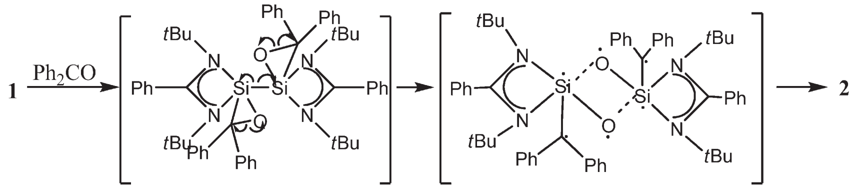
Scheme 1. Preparation of 2



1 **2**

Scheme 2. Suggested Mechanism for the Formation of 2



single bond and a lone pair of electrons on each Si atom ([PhC(N*t*Bu)$_2$]$_2$Si$_2$) (**1**).[9] The formal oxidation state of each silicon atom in **1** is +1, or according to the suggestion of Frenking et al., compound **1** contains three-valent silicon atoms of formal oxidation state +1.[10] Anyhow this is a new entry to the low-valent low-coordinate silicon compound and may serve as a building block in organosilicon chemistry. A further impetus came from the theoretical calculation,[11] which shows that **1** has two stereoactive lone pairs that prefer to remain nonbonded in each Si center and the Si−Si bond does not have multiple-bond character. As a result of this unprecedented electronic structure, we were interested in studying the chemistry of **1** with ketone. The question arises whether it is possible to obtain a [1+2] cycloaddition product or a cyclodisiloxane derivative from the reaction of **1** with benzophenone.

Results and Discussion

LSi(I)−Si(I)L was treated with benzophenone in THF at ambient temperature under stirring overnight. After removal of the solvent under vacuum, *n*-hexane was added and the reaction mixture was stirred for 12 h. After that the solution was concentrated and kept for crystallization, which affords colorless crystals of **2** suitable for X-ray crystallography (Scheme 1). The structure of **2** was confirmed by NMR spectroscopy, EI-mass spectrometry, and elemental analysis. The ^{1}H NMR spectrum exhibits a resonance (δ 1.27 ppm) that corresponds to the *t*Bu protons. A resonance at δ 4.1 ppm indicates the two C*H* protons. The ^{29}Si NMR spectrum shows a resonance at δ −86.25 ppm, which is comparable with that of the reported five-coordinate silicon compound[12] and differs distinctively from West's four-coordinate cyclodisiloxane (δ −22.02 ppm).[4c] The molecular ion is observed with the highest relative intensity in the EI-MS spectrum at *m*/*z* 884. Compound **2** is very well soluble in ether, THF, and toluene and partially soluble in *n*-hexane. It is stable in the solid state and in solution at room temperature under an inert atmosphere.

The mechanism for the formation of **2** is not clear at this moment, and intermediates could not be observed, but we propose that a [2+1] cycloaddition occurs as an initial step to give the respective three-membered SiCO cycles, which subsequently rearrange to the final product under hydrogen abstraction from THF (Scheme 2).[13a] To prove the hydrogen abstraction from the solvent unambiguously, we performed a NMR-scale reaction in THF-d_8, and we did not find any resonance for the C*H* proton. Furthermore a hydrogen abstraction from etheral solvent was also observed by Robinson et al. during the synthesis of diborane and diborene compounds.[13b] The cleavage of the Si−Si bond is not unexpected because So et al. showed recently that **1** is cleaved with Br$_2$ under formation of a heteroleptic bromo silylene.[11] But the most striking phenomenon is the removal of oxygen from ketone under formation of a Si−O−Si bond (C=O bond energy ~178 kcal/mol).[14] Moreover, it is also worth mentioning that during the reaction the formal oxidation state of Si has been changed from +1 to +4. There is no comparable example of oxidative addition at silicon so far known.

The molecular structure of **2**·2 toluene is shown in Figure 1.[15] Compound **2**·2 toluene crystallizes in the monoclinic space group *P*2$_1$/*n* (Table 1). The structure consists of a rectangular cyclodisiloxane ring orthogonal to a slightly distorted planar skeleton containing the silicons and their pendant nitrogens. The two independent Si−O bond lengths are very close to each other (167.91(11) and 171.82(10) pm) and are slightly larger than the normal bond lengths found for other cyclic siloxanes.[4b−d] A 2-fold symmetry axis passes through the centroid of the siloxane ring, which is almost planar (sum of the internal angles 360.02°). The endocyclic Si−O−Si bond angle in the four-membered ring is 95.08°, which is very close to the Si−O−Si bond angle (95.8°) in the *t*Bu$_4$Si$_2$O$_2$ ring reported by West et al.[4c] The

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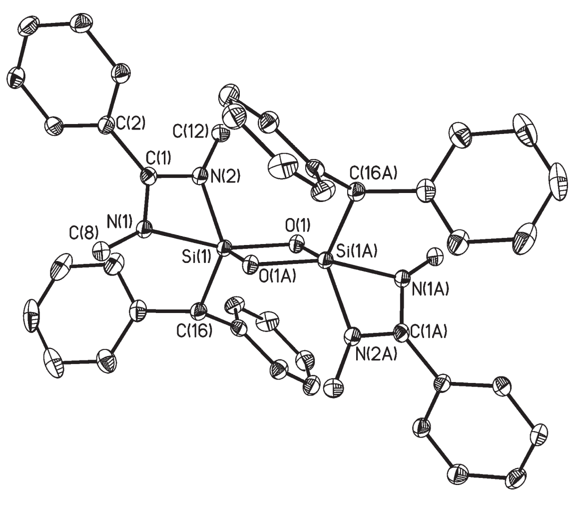
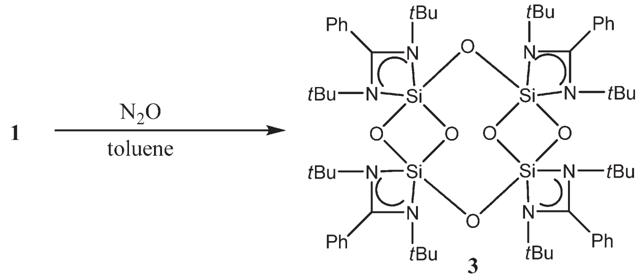


Figure 1. Crystal structure of **2**·2 toluene. Hydrogen atoms, methyl groups at C(8) and C(12), and two toluene molecules are not shown for clarity. Anisotropic displacement parameters are depicted at the 50% probability level. Selected bond distances (pm) and bond angles (deg): Si(1)−O(1A) 167.91(11), Si(1)−O(1) 171.82(10), Si(1)−N(2) 182.98(13), Si(1)−C(16) 193.17(15), Si(1)−N(1) 197.47(12), O(1)−Si(1A) 167.90(11); O(1A)−Si(1)−O(1) 84.93(5), O(1A)−Si(1)−N(2) 123.96(5), O(1)−Si(1)−N(2) 100.03(5), O(1A)−Si(1)−C(16) 117.07(6), O(1)−Si(1)−C(16) 101.77(6), N(2)−Si(1)−C(16) 116.28(6), O(1A)−Si(1)−N(1) 90.65(5), O(1)−Si(1)−N(1) 162.41(5), N(2)−Si(1)−N(1) 68.51(5), C(16)−Si(1)−N(1) 95.41(6), O(1A)−Si(1)−Si(1A) 43.07(3), O(1)−Si(1)−Si(1A) 41.86(3), N(2)−Si(1)−Si(1A) 119.58(4).

Table 1. Crystallographic and Structure Refinement Data at 100.0(2) K

parameter	**2**·2 toluene	**3**·toluene
empirical formula	$C_{70}H_{84}N_4O_2Si_2$	$C_{67}H_{100}N_8O_6Si_4$
fw	1069.59	1225.91
space group	$P2_1/n$	$P2_1/n$
a (Å)	12.4840(17)	10.7264(16)
b (Å)	11.4379(16)	28.415(4)
c (Å)	21.383(3)	23.012(3)
β (deg)	100.954(3)	101.979(2)
V (Å^3)	2997.6(7)	6861.2(18)
Z	2	4
ρ_{calcd} (g/cm^3)	1.185	1.187
F(000)	1152	2648
μ (mm^{-1})	0.108	0.141
θ range for data collection (deg)	1.94 to 27.10	1.15 to 26.37
reflns collected/unique [$I > 2\sigma(I)$]	60 807/6607	162 534/14 016
data/restraints/params	6607/1/362	14 016/219/861
Goof on F^2	1.021	1.019
R_1, wR_2 [$I > 2\sigma(I)$]	0.0405, 0.0918	0.0422, 0.0940
R_1, wR_2 (all data)	0.0569, 0.0999	0.0635, 0.1053
largest diff peak/hole (e Å^{-3})	0.322/−0.301	0.261/−0.337

Scheme 3. Preparation of 3



3

amidinate ligands and Ph_2CH groups are disposed above and below the Si_2O_2 ring in such a way that the Si centers exhibit trigonal-bipyramidal coordination sites.[16] To explain the axial and equatorial arrangement, we selected Si(1), N(2), O(1A), and O(1), which reside in the equatorial positions, whereas C(16) and N(1) occupy the axial positions of the trigonal-bipyramidal geometry. Another striking feature of this structure is the Si−Si distance of 250.63(8) pm, which is 6.38% longer than the normal Si−Si σ-bond distance (235 pm) and 3.73% longer compared to that in **1** (241 pm) and significantly longer than West's 1,1′,3,3′-tetramesitylcyclodisiloxane (231 pm).[4c] From these data it can be assumed that there is no bond between the two Si atoms. This assumption is also supported by MNDO calculations on the parent cyclodisiloxane, $H_4Si_2O_2$,[4b] which also provided no evidence for bonding between silicon atoms. In agreement with this, recent *ab initio* calculations on $H_4Si_2O_2$ indicate that the cyclodisiloxane is best described as containing four equivalent localized Si−O bonds with no appreciable σ-bonding between the silicon atoms.[5e,f] The calculated Si−O−Si bond angle for $H_4Si_2O_2$ is 91.5°, similar to that found for **2**, while the calculated Si···Si bond length (239 pm) is reasonably shorter than those in **2**. A possible qualitative explanation for the marked differences in bond length observed in **2** and West's 1,1′,3,3′-tetramesitylcyclodisiloxane is as follows: The 3p orbitals of π-symmetry on silicon have low electron density compared to the 2p orbitals on oxygen, so that the diagonal antibonding interactions between oxygens are stronger than between the silicon atoms, leading to the diamond-shaped distortion found for West's disiloxane,[4c] whereas in **2**, due to the presence of four nitrogen atoms, the electron density on silicon atoms is shifted toward the amidinato ligand, causing a longer Si−Si bond length. Here it is also worth pointing out that recently Driess and co-workers reported the formation of cyclodisiloxane, where the two silicon atoms, however, have different coordination numbers; one silicon atom is five- and the other one is four-coordinate,[17a] whereas in **2** both the Si centers are five-coordinate.[18]

After being successful in the preparation of the cyclodisiloxane derivative by treating **1** with benzophenone, we turned our focus toward N_2O. The latter is well-known to serve as a mono-oxygen donor. Recently Driess et al. reported the reaction of N_2O with siloxy silylene HSi(L′)-O-(L)Si and NHC-supported silylene NHC→L′Si [L′ = CH[(C=CH$_2$)CMe(NAr)$_2$], L = CH(CMeNAr)$_2$, Ar = 2,6-*i*Pr$_2$-C$_6$H$_3$],[17] respectively. In the first case a silanoic silylester resulted, whereas in the second case a NHC-supported silanone was isolated. Power and co-workers recently described the complete cleavage of the Cr−Cr quintiple bond, and instead a Cr_2O_2 ring was formed when Ar′CrCrAr′ (Ar′ = C$_6$H$_3$-2,6-(2,6-*i*Pr$_2$−C$_6$H$_3$)$_2$)[19] was reacted with N_2O. Following this we also demonstrated the conversion of LGeH to LGeOH (L = CH(CMeNAr)$_2$, Ar = 2,6-*i*Pr$_2$-C$_6$H$_3$) quantitatively by using N_2O as a mono-oxygen source.[20]

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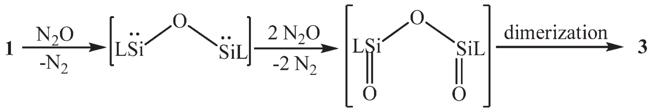
Scheme 4. Suggested Mechanism for the formation of 3



All these reactions instigated us to probe the reaction of **1** with N_2O. Exposure of a red solution of **1** in toluene to N_2O at room temperature led to rapid decoloration and formation of a colorless compound. Recrystallization of the latter in a toluene/*n*-hexane solution at room temperature furnished colorless crystals of **3** suitable for single-crystal X-ray diffraction (Scheme 3). To our surprise, **3** contains two four-membered disiloxane rings, which are bridged by two oxygen atoms. This is a new class of compounds that has not been reported so far. **3** was fully characterized by single-crystal X-ray diffraction, NMR spectroscopy, EI-MS spectrometry, and elemental analysis. In the ^{1}H NMR spectrum two types of resonances were observed, one for *t*Bu protons and another for the phenyl rings. In the ^{29}Si NMR spectrum a sharp resonance was outlined (δ −111.02 ppm) that corresponds to the five-coordinate silicon atom[12] and differs distinctly from that of **2** (δ −86.25 ppm) and Driess' cyclodisiloxane (δ −60.7 and −119.2 ppm).[17a] The molecular ion is observed with the highest relative intensity in the EI-MS spectrum at *m*/*z* 1132. All the silicon atoms in **3** are five-coordinate.

Like **2**, the mechanism for the formation of **3** is unknown, but it can be suggested that the Si−Si bond is cleaved under insertion of an oxygen atom from N_2O. Then each of the lone pairs of electrons at silicon react with N_2O to give the respective Si=O, which *in situ* dimerizes to afford **3** due to the highly polar nature of $Si^{\delta+}{=}O^{\delta-}$ (Scheme 4).[5h]

The molecular structure of **3**·toluene was unequivocally established by single-crystal X-ray diffraction (Figure 2).[15] **3**·toluene crystallizes in the monoclinic space group $P2_1/n$ (Table 1). Selected bond lengths and bond angles are given in the legend of Figure 2. The most important feature of **3**·toluene is that two four-membered rings are connected by two oxygen atoms. The ring actually consists of two four-membered disiloxane rings that are parallel to each other and connected by a bridging oxygen atom. The amidinato ligands are each arranged orthogonally to the four-membered disiloxane ring. All the silicon atoms are five-coordinate and exhibit a trigonal-bipyramidal geometry. Three sites of each silicon atom are occupied by the three oxygen atoms, whereas the nitrogen atoms from the amidinato ligand occupy the remaining two coordination sites. To explain the axial and equatorial arrangement of the silicon atoms, we chose one silicon atom in the ring designated as Si(4). From the bond length and angle data it is revealed that N(7) and O(3) reside in the axial positions and O(1), O(4), and N(8) occupy the equatorial positions. The sum of angles between the equatorial atoms and Si(4) is 357.9°, and the two axial atoms include an angle of 159.5° with Si(4). The arrangement holds true for all the silicon atoms in the ring where one oxygen atom of the disiloxane moiety and one nitrogen atom from the amidinato ligand occupy axial positions and two oxygen atoms and another nitrogen atom from the ligand occupy equatorial positions. It is noticeable that the Si−N as well as the Si−O bond lengths differ significantly depending on whether equatorial or axial positions are occupied. The Si−N distances range from 197.1 to 201.9 pm for axial nitrogen atoms while the equatorial Si−N bond lengths are between 183.8 and 185.2 pm and thus significantly shorter. The Si−O bond lengths in the disiloxane rings exhibit a similar behavior, with axial Si−O bond lengths ranging from 172.0 to 172.8 pm and shorter equatorial Si−O bond lengths ranging from 165.8 to 166.5 pm. All these Si−O bond lengths are quite similar to those found for **2** and HSi(L′)-O-(L)Si.[17a]

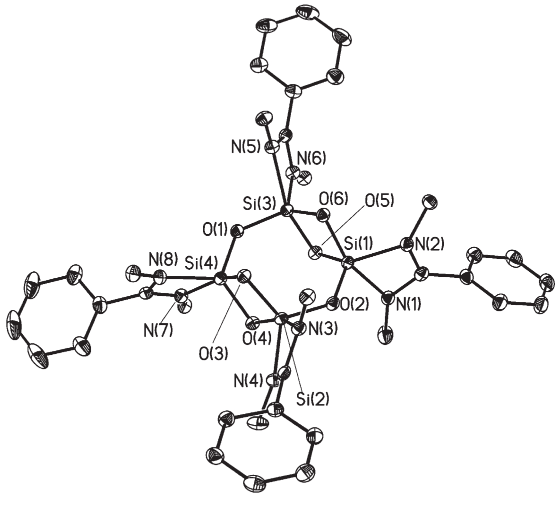


Figure 2. Crystal structure of **3**·toluene. Hydrogen atoms as well as methyl groups and the toluene molecule are omitted for clarity. Selected bond distances (pm) and bond angles (deg) with standard deviations: O(1)−Si(3) 164.69(13), O(1)−Si(4) 165.48(13), O(2)−Si(1) 164.55(13), O(2)−Si(2) 164.94(13), O(3)−Si(2) 166.50(13), O(3)−Si(4) 172.82(13), O(4)−Si(4) 165.77(13), O(4)−Si(2) 172.41(13), O(5)−Si(1) 166.33(13), O(5)−Si(3) 172.04(13), O(6)−Si(3) 165.90(13), O(6)−Si(1) 172.52(13), N(1)−Si(1) 197.10(16), N(2)−Si(1) 185.24(16), N(3)−Si(2) 198.55(16), N(4)−Si(2) 183.97(16), N(5)−Si(3) 201.91(16), N(6)−Si(3) 183.77(16), N(7)−Si(4) 198.57(16), N(8)−Si(4) 184.80(16); Si(3)−O(1)−Si(4) 129.96(8), Si(1)−O(2)−Si(2) 130.94(8), Si(2)−O(3)−Si(4) 94.28(6), Si(4)−O(4)−Si(2) 94.70(6), Si(1)−O(5)−Si(3) 94.28(6), Si(3)−O(6)−Si(1) 94.26(6), O(2)−Si(1)−O(5) 117.48(7), O(2)−Si(1)−O(6) 102.92(6), O(5)−Si(1)−O(6) 85.25(6), O(2)−Si(1)−N(2) 113.48(7), O(5)−Si(1)−N(2) 127.11(7), O(6)−Si(1)−N(2) 96.67 (7), O(2)−Si(1)−N(1) 96.71(7), O(5)−Si(1)−N(1) 92.40(7), O(6)−Si(1)−N(1) 158.96(7), N(2)−Si(1)−N(1) 68.21(7), O(2)−Si(2)−O(3) 117.04(7), O(2)−Si(2)−O(4) 101.85(6), O(3)−Si(2)−O(4) 85.15(6), O(2)−Si(2)−N(4) 116.65(7), O(3)−Si(2)−N(4) 124.52(7), O(4)−Si(2)−N(4) 96.82(7), O(2)−Si(2)−N(3) 96.58(6).

Conclusion

We have prepared a four-membered Si_2O_2 ring with five-coordinate silicon atoms. Compound **2** is formed by oxidative addition of benzophenone under cleavage of the ketone bond and hydrogen abstraction from THF. Furthermore we reacted **1** with N_2O to afford compound **3** with two four-membered rings bridged by two oxygen atoms. The composition and constitution of **2** and **3** have been supported by NMR spectroscopy, EI-MS spectrometry, and single-crystal X-ray diffraction.

Experimental Section

All manipulations were carried out in an inert atmosphere of dinitrogen using standard Schlenk techniques and in a dinitrogen-filled glovebox. Solvents were purified by MBRAUN solvent purification system MB SPS-800. **1** was prepared by literature methods.[9] All chemicals purchased from Aldrich were used without further purification. ^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded with Bruker Avance DPX 200 or Bruker Avance DRX 500 spectrometers. The ^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded in C_6D_6. The chemical shifts δ are given relative to $SiMe_4$. EI-MS spectra were obtained using a Finnigan MAT 8230 instrument. Elemental analyses were performed by the Institut für Anorganische Chemie, Universität Göttingen. Melting point was measured in a sealed glass tube on a Büchi B-540 melting point apparatus.

Preparation of 2. THF (20 mL) was added to a mixture of **1** (0.5 g, 0.96 mmol) and benzophenone (0.35 g, 1.92 mmol) at ambient temperature. The mixture was stirred overnight. The volatiles were removed *in vacuo*, and *n*-hexane (20 mL) was added to the residue. The reaction mixture was once again stirred overnight. The *n*-hexane was removed under vacuum, toluene (5 mL) was added to the reaction mixture, and the solution was concentrated and stored at room temperature for two days to yield colorless crystals of **2**·2toluene (0.22 g, 26%). Mp: 165−170 °C. For the elemental analysis, **2**·2toluene was treated under vacuum to remove the two toluene molecules. Anal. Calcd for **2**·toluene, $C_{63}H_{76}N_4O_2Si_2$ (976.55): C, 77.41; H, 7.84; N, 5.73. Found: C, 77.56; H, 8.04; N, 5.35. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 1.27 (s, 36 H, *t*Bu), 4.1 (s, 2H, *C*H), 7.26−7.33 (m, 10 H, Ph); 7.52−7.83 ppm (m, 10 H, Ph). ^{13}C{^{1}H} NMR (125.75 MHz, C_6D_6, 25 °C): δ 30.1(C*Me*$_3$), 37.5 (*C*H), 57.2 (*C*Me$_3$), 128.5, 128.9, 129.4, 129.9, 130.2, 133.0 (Ph), 166.45 ppm (NCN). ^{29}Si{^{1}H} NMR (99.36 MHz, C_6D_6, 25 °C): δ −86.248. EI-MS: *m*/*z* 884 [M^{+}] (100%).

Preparation of 3. Dry N_2O was bubbled into a solution of **1** (0.11 g, 0.21 mmol) in toluene (20 mL) at room temperature. After 5 min the gas flow of N_2O was disconnected, and all the volatiles were removed under vacuum. The residue was treated with *n*-hexane (10 mL) and stirred overnight. The *n*-hexane was removed under vacuum, toluene (15 mL) was added to the reaction mixture, and the solution was concentrated and stored at room temperature to yield colorless crystals of **3**·toluene (0.12 g, 50%). Mp: 168−175 °C. For the elemental analysis **3**·toluene was kept under vacuum overnight to remove the toluene. Anal. Calcd for $C_{60}H_{92}N_8O_6Si_4$ (1132.62): C, 63.56; H, 8.18; N, 9.88. Found: C, 64.71; H, 8.55; N, 9.09. ^{1}H NMR (500 MHz, C_6D_6, 25 °C): δ 1.58 (s, 36 H, *t*Bu), 6.94−7.14 (m, 20 H, Ph). ^{13}C{^{1}H} NMR (125.75 MHz, C_6D_6, 25 °C): δ 33.1(C*Me*$_3$), 53.5 (*C*Me$_3$), 125.6, 127.6, 128.3, 128.5, 128.8, 129.3, 135.9 (Ph), 171.23 ppm (NCN). ^{29}Si{^{1}H} NMR (99.36 MHz, C_6D_6, 25 °C): δ −111.02. EI-MS: *m*/*z* 1132 [M^{+}] (100%).

Crystal Structure Determination. Shock-cooled crystals were selected and mounted under a nitrogen atmosphere using the X-TEMP.[15] The data for **3**·toluene were collected at 100(2) K on a INCOATEC Mo Microsource[21] with Quazar mirror optics and an APEX II detector on a D8 goniometer. The data of **2**·2toluene were measured on a Bruker TXS-Mo rotating anode with Helios mirror optics and an APEX II detector on a D8 goniometer. Both diffractometers were equipped with a low-temperature device and used Mo Kα radiation, λ = 71.073 pm. The data of **2**·2toluene and **3**·toluene were integrated with SAINT,[22] and an empirical absorption (SADABS) was applied.[23] The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares methods against F^2 (SHELXL-97).[24] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically on calculated positions using a riding model with their U_{iso} values constrained to equal 1.5 times the U_{eq} of their pivot atoms for terminal sp^3 carbon atoms and 1.2 times U_{eq} for all other carbon atoms. Disordered moieties were refined using bond length restraints and isotropic displacement parameter restraints.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. The crystal data are listed in Table 1. Copies of the 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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Supporting Information Available: CIF for **2**·2toluene and **3**·toluene. This material is available free of charge via the Internet at http://pubs.acs.org.

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