Organometallics **2002,** *21,* 3827−3830 3827

The Sodium Siloxides ($(t\mathrm{Bu}_3\mathrm{SiONa})_4$) and ($(t\mathrm{Bu}_2\mathrm{PhSiONa})_4$): Synthesis and X-ray Crystal Structure Analysis

Hans-Wolfram Lerner,*,† Stefan Scholz,† and Michael Bolte‡

Institut für Anorganische Chemie and Institut für Organische Chemie,
Johann Wolfgang Goethe-Universität Frankfurt am Main, Marie-Curie-Strasse 11,
60439 Frankfurt am Main, Germany

Received April 22, 2002

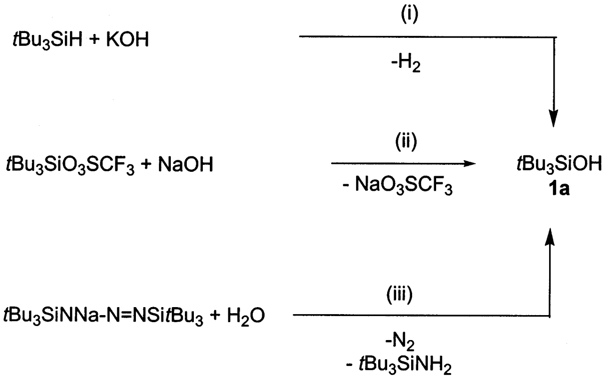
Summary: The sodium siloxides ($(t\mathrm{Bu}_3\mathrm{SiONa})_4$) and ($(t\mathrm{Bu}_2\mathrm{PhSiONa})_4$) can be synthesized almost quantitatively from the reaction of the sodium silanides $t\mathrm{Bu}_3\mathrm{SiNa}$ and $t\mathrm{Bu}_2\mathrm{PhSiNa}$ with N_2O in tetrahydrofuran at −78 °C. ($(t\mathrm{Bu}_3\mathrm{SiONa})_4$) and ($(t\mathrm{Bu}_2\mathrm{PhSiONa})_4$) are the first structurally characterized sodium siloxides featuring a heterocubane framework in the solid state. X-ray quality crystals of the supersilanol, $t\mathrm{Bu}_3\mathrm{SiOH}$ (monoclinic, C2/c), were obtained from the thermolysis of $t\mathrm{Bu}_3\mathrm{SiNaN{-}N{=}NSi}t\mathrm{Bu}_3$ in the presence of water.

Introduction

Low-coordinate early transition metal complexes containing Si−O−M units have attracted recent attention due to their chemical properties.[1] The angle of the Si−O−M linkage and the metal−oxygen bond length are the typical criteria for assessing the metal−siloxide bond order. An Si−O−M bond angle that is near linearity indicates a significant π-interaction. In this case, the siloxide can act as a six-electron donor similar to cyclopentadienide. Using bulky ligands such as cyclopentadienide or tri-*tert*-butylsiloxide (supersiloxide), $t\mathrm{Bu}_3\mathrm{SiO}^-$, low-coordinate, reactive metal centers can be stabilized. Previous investigations indicated supersiloxide to possess a cone angle greater than 120° (cyclopentadienide ~130°).[2]

Tri-*tert*-butylsilanol (supersilanol), $t\mathrm{Bu}_3\mathrm{SiOH}$, was invented by Dexheimer, Spialter, and Weidenbruch more than 20 years ago and is today well-established as a ligand in coordination chemistry.[3] Several syntheses of supersilanol, $t\mathrm{Bu}_3\mathrm{SiOH}$, have recently been reported, as shown in Scheme 1: (i) reaction of supersilane, $t\mathrm{Bu}_3\mathrm{SiH}$, with KOH in methanol,[4] (ii) treatment of supersilyltriflate, $t\mathrm{Bu}_3\mathrm{SiO}_3\mathrm{SCF}_3$, with NaOH;[5] and (iii) thermolysis of $t\mathrm{Bu}_3\mathrm{SiNaN{-}N{=}NSi}t\mathrm{Bu}_3$, sodium bissupersilyltriazenide, in the presence of water.[6]

Scheme 1



In this paper, the syntheses and structural characterization of the sodium siloxides $t\mathrm{Bu}_3\mathrm{SiONa}$ and $t\mathrm{Bu}_2\mathrm{PhSiONa}$ are described. When $t\mathrm{Bu}_2\mathrm{PhSiONa}$ is employed as a ligand of transition metal complexes, some novel peculiar properties can be expected. Perhaps the most interesting feature of the new ligand, $t\mathrm{Bu}_2\mathrm{PhSiO}^-$, is its ability to coordinate a second metal center via its phenyl group. Finally we report here the crystal structure of a supersilanol adduct with 18-crown-6 (**1a(18-crown-6)**).

Results and Discussion

In contrast to the well-established trimethylsiloxides and tris(trimethylsilyl)siloxides[7] (hypersilylsiloxides), only a limited number of supersiloxides have been structurally characterized by X-ray crystallography. Crystals of the supersilanol adduct **1a(18-crown-6)**

---

* Corresponding author. Fax: +49-69798-29260. E-mail: lerner@chemie.uni-frankfurt.de.

† Institut für Anorganische Chemie.

‡ Institut für Organische Chemie.

(1) (a) Wolczanski, P. T. *Polyhedron* **1995**, *14*, 3335. (b) Strazisar, S. A.; Wolczanski, P. T. *J. Am. Chem. Soc.* **2001**, *123*, 4728. (c) Feher, F. J.; Budzichowski, T. A. *Polyhedron* **1995**, *14*, 3239. (d) Johnson, B. F. G. *J. Organomet. Chem.* **2000**, *596*, 221. (e) Covert, K. J.; Neithammer, D. R.; Zonnevylle, M. C.; LaPointe, R. E.; Schaller, C. P.; Wolczanski, P. T. *Inorg. Chem.* **1991**, *30*, 2494. (f) Cundari, T. R. *J. Am. Chem. Soc.* **1992**, *114*, 7879. (g) Schaller, C. P.; Wolczanski, P. T. *Inorg. Chem.* **1993**, *32*, 131. (h) Feher, F. J.; Blanski, R. L. *J. Chem. Soc., Chem. Commun.* **1990**, 1614. (i) Feher, F. J.; Walzer, J. F.; Blanski, R. L. *J. Am. Chem. Soc.* **1991**, *113*, 3618.

(2) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

(3) Marcinec, B.; Maciejewski, H. *Coord. Chem. Rev.* **2001**, *223*, 301.

(4) (a) Dexheimer, E. M.; Spialter, L.; Smithson, L. D. *J. Organomet. Chem.* **1975**, *102*, 21. (b) Weidenbruch, M.; Peter W.; Streichen, R. *J. Organomet. Chem.* **1977**, *141*, 9. (c) Weidenbruch, M.; Pierrard C.; Pesel, H. *Z. Naturforsch.* **1978**, *33b*, 1468. (d) Weidenbruch, M.; Pesel, H.; von Hien, D. *Z. Naturforsch.* **1980**, *35b*, 31.

(5) Lerner, H.-W.; Wiberg, N.; Bolte, M.; Nöth, H.; Knizek, J. *Z. Naturforsch.* **2002**, *57b*, 177, and references therein.

(6) (a) Kühnel, E.; Lerner, H.-W.; Wagner, M.; Wiberg, N.; Bolte, M.; Polborn, K. Unpublished work. (b) Wiberg, N.; Karampatses, P.; Kühnel, E.; Veith, M.; Huch, V. *Z. Anorg. Allg. Chem.* **1988**, *562*, 91.

(7) (a) For an overview see ref 3. (b) Chesnokova, T. A.; Zhezlova, E. V.; Kornev, A. N.; Fedotova, Y. V.; Yana, V.; Zakharov, L. N.; Fukin, G. K.; Kursky, Y. A.; Mushtina, T. G.; Domrachev, G. A. *J. Organomet. Chem.* **2002**, *642*, 20. (c) Kornev, A. N.; Chesnokova, T. A.; Zhezlova, E. V.; Fukin, G. K.; Zakharov, L. N.; Domrachev, G. A. *Dokl. Akad. Nauk* **1999**, *369*, 203. (d) Kornev, A. N.; Chesnokova, T. A.; Zhezlova, E. V.; Zakharov, L. N.; Fukin, G. K.; Kursky, Y. A.; Domrachev, G. A.; Lickiss, P. D. *J. Organomet. Chem.* **1999**, *587*, 113. (e) Kornev, A. N.; Chesnokova, T. A.; Semenov, V. V.; Zhezlova, E. V.; Zakharov, L. N.; Klapshina, L. G.; Domrachev, G. A.; Rusakov, V. S. *J. Organomet. Chem.* **1997**, *547*, 113. (f) Kornev, A. N.; Chesnokova, T. A.; Semenov, V. V.; Kurskii, Y. A. *Izv. Akad. Nauk, Ser. Khim.* **1995**, *6*, 1146.

10.1021/om020318v CCC: $22.00 © 2002 American Chemical Society
Publication on Web 08/01/2002

Table 1. Selected Data for 1a, 1b, 2a, 2a(THF)$_2$, and 2b

	^{1}H NMR (C_6D_6), δ	^{13}C NMR (C_6D_6), δ	^{29}Si NMR (C_6D_6), δ
1a	1.082 (s; 3 *t*Bu)	22.7 (s; *C*Me$_3$), 29.8 (s; C*Me$_3$*)	9.80 (s; Si*t*Bu$_3$)
1b	0.970 (s; 2 *t*Bu), 7.161 (m; 3H o/p-Ph), 7.599 (m; 2H m-Ph)	20.5 (s; *C*Me$_3$), 28.2 (s; C*Me$_3$*), 128.4 (s; m-Ph), 129.2 (s; p-Ph), 134.8 (m; o-Ph), 136.6 (s; i-Ph)	2.02 (s; SiPh*t*Bu$_2$)
2a	1.176 (s; 3 *t*Bu)	23.4 (s; *C*Me$_3$), 31.5 (s; C*Me$_3$*).	−6.17 (s; Si*t*Bu$_3$).
2a(THF)$_2$[11]	1.161 (s; 3 *t*Bu), 1.412 (m; 4 CH$_2$), 3.590 (m; 4 OCH$_2$)	23.4 (s, 3 *C*Me$_3$), 31.6 (s, 3 C*Me*$_3$), 25.3 (s, *C*H$_2$), 68.0 (s, O*C*H$_2$)	−5.10 (s, Si*t*Bu$_3$)
2b	1.076 (s; 2 *t*Bu), 7.198 (m; 3H o/p-Ph), 7.736 (m; 2H m-Ph)	21.0 (s; *C*Me$_3$), 29.5 (s; C*Me$_3$*), 128.1 (s; m-Ph), 129.2 (s; p-Ph), 134.3 (m; o-Ph), 138.0 (s; i-Ph)	−6.62 (s; SiPh*t*Bu$_2$)

Scheme 2

$$10\ tBu_3SiNa + 6\ O_2 \xrightarrow[-2\ NaO_2]{(i)} 8\ tBu_3SiONa + tBu_3Si\text{-}SitBu_3$$

$$R_3SiNa + N_2O \xrightarrow[-N_2]{(ii)} R_3SiONa$$

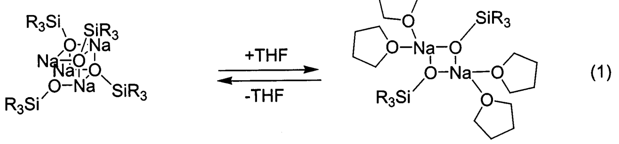
2a: $R_3Si = tBu_3Si$
2b: $R_3Si = tBu_2PhSi$

were obtained from the thermolysis of $tBu_3SiNaN{-}N{=}NSitBu_3$ in the presence of water, as indicated in Scheme 1.

The synthesis of tBu_3SiONa was achieved in two different ways, as depicted in Scheme 2: oxidation of (i) tBu_3SiNa[8] with O_2 at ambient temperature; (ii) tBu_3SiNa with N_2O at −78 °C.

The synthesis of **2a** according to method 2 is preferable to method 1, because **2a** is obtained in high purity and very good yield without $tBu_3Si{-}SitBu_3$ as byproduct. Obviously, in the solution the bulky silanide, tBu_3SiNa, undergoes Si−O bond forming reactions with N_2O as H_3Si^- or Me_3Si^- does in the gas phase. Ab initio calculations for the reaction of H_3Si^- with N_2O suggest a complex reaction pathway.[9]

In a similar way, the siloxide **2b** can be obtained almost quantitatively from the sodium silanide $tBu_2PhSiNa$[10] with N_2O in tetrahydrofuran at −78 °C. Removal of the solvent in vacuo gave the solid siloxides **2a** and **2b**, which were extracted with heptane. These heptane extracts yielded colorless crystals of the siloxides **2a** and **2b**, which are still only moderately sensitive to moisture. The tetrahydrofuran adduct **2a** could be crystallized from a solution of **2a** in tetrahydrofuran or in pentane/tetrahydrofuran (see eq 1).[11]



(1)

2a **2a(THF)$_2$**

$R_3Si = tBu_3Si$

For the preparation of siloxides it is generally advantageous to combine the appropriate silanides and N_2O at low temperature. For the synthesis of **1a** and **1b**, the sodium siloxides **2a** and **2b** were protonated with 1 equiv of water as indicated in eq 2.

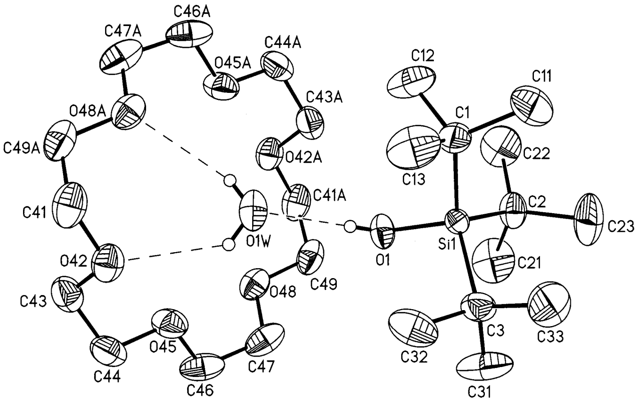


Figure 1. Thermal ellipsoid plot of **1a** showing the atom-numbering scheme. The displacement ellipsoids are drawn at the 50% probability level.

$$R_3SiONa + H_2O \xrightarrow{-NaOH} R_3SiOH \qquad (2)$$

2a: $R_3Si = tBu_3Si$
2b: $R_3Si = tBu_2PhSi$

The NMR spectra of **2a** and **2b** exhibit the same general features. The most remarkable difference between the sodium siloxides **2a** and **2b** on one hand and the silanols **1a** and **1b** on the other hand is manifested in an upfield shift of the ^{29}Si resonances of **2a** and **2b**. In comparison to the ^{1}H NMR spectra of sodium siloxides, a significant upfield shift of the *t*Bu proton resonance is observed for the silanols **1a** and **1b**. Table 1 shows the NMR data in detail.

Figure 1 represents the molecular structure of the silanol **1a**. **1a** (monoclinic, *C*2/*c*) cocrystallizes in an equimolar ratio with 18-crown-6 and water. The distance of 1.6407(14) Å represents a characteristic value for an O−Si bond. The crystal packing shows three intermolecular O···H···O contacts between the silanol, water, and the crown-ether (O···H···O distances: O(1)−O(1W) 2.715(2) Å, O(42)−O(1W) 2.982(2) Å, O(48A)−O(1W) 3.040(2) Å). The crystal structure of **2a** is shown in Figure 2 (**2b** is analogously structured to **2a**); the selected bond lengths and angles are listed in Table 3. X-ray quality crystals of **2a** (triclinic, $P\bar{1}$) and **2b** (triclinic, $P\bar{1}$) were grown from heptane. The central cores of sodium siloxides **2a** and **2b** possess a distorted heterocubane structure. The corners of these cubes are alternately occupied by O and Na atoms (**2a**: O−Na−O 98.2(2)°, Na−O−Na 81.4(2)°; **2b**: O−Na−O 96.1(2)°,

---

(8) Wiberg, N.; Amelunxen, K.; Lerner, H.-W.; Schuster, H.; Nöth, H.; Krossing, I.; Schmidt-Amelunxen, M.; Seifert, T. *J. Organomet. Chem.* **1997**, *542*, 1.

(9) Sheldon, C. S.; Bowie, J. H.; DePuy, C. H.; Damrauer, R. *J. Am. Chem. Soc.* **1986**, *108*, 6794.

(10) Lerner, H.-W.; Scholz, S.; Bolte, M. *Z. Anorg. Allg. Chem.* **2001**, *627*, 1638.

(11) Lerner, H.-W.; Wiberg, N.; Borrmann, H.; Simon, A. Unpublished work: Crystal data for $tBu_3SiONa(THF)_2$: $C_{20}H_{43}NaO_3Si$, monoclinic, space group $P2_1/c$, a = 23.506(5) Å, b = 17.512(4) Å, c = 23.624(5) Å, α = 90°, β = 105.41(3)°, γ = 90°.

Table 2. Crystal Data and Structure Refinement for 1a, 2a, 2a(tBu$_3$SiSitBu$_3$)$_{0.5}$, and 2b

	1a	2a(tBu$_3$SiSitBu$_3$)$_{0.5}$	2a	2b
empirical formula	$C_{18}H_{42}O_5Si$	$C_{63}H_{138}N_4O_4Si_5$	$C_{48}H_{108}Na_4O_4Si_4$ *(C_7H_{16})	$C_{56}H_{92}Na_4O_4Si_4$
color	colorless	colorless	colorless	colorless
shape	plate	block	plate	needle
fw	366.61	1192.14	1003.76	1033.62
cryst syst	monolinic	cubic	triclinic	triclinic
space group	$C2/c$	$P2_13$	$P\bar{1}$	$P\bar{1}$
a, Å	35.058(3)	24.612(3)	13.182(2)	12.288(2)
b, Å	8.7226(8)	24.612(3)	13.297 (2)	12.335(2)
c, Å	15.150(1)	24.612(3)	21.319(3)	24.072(3)
α, deg	90	90	73.45(1)	96.53(1)
β, deg	100.583(7)	90	87.01(1)	96.44(1)
γ, deg	90	90	62.62(1)	111.75(1)
volume, (Å^3), Z	4554.0(6), 8	14909(3), 8	3167.1(8), 2	3319.5(9), 2
density(calcd), Mg/m^3	1.069	1.062	1.053	1.034
abs coeff μ(Mo Kα), mm^{-1}	0.124	0.159	0.158	0.153
F(000)	1632	5296	1114	1120
cryst size, mm^3	$0.73 \times 0.71 \times 0.28$	$0.32 \times 0.28 \times 0.16$	$0.20 \times 0.20 \times 0.08$	$0.18 \times 0.10 \times 0.08$
diffractometer	Siemens SMART-CCD	Siemens SMART-CCD	Stoe-IPDS-II	Stoe-IPDS-II
θ-range, deg	2.41–27.48	1.43–25.33	1.79–25.03	0.86–25.24
index ranges	$-44 \leq h \leq 44$, $-10 \leq k \leq 11$, $-19 \leq l \leq 18$	$-29 \leq h \leq 29$, $-29 \leq k \leq 29$, $-29 \leq l \leq 29$	$-14 \leq h \leq 15$, $-15 \leq k \leq 15$, $-25 \leq l \leq 25$	$-14 \leq h \leq 14$, $-14 \leq k \leq 14$, $-28 \leq l \leq 28$
no. of reflns collected	39 713	150 838	36 569	30 066
no. of ind reflns	5141	9115	11 178	11 873
R(int)	0.0385	0.1526	0.0981	0.1343
abs corr	empirical, SADABS	empirical, SADABS	empirical, MULABS	empirical, MULABS
$T_{\min}$, $T_{\max}$	0.915, 0.966	0.951, 0.975	0.969, 0.988	0.973, 0.988
no. of data/restraints/ params	5141/0/229	9115/0/457	11 178/0/577	11 873/23/650
goodness of fit on F^2	1.026	1.007	0.892	0.778
final R indices [$I > 2\sigma(I)$], R1, wR2	0.0541, 0.1483	0.0611, 0.1051	0.0965, 0.2152	0.0777, 0.1914
largest diff peak/hole, e Å^{-3}	0.864, −0.329	0.229, −0.247	0.737, −0.466	1.071, −0.422

Na–O–Na 83.6(2)°). In and between both compounds, no significant variations between the O–Si bonds are observed (**2a**: O–Si 1.612(5) Å; **2b**: O–Si 1.617(5) Å). However, the O–Si distances in **2a** and **2b** are shorter than in **1a**. **2a** cocrystallizes with heptane in the triclinic space group $P\bar{1}$ and with tBu$_3$Si–SitBu$_3$ in the cubic space group $P2_13$.

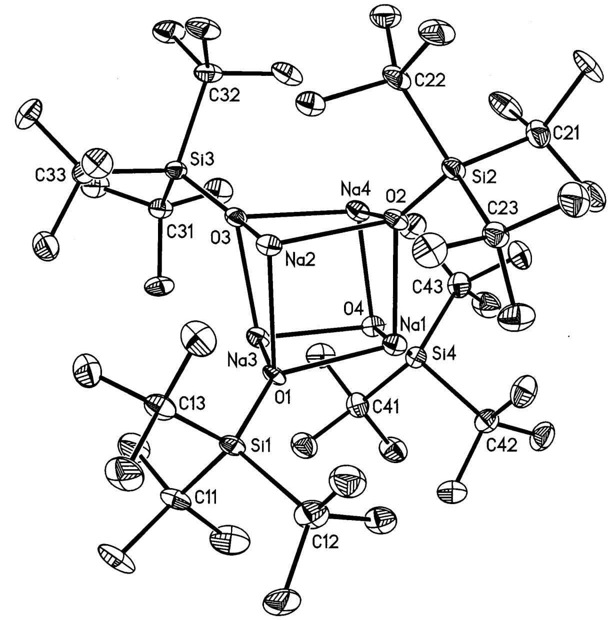


Figure 2. Thermal ellipsoid plot of **2a** showing the atom-numbering scheme. The displacement ellipsoids are drawn at the 50% probability level. **2b** is analogously structured to **2a**.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 1a[a]

Si(1)–O(1)	1.6407(14)
Si(1)–C(3)	1.917(2)
Si(1)–C(2)	1.920(2)
Si(1)–C(1)	1.924(2)
O(1)–H(1)	0.72(3)
O(1)–Si(1)–C(3)	107.14(9)
O(1)–Si(1)–C(2)	102.53(8)
O(1)–Si(1)–C(1)	108.73(8)
C–Si–C	112.58(10) (av)

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x+1/2$, $-y+3/2$, $-z+1$.

Table 4. Selected Bond Lengths (average) (Å) and Angles (av) (deg) for 2a and 2b[a]

	2a	2b
Na–O	2.308(6)	2.294(6)
O–Si	1.612(5)	1.617(5)
Si–C	1.950(10)	1.913(12)
O–Na–O	98.2(2)	96.1(2)
Na–O–Na	81.4(2)	83.6(2)
Si–O–Na	131.2(3)	128.7(3)
C–Si–C	109.4(4)	108.6(7)

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x+1$, $-y$, $-z+1$.

The supersilanol **1a** shows a C–Si–C angle greater than 110° (**1a**: 112.58(10)°), indicating a positively polarized Si atom.[12] The smaller C–Si–C angle (109.4(4)°) in the siloxide **2a** indicates that more negative charge than in **1a** is located at the silicon center.

---

(12) (a) Wiberg, N.; Amelunxen, K.; Lerner, H.-W.; Nöth, H.; Appel, A.; Knizek, J.; Polborn, K. *Z. Anorg. Allg. Chem.* **1997**, *623*, 1861. (b) Wiberg, N. *Coord. Chem. Rev.* **1997**, *163*, 217.

Experimental Section

General Procedures. All experiments were carried out under dry argon with strict exclusion of air and moisture using standard Schlenk techniques. $t\mathrm{Bu_3SiNa}$,[8] $t\mathrm{Bu_2PhSiNa}$,[10] and **1a(18-crown-6)**[11] were prepared according to literature procedures. The solvents (benzene, heptane, toluene, tetrahydrofuran) were distilled from sodium/benzophenone prior to use.

The NMR spectra were recorded on a Bruker AM 250, a Bruker DPX 250, and a Bruker AMX 400 spectrometer. The ^{29}Si NMR spectra were recorded using the INEPT pulse sequence with empirically optimized parameters for polarization transfer from the *t*Bu substituents.

Synthesis of ($t\mathbf{Bu_3SiONa}$)$_4$ (2a). $\mathrm{N_2O}$ (25.0 mmol) was passed through a cooled (−78 °C) solution of $t\mathrm{Bu_3SiNa}$ in tetrahydrofuran (10 mL, 0.5 M, 2.5 mmol). The reaction mixture became colorless. After heating to room temperature the solvent was removed in vacuo. The solid reaction product was extracted into 10 mL of heptane. X-ray quality crystals of **2a** were grown from this heptane solution at −25 °C. Yield: 95%. Selected data for **2a**: thermal decomposition of **2a**: 107 °C; NMR data are listed in Table 1. Anal. Calcd for $\mathrm{C_{12}H_{27}SiONa}$ (238.42): C, 60.45; H, 11.42. Found: C, 60.54; H, 11.23.

Synthesis of ($t\mathbf{Bu_2PhSiONa}$)$_4$ (2b). 2b was prepared similary to **2a** from $t\mathrm{Bu_2PhSiNa}$ (1.6 mmol) and $\mathrm{N_2O}$ (16.0 mmol). Yield: 93%. Selected data for **2b**: thermal decomposition of **2b**: 95 °C; NMR data are listed in Table 1. Anal. Calcd for $\mathrm{C_{14}H_{23}SiONa}$ (258.41): C, 65.07; H, 8.97. Found: C, 65.59; H, 9.04.

Synthesis of $t\mathbf{Bu_3SiOH}$ (1a). To a solution of **2a** (0.097 g, 0.41 mmol) in 10 mL of $\mathrm{CH_2Cl_2}$ was added 10 mL of a saturated aqueous solution of $\mathrm{(NH_4)_2SO_4}$. This reation mixture was well-shaken in a separation funnel. From the organic layer all volatile compounds were removed in vacuo, leaving a colorless oil behind. Yield: 92%. NMR data for **1a** are listed in Table 1.

Synthesis of $t\mathbf{Bu_2PhSiOH}$ (1b). 1b was prepared similary to **1a** from $t\mathrm{Bu_2PhSiONa}$ (0.071 g, 0.28 mmol) and $\mathrm{H_2O}$ (16.0 mmol). Yield: 94%. NMR data for **1b** are listed in Table 1.

Reaction of $t\mathbf{Bu_3SiNa}$ with Oxygen. Through a solution of $t\mathrm{Bu_3SiNa(THF)}_n$ (1.0 mmol) in 5 mL of benzene a stream of oxygen gas was passed at ambient temperature. After 30 min **2a** and as minor products superdisilane, $t\mathrm{Bu_3SiSi}t\mathrm{Bu_3}$,[13] and supersilane, $t\mathrm{Bu_3SiH}$,[13] were formed (^{1}H, ^{13}C, ^{29}Si NMR spectroscopical control molar ratio: 4:2:1). X-ray quality crystals of **2a(tBu$_3$SiSitBu$_3$)$_{0.5}$** were grown by storing this benzene solution at room temperature. $t\mathrm{Bu_3SiSi}t\mathrm{Bu_3}$: ^{1}H NMR ($\mathrm{C_6D_6}$, internal TMS): δ 1.363 (s; 6 *t*Bu). ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$, internal TMS): δ 27.3 (s; *C*Me$_3$), δ 34.6 (s; C*Me$_3$*). ^{29}Si{^{1}H}-NMR ($\mathrm{C_6D_6}$, external TMS): δ 35.4 (s; 2 Si*t*Bu$_3$). $t\mathrm{Bu_3SiH}$: ^{1}H NMR ($\mathrm{C_6D_6}$, internal TMS): δ 1.118 (s; 3 *t*Bu), δ 3.504 (s; 1 SiH). ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$, internal TMS): δ 21.0 (s; *C*Me$_3$), δ 30.8 (s; C*Me$_3$*). ^{29}Si{^{1}H}NMR ($\mathrm{C_6D_6}$, external TMS): δ 17.8 (s; Si*t*Bu$_3$).

X-ray Structure Determination. Data Collection: Stoe-IPDS-II and Siemens CCD three-circle diffractometer, graphite-monochromated Mo Kα radiation; T = 173 K, empirical absorption correction using SADABS,[14] structure solution by direct methods,[15] structure refinement by full-matrix least-squares on F^2 with SHELXL-97.[16] Hydrogen atoms were placed on ideal positions and refined with fixed isotropic displacement parameters using a riding model.

Acknowledgment. We are grateful to Professor M. Wagner, University of Frankfurt, for his generous support and to the University of Frankfurt for financial funding.

Supporting Information Available: The structures of **2b** and **2a(tBu$_3$SiSitBu$_3$)$_{0.5}$**, tables of X-ray parameters, atomic coordinates and thermal parameters, and bond distances and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

OM020318V

---

(13) Identified by comparison with the NMR data of an authentic sample, which was prepared according to a literature procedure.[8]

(14) Sheldrick, G. M. *SADABS*, a Program for Empirical Absorption Correction of Area Detector Data; University of Göttingen, Germany, 1996.

(15) Sheldrick, G. M. *Acta Crystallogr. A* **1990**, *46*, 467**.**

(16) Sheldrick, G. M. *SHELXL-97*, A Program for the Refinement of Crystal Structures; University of Göttingen, Germany, 1997.