Organometallics **2002,** *21,* 3485−3488

Siloxy Titanocene and Zirconocene Complexes Derived from the Ferriomethyl-Silanol $Cp(OC)_2Fe-CH_2-SiMe_2OH$: Synthesis and Structure of $Cp(OC)_2Fe-CH_2-SiMe_2O-M(Cl)Cp_2$ (M = Ti, Zr) and $[Cp(OC)_2Fe-CH_2-SiMe_2O]_2-ZrCp_2$[†]

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Received May 13, 2002

*Summary: The Et_3N-assisted condensation of the ferriomethyl-silanol $Cp(OC)_2Fe-CH_2-SiMe_2OH$ (**1**) with 1 equiv of Cp_2MCl_2 (M = Ti (**2a**), Zr (**2b**)) leads to the formation of the iron fragment substituted heterosiloxanes $Cp(OC)_2Fe-CH_2-SiMe_2O-M(Cl)Cp_2$ (M = Ti (**3a**), Zr (**3b**)). The bis(siloxy) zirconium complex $[Cp(OC)_2Fe-CH_2-SiMe_2O]_2-ZrCp_2$ (**4**) is obtained by further condensation of the M−Cl functionality of **3b** with **1**. The new compounds have been identified spectroscopically, and in addition, **3b** and **4** have been structurally characterized by single-crystal X-ray diffraction methods.*

Introduction

Metallo-siloxanes with an Si−O−M unit have attracted considerable interest in recent years.[1] This is mainly due to their ability to serve as model compounds for the structural and mechanistical elucidation of metal-catalyzed transformations occurring at the surface of a heterogenized catalyst.[2] Due to the great industrial importance of group 4 metal compounds in catalytic processes, e.g. in alkene epoxidation or olefin polymerization,[3] the main interest was focused on the synthesis of group 4 metallo-siloxanes, especially those deriving from bis(cyclopentadienyl)-substituted titanium and zirconium compounds.[4]

The first syntheses of group 4 metallo-siloxanes involved simple complexes of the type $L_nM-O-SiR_3$, resulting from the reaction of triorganosilanols with suitable organotitanium and -zirconium complexes.[1a] In a typical reaction the metallo-siloxanes $Cp_2Zr(OSiR_3)_2$ (R = Et, Ph) are obtained from dimethylzirconocene and 2 equiv of the triorganosilanols,[4a] whereas the equimolar reaction of Ph_3SiOH with Cp_2MCl_2 (M = Ti, Zr) in the presence of piperidine yielded the chloro functional species $Cp_2M(Cl)OSiPh_3$.[4b] Other synthetic procedures for the preparation of transition-metal heterosiloxanes involve the condensation of organosilanols with transition-metal alkoxides or -amides with elimination of alcohol or amine, respectively, as well as the reaction of transition-metal chloro complexes with organosilanolates.[1a,c]

The developments in the synthesis of stable organosilanediols and -triols and incompletely condensed silsesquioxanes have led to the successful generation of new cyclic or polyhedral metallo-siloxanes.[1b−e]

Recently, we have described the ferriomethyl-substituted silanol $Cp(OC)_2Fe-CH_2-SiMe_2OH$[5] with a bridging CH_2 group between the metal fragment and the silanol unit. This type of metallo-silanol is characterized

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[†] Synthesis and Reactivity of Silicon Transition Metal Complexes, 53. This paper is also Metallo-Silanols and Metallo-Siloxanes, 25. Part 52/24: ref 5b.

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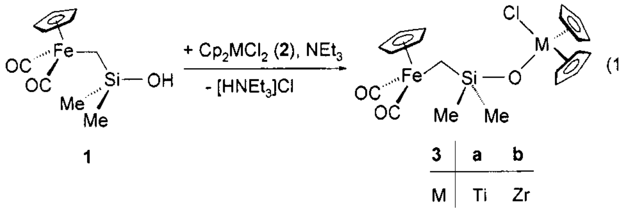
10.1021/om020385p CCC: $22.00

by an enhanced reactivity in condensation reactions compared to the analogous Fe−Si system.[6] We have now examined the reactivity of this novel silanol, which can be considered as a derivative of trimethylsilanol with a methyl hydrogen substituted by the $Cp(OC)_2Fe$ fragment, toward condensation with titanocene and zirconocene dichlorides, respectively. This procedure should give access to a novel class of multinuclear heterosiloxanes with a C−Si−O bridge between different transition-metal fragments. In the present work, the synthesis of these di- and trinuclear titanium and zirconium heterosiloxanes is presented as well as the structure of the zirconium compounds in the solid state.

Results and Discussion

The condensation reaction of $Cp(OC)_2Fe-CH_2-SiMe_2-OH$ (**1**) with titanocene and zirconocene dichloride, respectively (**2a**,**b**) in toluene in the presence of the auxiliary base triethylamine at room temperature leads to the heterosiloxanes $Cp(OC)_2Fe-CH_2-SiMe_2O-M(Cl)Cp_2$ (M = Ti (**3a**), Zr (**3b**)) in good yields of 86% and 64%, respectively (eq 1). The reaction time of 24 h reveals the higher reactivity of the silanol **1** in condensation reactions compared to that of the ferriosilanol $Cp(OC)_2Fe-SiMe_2OH$[6] and the tungsten−silanol $Cp(OC)_2(Me_3P)W-SiMe_2OH$, which have been used in a preliminary study for condensation with Cp_2MCl_2 (M = Ti, Zr) and $CpTiCl_3$.[7] In these transformations, a reaction time of 2−4 days was necessary, providing the heterosiloxanes in yields only up to 60%.



3	a	b
M	Ti	Zr

In the case of the titanium derivative **3a** using a 1:1 stoichiometry of **1** and **2a** the reaction takes place in a controlled manner; i.e., the second Ti−Cl function does not become involved in the reaction, whereas in the synthesis of the zirconium compound **3b**, even using a 2-fold excess of Cp_2ZrCl_2 (**2b**), the trinuclear species $[Cp(OC)_2Fe-CH_2-SiMe_2O]_2ZrCp_2$ (**4**) is formed in ca. 15% yield, which reveals the higher reactivity of the remaining M−Cl functionality in **3b** compared to **3a**. This difference in reactivity of analogous titanium and zirconium complexes has previously been observed in the synthesis of the siloxy metal complexes $Cp''M(X_2)(OSiPh_3)$ and $Cp''M(X)(OSiPh_3)_2$ ($Cp'' = C_5H_3(SiMe_3)_2$; M = Ti, Zr).[8] **3b** can be isolated in pure form by repeated low-temperature fractional crystallization.

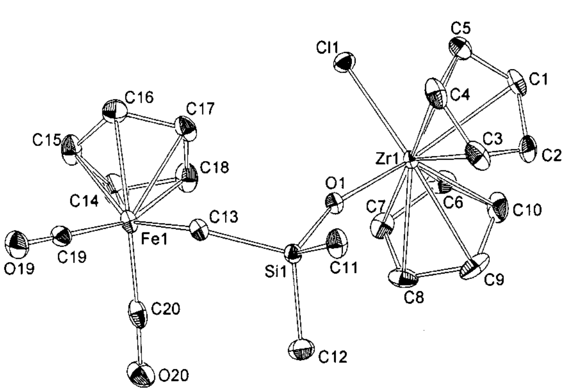
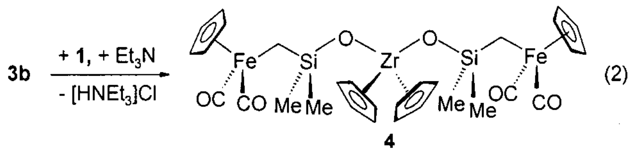


Figure 1. ORTEP plot of $Cp(OC)_2Fe-CH_2-SiMe_2-O-Zr(Cl)Cp_2$ (**3b**). Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Zr(1)−O(1), 1.9621(10); Zr(1)−Cl(1), 2.4747(4); O(1)−Si(1), 1.6490(11); Fe(1)−C(13), 2.0783(15); O(1)−Zr(1)−Cl(1), 99.29(3); Z(Cp1)−Zr(1)−Z(Cp2), 127.3(1); Si(1)−O(1)−Zr(1), 160.61(7); Si(1)−C(13)−Fe(1), 122.01(7); C(19)−Fe(1)−C(20), 92.47(7); Cl(1)−Zr(1)−O(1)−Si(1), −167.49(19); Zr(1)−O(1)−Si(1)−C(13), 166.45(18); O(1)−Si(1)−C(13)−Fe(1), 52.89(10).

The trinuclear heterosiloxane **4** can be obtained in pure form from the equimolar reaction of **3b** and **1** in diethyl ether after 68 h at room temperature in a yield of 98% (eq 2).



3a,**b** and **4** are isolated as orange (**3a**) and yellow (**3b**, **4**) microcrystalline solids with melting points of 60 °C (**3a**), 48 °C (**3b**), and 77 °C (**4**), respectively. They are only slightly soluble in aliphatic solvents such as *n*-pentane; better solubility is shown in aromatic solvents such as benzene and toluene or ethereal solvents such as diethyl ether and THF. The chloro functional species **3a**,**b** can be stored under an atmosphere of dinitrogen at −20 °C. At room temperature, partial decomposition is found after a few weeks, shown significantly by the darkening of the solids. The trinuclear species **4** reveals a higher stability and can be stored at room temperature under an atmosphere of dinitrogen for several months. It can also be handled for brief periods in air without significant decomposition.

3a,**b** and **4** show the characteristic upfield signals of the CH_2 unit detected between −0.20 and −0.31 ppm in the ^1H NMR spectra (C_6D_6) and between −21.18 and −22.60 ppm in the ^{13}C NMR spectra. In the ^{29}Si NMR spectra the signal of the titanio-heterosiloxane **3a** is nearly identical with that of the starting ferriomethylsilanol **1** (21.91 ppm (**3a**) vs 21.77 ppm (**1**)),[5] whereas the signals of the zirconium compounds **3b** and **4** are shifted 4−8 ppm to higher field (18.03 (**3b**) and 14.21 (**4**) ppm).

Pale yellow crystals of **3b** and **4**, suitable for X-ray analysis, could be obtained from saturated solutions from *n*-pentane at 0 °C.

The crystal structures (Figures 1 and 2) reveal a distorted pseudo-tetrahedral ligand environment around the zirconium atom with the largest angle between the

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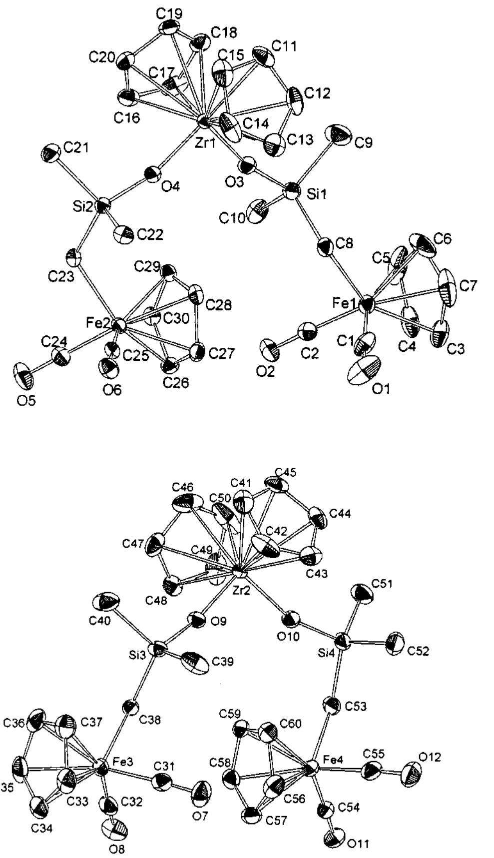

Figure 2. ORTEP plot of the two crystallographically independent molecules of $[Cp(OC)_2Fe-CH_2-SiMe_2-O]_2-ZrCp_2$ (**4**). Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Zr1−O3, 1.9545(13); Zr1−O4, 1.9707(13); Zr2−O9, 1.9677(12); Zr2−O10, 1.9724(14); Si1−O3, 1.6441(14); Si2−O4, 1.6361(14); Si3−O9, 1.6377(13); Si4−O10, 1.6350(15); Fe1−C8, 2.085(2); Fe2−C23, 2.0893(19); Fe3−C38, 2.0968(18); Fe4−C53, 2.083(2); Cp(Z)−Zr1−Cp(Z), 127.06; Cp(Z)−Zr2−Cp(Z), 126.70; O3−Zr1−O4, 100.90(5); O9−Zr2−O10, 100.89(6); Zr1−O3−Si1, 167.50(9); Zr1−O4−Si2, 165.33(8); Zr2−O10−Si4, 161.69(9); Zr2−O9−Si3, 167.84(9); Fe1−C8−Si1, 119.47(11); Fe2−C23−Si2, 118.43(10); Fe4−C53−Si4, 118.58(11); Si3−C38−Fe3, 119.06(10); Zr1−O3−Si1−C8, 109.5(4); Zr1−O4−Si2−C23, 139.3(3); Zr2−O9−Si3−C38, 154.6(4); Zr2−O10−Si4−C53, −153.7(3); O3−Zr1−O4−Si2, −172.3(3); O4−Zr1−O3−Si1, −167.9(4); O9−Zr2−O10−Si4, −166.0(3); O10−Zr2−O9−Si3, 155.1(4).

cyclopentadienyl groups (127.3° (**3b**); 127.06°/126.70° (**4**)) and the smallest one between the two other ligands (Cl1−Zr1−O1, 99.29(3)° (**3b**); O3−Zr1−O4, 100.90(5)°/O9−Zr2−O10, 100.89(6)° (**4**)), typical for d^0 complexes of the type Cp_2MX_2.[9] The Zr−O bond distances (1.9621(10) Å (**3b**); 1.9545(13)−1.9724(14) Å (**4**)) are significantly shortened compared to the sum of the covalent radii of zirconium and oxygen (2.26 Å) and are in the range of the values found in the related zirconocene siloxy complexes $Cp_2Zr(Cl)OSiPh_3$ (average 1.965(6) Å)[4b] and $[Cp_2Zr(\mu\text{-}OSiPh_2O)]_2$ (average 1.977(3) Å)[4c] as well as in the zirconocene alkoxy complex $Cp_2Zr(O\text{-}t\text{Bu})Ru(CO)_2Cp$ (1.91 Å)[10] or in the oxo-bridged zirconocene complexes $[Cp_2ZrR]_2O$ (R = Cl,[11a] Me,[11b] SPh[11c]) and $[Cp_2ZrO]_3$[11d] (1.94−1.96 Å), in which a Zr=O double bond is suggested. This is also in good accordance with the large Zr−O−Si bond angles of 160.61(7)° (**3b**) and 161.69(9)−167.84(9)° (**4**), which reveal a significant $d_\pi(Zr)-p_\pi(O)$ bond interaction typical for R_3SiO ligands at electron-deficient metal centers.[12]

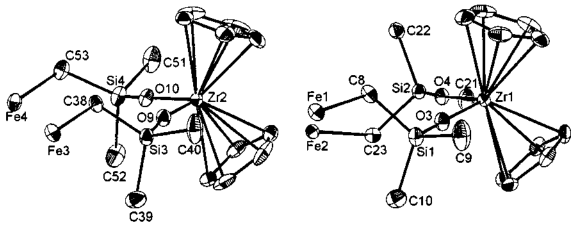

Figure 3. View of the arrangement of the $Zr(OSiCFe)_2$ backbone of the two molecules of **4**: (left) chair isomer; (right) twist isomer.

All Si−O bond lengths of **3b** and **4** lie in the normal range between 1.6350(15) and 1.6490(13) Å and are only slightly shortened compared to the Si−O bond distance of the ferriomethyl-silanol **1** (1.6599(13)/1.6558(13) Å).[5] The Zr−Cl bond length of **3b**, with a value of 2.4747(4) Å, is only slighty elongated compared to that of Cp_2ZrCl_2 (2.44 Å).[13]

In the case of **4**, two crystallographically independent molecules are found in the asymmetric unit, which show a difference in the conformation of the $Zr(OSiCFe)_2$ backbone (Figure 3). In the one case a chair-like arrangement is found with a mirror plane including Zr2 and the bisector of the O10−Zr2−O9 angle. In the other case a twist conformation can be observed with approximately C_2 symmetry of the $Zr(OSiCFe)_2$ unit.

Experimental Section

General Considerations. All manipulations were performed under an atmosphere of purified and dried nitrogen using standard Schlenk-type techniques. Solvents were dried according to conventional procedures, distilled, and saturated with N_2 prior to use. NMR spectra were recorded at room temperature on a JEOL JNM-LA 300 spectrometer. All chemical shifts are in ppm referenced to solvent signals (^1H and ^{13}C) or to the external standards H_3PO_4 (^{31}P) and TMS (^{29}Si). IR spectra were recorded using a Perkin-Elmer 283 grating spectrometer. Samples were prepared as solutions in a NaCl cell. Melting points were obtained by differential thermoanalysis (Du Pont 9000 Thermal Analysis System). Elemental analyses were performed in the laboratories of the Institut für Anorganische Chemie der Universität Würzburg. The starting materials $Cp(CO)_2Fe-CH_2-SiMe_2OH$[5] and Cp_2MCl_2 (M = Ti,[14a] Zr[14b]) were prepared according to literature procedures.

Synthesis of $Cp(OC)_2Fe-CH_2-SiMe_2O-Ti(Cl)Cp_2$ (3a). A solution of 110 mg (0.41 mmol) of $Cp(OC)_2Fe-CH_2-SiMe_2\text{-}OH$ (**1**) and 50 mg (0.49 mmol) of Et_3N in 80 mL of toluene was treated with 99 mg (0.49 mmol) of Cp_2TiCl_2 and stirred for 24 h at room temperature. The reaction mixture was filtered through a Celite pad and the filtrate evaporated in vacuo. The orange-brown residue was extracted five times with *n*-pentane (each 10 mL), and the combined extracts were

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reduced in volume to 8 mL. **3a** was crystallized at −80 °C and dried in vacuo. Yield: 187 mg (86%) of an orange, microcrystalline solid. Mp: 60 °C dec. ^{1}H NMR (300.4 MHz, C_6D_6): δ 5.97 (s, 10 H, $(H_5C_5)_2Ti$), 4.25 (s, 5 H, $(H_5C_5)Fe$), 0.31 (s, 6 H, H_3C), −0.22 ppm (s, 2 H, H_2C). $^{13}C\{^{1}H\}$ NMR (75.5 MHz, C_6D_6): δ 218.23 (s, CO), 117.00 (s, $(C_5H_5)_2Ti$), 85.10 (s, C_5H_5-Fe), 3.51 (s, CH_3), −22.52 ppm (s, CH_2). $^{29}Si\{^{1}H\}$ NMR (59.6 MHz, C_6D_6): δ 21.91 ppm (s). IR (THF): $\tilde{\nu}$(CO) 2003 (s), 1946 (vs) cm^{-1}. Anal. Calcd for $C_{20}H_{23}ClFeO_3SiTi$: C, 50.18; H, 4.84. Found: C, 49.78; H, 4.96.

Synthesis of $Cp(OC)_2Fe-CH_2-SiMe_2O-Zr(Cl)Cp_2$ (3b). This compound was prepared as described in the synthesis of **3a** from 321 mg (1.21 mmol) of $Cp(OC)_2Fe-CH_2-SiMe_2OH$ (**1**), 605 mg (2.07 mmol) of Cp_2ZrCl_2 (**2b**), and 292 mg (2.88 mmol) of Et_3N in 60 mL of toluene with stirring for 24 h at room temperature. The combined *n*-pentane extracts were reduced in volume to 20 mL and stored at −80 °C. **3b** crystallizes as a yellow solid, which contains small amounts of the trinuclear compound $[Cp(OC)_2Fe-CH_2-SiMe_2O]_2-ZrCp_2$ (**4**). Recrystallization from 20 mL of *n*-pentane/diethyl ether (4:1) at −30 °C affords pure **3b**. Yield: 404 mg (64%) of a yellow microcrystalline solid. Mp: 48 °C. ^{1}H NMR (300.4 MHz, C_6D_6): δ 6.01 (s, 10H, $(H_5C_5)_2Zr$), 4.27 (s, 5H, $(H_5C_5)Fe$), 0.27 (s, 6H, H_3C), −0.31 ppm (s, 2H, H_2C). $^{13}C\{^{1}H\}$ NMR (75.5 MHz, C_6D_6): δ 218.17 (s, CO), 113.94 (s, $(C_5H_5)_2Zr$), 85.01 (s, C_5H_5-Fe), 3.76 (s, CH_3Si), −22.60 ppm (s, CH_2). $^{29}Si\{^{1}H\}$ NMR (59.6 MHz, C_6D_6): δ 18.03 ppm (s). IR (*n*-pentane): $\tilde{\nu}$(CO) 2000 (s), 1956 cm^{-1} (vs). Anal. Calcd for $C_{20}H_{23}ClFeO_3SiZr$: C, 46.02; H, 4.44. Found: C, 46.15; H, 4.63.

Synthesis of $[Cp(OC)_2Fe-CH_2-SiMe_2O]_2ZrCp_2$ (4). A solution of 171 mg (0.33 mmol) of $Cp(OC)_2Fe-CH_2-Si(Me_2)O-Zr(Cl)Cp_2$ (**3b**) and 73 mg (0.72 mmol) of Et_3N in 40 mL of diethyl ether was treated with a solution of 95 mg (0.36 mmol) of $Cp(OC)_2Fe-CH_2-SiMe_2OH$ (**1**) in 10 mL of diethyl ether and stirred for 68 h at room temperature. All volatiles were removed in vacuo, and the residue was treated with 20 mL of *n*-pentane. The reaction mixture was filtered through a Celite pad, and the filtrate was reduced in volume to 5 mL, in which **4** precipitates as a yellow powder. The supernatant liquid was cooled to 0 °C, upon which additional **4** was obtained. The combined solids were dried in vacuo. Yield: 242 mg (98%) of a yellow microcrystalline powder. Mp: 77 °C. ^{1}H NMR (300.4 MHz, C_6D_6): δ 6.12 (s, 10H, $(H_5C_5)_2Zr$), 4.27 (s, 10H, $(H_5C_5)Fe$), 0.32 (s, 12H, H_3CSi), −0.20 ppm (s, 4H, H_2C). $^{13}C\{^{1}H\}$ NMR (75.5 MHz, C_6D_6): δ 218.19 (s, CO), 112.45 (s, $(C_5H_5)_2Zr$), 84.93 (s, C_5H_5Fe), 4.08 (s, CH_3Si), −21.18 ppm (s, CH_2). $^{29}Si\{^{1}H\}$ NMR (59.6 MHz, C_6D_6): δ 14.21 ppm (s). IR (*n*-pentane): $\tilde{\nu}$(CO) 2001 (s), 1958 cm^{-1} (vs). Anal. Calcd for $C_{30}H_{36}Fe_2O_6Si_2Zr$: C, 47.94; H 4.83. Found: C, 47.60; H, 4.81.

X-ray Crystal Structure Analyses of 3b and 4. The intensities were measured with a Nonius-Kappa CCD diffractometer (Mo Kα radiation, λ = 0.710 73 Å, graphite monochromator) at T = 123(2) K (**3b**) and 133(2) K (**4**). The structures were solved by direct methods (Patterson methods)[15] (SHELXS-97) and refined by least-squares methods based on F^2 with all measured reflections (SHELXL-97) (full-matrix least-squares on F^2).[16] Non-hydrogen atoms were refined anisotropically, and H atoms were localized by difference electron density and refined using a "riding" model. An empirical absorption correction was applied.

Crystal data for **3b**: $C_{20}H_{23}ClFeO_3SiZr$; $M_r = 521.99$; monoclinic, space group $P2_1/c$; $a = 12.1178(1)$ Å, $b = 11.5202(1)$ Å, $c = 14.8496(1)$ Å, $\beta = 90.370(1)°$, $V = 2072.95(3)$ Å^3, $D_c = 1.673$ g cm^{-3}, $Z = 4$; full-matrix least-squares on F^2 with R1 = 0.0163 and wR2 = 0.0423 for 3649 symmetry-independent reflections.

Crystal data for **4**: $C_{30}H_{36}Fe_2O_6Si_2Zr$; $M_r = 751.69$; triclinic, space group $P\bar{1}$, $a = 13.0206(8)$ Å, $b = 14.0946(8)$ Å, $c = 19.5383(12)$ Å, $\alpha = 82.7700(10)°$, $\beta = 84.9360(10)°$, $\gamma = 66.2950(10)°$, $V = 3254.2(3)$ Å^3, $D_c = 1.534$ g cm^{-3}, $Z = 4$; full-matrix least-squares on F^2 with R1 = 0.0308 and wR2 = 0.0755 for 14 670 symmetry-independent reflections.

Acknowledgment. We gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft (Schwerpunktprogramm "Spezifische Phänomene in der Siliciumchemie") as well as from the Fonds der Chemischen Industrie.

Supporting Information Available: Tables of crystal data and refinement parameters, bond lengths and angles, and positional and thermal parameters for **3b** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM020385P

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