Inorg. Chem. **2003**, *42*, 970–973

Inorganic Chemistry

Article

Synthesis and X-ray Crystal Structure of $[(THF)Zn(O_2(OH)SiR)]_4$ (R = $(2,6\text{-}i\text{-}Pr_2C_6H_3)N(SiMe_3)$): Enroute to Larger Aggregates[†]

Ganapathi Anantharaman,[‡] Herbert W. Roesky,*,[‡] Hans-Georg Schmidt,[‡] Mathias Noltemeyer,[‡] and Jiri Pinkas[§]

Institut für Anorganische Chemie der Universität Göttingen, Tammannstrasse 4,
D-37077 Göttingen, Germany, and Department of Inorganic Chemistry,
Masaryk University, CZ-61137 Brno, Czech Republic

Received August 14, 2002

Reaction of aminosilanetriol $RSi(OH)_3$ (**1**) (R = $(2,6\text{-}i\text{-}Pr_2C_6H_3)N(SiMe_3)$) with diethyl zinc at room temperature in 1:1 stoichiometric ratio affords $[(THF)Zn(O_2(OH)SiR)]_4$ (**2**) (R = $(2,6\text{-}i\text{-}Pr_2C_6H_3)N(SiMe_3)$) in good yield. The single-crystal X-ray diffraction studies reveal that **2** is monoclinic, $P2_1$, with $a = 17.117(3)$ Å, $b = 16.692(5)$ Å, $c = 17.399(4)$ Å, $\alpha = \gamma = 90°$, $\beta = 91.45(7)°$, and $Z = 2$. The molecular structure of **2** contains two puckered eight-membered $Zn_2Si_2O_4$ rings, which are connected by the Zn–O bonds and form two planar four-membered Zn_2O_2 rings. Compound **2** contains an unreacted hydroxyl group on each silicon atom, and hence, we carried out the reactions of **2** with dimethylzinc and methyllithium to form $[Zn_4(THF)_4(MeZn)_4(O_3SiR)_4]$ (**3**) (R = $(2,6\text{-}i\text{-}Pr_2C_6H_3)N(SiMe_3)$) and $[(L)ZnLi(O_3SiR)]_4$ (**4**) (L = $1,4\text{-}(Me_2N)_2C_6H_4$, R = $(2,6\text{-}i\text{-}Pr_2C_6H_3)N(SiMe_3)$), respectively. This suggested that **2** could be an intermediate product formed during the synthesis of **3** and **4**.

Introduction

The Si−O−M linkages are the basic structural units present in the naturally occurring silicate minerals in the earth's crust and in the synthetic zeolites. The type of the Si−O linkages predominantly determines the structure of these minerals and the nature of the metal atoms; they can form cyclic, chain, and sheet type structures or three-dimensional frameworks as in zeolites.[1] The presence of a metal in the siloxane framework increases the thermal stability and improves the catalytic and conducting properties. The studies on metal-incorporated zeolites and metal-doped silica surfaces, used as catalysts, emerged as an important topic of research in last two decades.[2−5] Moreover, the introduction of zinc species into H−ZSM-5 increases the rate and selectivity of the aromatization reaction of alkanes. Also, Zn/H−ZSM-5 is used as a catalyst due to the Lewis acidic nature of the zinc atoms, for the conversion of methyl halides to hydrocarbons and for the dehydrofluorination of

---

* To whom correspondence should be addressed. E-mail: hroesky@gwdg.de. Fax: +49-551-393373.

[†] Dedicated to Professor Lev Yagupolskii on the occasion of his 80th birthday.

[‡] Universität Göttingen.

[§] Masaryk University.

(1) (a) Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, 5th ed.; John Wiley and Sons: New York, 1999. (b) Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Clarendon Press: Oxford, U.K., 1984. (c) Baerlocher, C.; Meier, W. M.; Olson, D. H. *Atlas of Zeolite Framework Types*, 5th ed.; Elsevier: Amsterdam, 2001.

(2) (a) Yermanov, Y. I.; Kuznetsov, B. N.; Zakharov, V. A. *Catalysis by Supported Complexes*; Elsevier: Amsterdam, 1981. (b) Seiyama, T.; Tanabe, K. *New Horizons in Catalysis*; Elsevier: Amsterdam, 1980. (c) Harley, F. R. *Supported Metal Complexes*; Reidel: Boston, MA, 1985. (d) Cornils, B.; Hermann, W. A. *Applied Homogeneous Catalysis with Organometallic Compounds*; VCH: Weinheim, Germany, 1996.

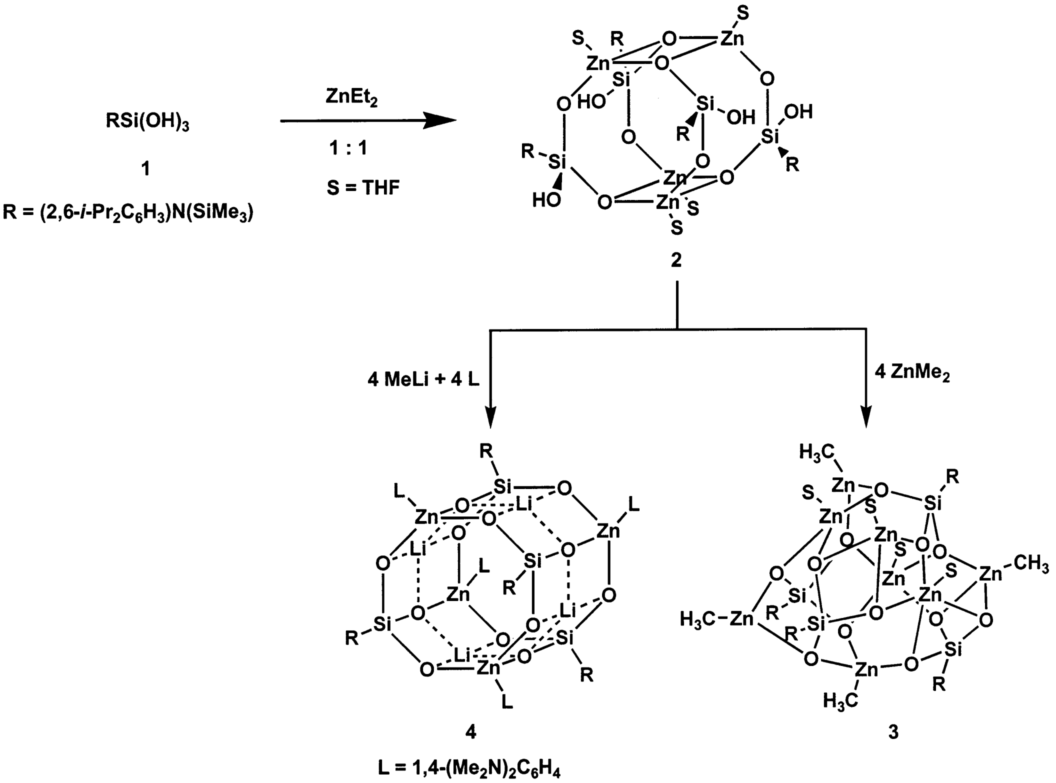
(3) (a) Frash, M. V.; van Santen, R. A. *Phys. Chem. Chem. Phys.* **2000**, *2*, 1085. (b) Kumar N.; Linfors, L.-E. *Catal. Lett.* **1996**, *38*, 239. (c) Bhaumik, A.; Kumar, R. *J. Chem. Soc., Chem. Commun.* **1995**, 869. (d) Zhao, D.; Goldfarb, D. *J. Chem. Soc., Chem. Commun.* **1995**, 875. (e) Gao, H.; Suo, J.; Li, S. *J. Chem. Soc., Chem. Commun.* **1995**, 835. (f) Serano, D. P.; Li, H.-X.; Davis, M. E. *J. Chem. Soc., Chem. Commun.* **1992**, 745. (g) Ono, Y. *Catal. Rev.*—*Sci. Eng.* **1992**, *34*, 179. (h) Cauqui, J. J.; Calvino, G.; Cifredo, L.; Esquivias, J. M.; Rodríguez-Izquierdo, J. *J. Non-Cryst. Solids* **1992**, *147/148*, 758. (i) Reddy, J. S.; Kumar, R. *J. Catal.* **1991**, *130*, 440. (j) Reddy, J. S.; Kumar, R.; Ratnasamy, P. *Appl. Catal.* **1990**, *58*, L1.

(4) (a) Perego, G.; Ballassi, G.; Corno, C.; Tamarasso, M.; Buonuomo, F.; Esposito, A. In *Studies in Surface Science and Catalysis, New Developments in Zeolite Science and Technology*; Muratami, Y., Iijima, A., Word, J. W., Eds.; Elsevier: Amsterdam, 1986. (b) Boccuti, M. R.; Rao, K. M.; Zecchina, A.; Leofanti, G.; Petrini, G. In *Structure and Reactivity of Surfaces*; Morterra, C., Zecchina, A., Costa, G., Eds.; Elsevier: Amsterdam, 1989; p 133.

(5) (a) Biscardi, J. A.; Meitzner, G. D.; Iglesia, E. *J. Catal.* **1998**, *179*, 192. (b) Circolo, M. F.; Norby, P.; Hanson, J. C.; Corbin, D. R.; Grey, C. P. *J. Phys. Chem. B* **1999**, *103*, 346. (c) Murray, D. K.; Howard, T.; Goguen, P. W.; Krawietz, T. R.; Haw, J. F. *J. Am. Chem. Soc.* **1994**, *116*, 6354. (d) Murray, D. K.; Chang, J. W.; Haw, J. F. *J. Am. Chem. Soc.* **1993**, *115*, 4732. (e) Isao, M.; Czarny, Y. Z.; Oszczudlowski, J. *J. Appl. Chem.* **1991**, *3*, 187.

10.1021/ic020514u CCC: $25.00

Scheme 1. Synthesis of Zinc Siloxane Starting from Aminosilanetriol **1**



Freons. Although the catalytic properties of the Zn/H−ZSM-5 system are reported, no structural investigation of the catalytic center has been described.[5] Earlier, the studies on metallasiloxanes have shown that these compounds are equally important because of their ability to act as model compounds for the complex zeolite systems.[6]

Currently, we have focused our attention on the formation of larger aggregates from smaller molecules. In recent years we have successfully synthesized a variety of organic soluble metallasiloxanes[6a,7] and metallaphosphonates,[8] starting from aminosilanetriol **1** and alkyl phosphonic acids with metal alkyls. Some of the structures of these products are comparable with the secondary building units (SBUs) of the naturally occurring molecular sieves and zeolite systems. Furthermore, these compounds can be utilized as precursors for the corresponding metal-containing silicate systems.[7] Consequently, we have been interested in synthesizing aggregates of zinc siloxanes to mimic condensation processes.

There are several methods reported for the synthesis of zinc siloxanes starting from monosilanol with alkyl- or amido-substituted zinc derivatives.[9] However, the degree of aggregation in these compounds is limited to a cubic tetranuclear zinc siloxane. Earlier, we have reported an oligomeric zinc siloxane compound [(L)ZnLi(O$_3$SiR)]$_4$ (**4**) (L = 1,4-(Me$_2$N)$_2$C$_6$H$_4$, R = (2,6-*i*-Pr$_2$C$_6$H$_3$)N(SiMe$_3$)) prepared from dimethylzinc, methyllithium, and kinetically stable aminosilanetriol **1** (Scheme 1).[10] Instead of using methyllithium in **4**, the addition of an excess of dimethylzinc to **1** (2:1 ratio) afforded the so far largest aggregate of zinc siloxane [Zn$_4$(THF)$_4$(MeZn)$_4$(O$_3$SiR)$_4$] (**3**) (R = (2,6-*i*-Pr$_2$C$_6$H$_3$)N(SiMe$_3$)). This result has been reported in a communication.[11] Subsequently, we were interested in the product from the reaction between zinc alkyl and **1** in a 1:1 stoichiometric ratio. In this case we have obtained tetrameric zinc siloxane [(THF)Zn(O$_2$(OH)SiR)]$_4$ (**2**) containing an unreacted OH group on each silicon atom. Herein we wish to report on the synthesis and single-crystal X-ray diffraction studies of compound **2**. Further, we have reported the synthesis of **3** and **4** starting from **2**. It is to be noted that all three compounds (**2**−**4**) have the same stoichiometric ratio of zinc to silicon with respect to the starting material.

---

(6) (a) Murugavel, R.; Voigt, A.; Walawalkar, M. G.; Roesky, H. W. *Chem. Rev.* **1996**, *96*, 2205. (b) Voronkov, M. G.; Maletina, E. A.; Roman, V. K. *Heterosiloxanes* (*Soviet Scientific Review Supplement, Series Chemistry, Vol. 1*); Academic Press: London, 1988. (c) Feher, F. J.; Budzichowski, T. A. *Polyhedron* **1995**, *14*, 3239.

(7) (a) Murugavel, R.; Chandrasekhar, V.; Roesky, H. W. *Acc. Chem. Res.* **1996**, *29*, 183. (b) Murugavel, R.; Bhattacharjee, M.; Roesky, H. W. *Appl. Organomet. Chem.* **1999**, *13*, 227 and further references therein.

(8) (a) Walawalkar, M. G.; Roesky, H. W.; Murugavel, R. *Acc. Chem. Res.* **1999**, *32*, 117 and further references therein. (b) Chakraborthy, D.; Horchler, S.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G. *Inorg. Chem.* **2000**, *39*, 3995. (c) Roesky, H. W. *Solid State Sci.* **2001**, *3*, 777.

(9) (a) Schindler, F.; Schmidbaur, H. *Angew. Chem.* **1967**, *79*, 697; *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 683. (b) Schindler, F.; Schmidbaur, H. *Angew. Chem.* **1965**, *77*, 865; *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 876. (c) Driess, M.; Merz, K.; Rell, S. *Eur. J. Inorg. Chem.* **2000**, 2517. (d) Su, K.; Tilley, T. D.; Sailor, M. J. *J. Am. Chem. Soc.* **1996**, *118*, 3459.

(10) Anantharaman, G.; Reddy, N. D.; Roesky, H. W.; Magull, J. *Organometallics* **2001**, *20*, 5777.

(11) Anantharaman, G.; Roesky, H. W.; Magull, J. *Angew. Chem.* **2002**, *114*, 1274; *Angew. Chem., Int. Ed.* **2002**, *41*, 1226.

Experimental Section

General Procedure. All manipulations were performed on a vacuum line or in the glovebox under a purified N_2 atmosphere. Solvents were distilled from Na/benzophenone ketyl prior to use. Dimethylzinc (2 M solution in toluene), diethylzinc (1.1 M solution in toluene), and *N*,*N*,*N*′,*N*′-tetramethyl-l,4-phenylenediamine (L) were purchased from Aldrich and used as received. Alkylzinc comounds were pyrophoric; hence, they were handled in a efficient fumehood by wearing adequate protective clothing. Methyllithium was purchased from Acros (1.6 M solution in toluene) and used as received. The aminosilanetriol **1** was prepared as described in the literature.[12] Elemental analyses were performed by the Analytisches Labor des Instituts für Anorganische Chemie, der Universität Göttingen. NMR spectra were recorded on a AM200 and Bruker Avance 500 instrument. Chemical shifts are reported in ppm with reference to TMS. IR spectra were recorded on a Bio-Rad FTS-7 spectrometer in Nujol mull. Melting points were measured in a sealed glass tube and were not corrected.

Synthesis of 2. A solution of $RSi(OH)_3$ (**1**) (2.0 g, 6.1 mmol) in THF/hexane (5 mL, 40 mL) was added to a solution of $ZnEt_2$ (5.6 mL of a 1.1 M solution in toluene, 6.1 mmol) in hexane (10 mL) at room temperature. After the evolution of ethane gas ceased, the resulting solution was further stirred for 16 h at room temperature. The volatile components were removed, and the residue was dried for 6 h under vacuum. The remaining solid was washed with hexane (5 mL). Colorless crystals of **2** were obtained in toluene (5 mL) at room temperature (1.85 g, 62%). Mp: 162−165 °C. ^1H NMR (500 MHz, $CDCl_3$, TMS): δ 0.03 (s, 36H; Si*Me*$_3$), 1.10 (d, 24H; J = 6.7 Hz, $CH(CH_3)(CH_3)$), 1.17 (d, 24H; J = 6.7 Hz, $CH(CH_3)(CH_3)$), 1.68 (br, 16H; OCH_2CH_2), 2.35 (s, 3H; $H_3CC_6H_5$), 3.62 (br, 16H; OCH_2), 3.70 (m, 8H; J = 6.7 Hz, $CH(CH_3)_2$), 6.94 (m, 12H; aromatic), 7.2 (m, 12H; $H_3CC_6H_5$). ^{13}C NMR (50.32 MHz, $CDCl_3$, TMS): δ 2.14 ($Si(CH_3)_3$), 21.45 ($C_6H_5CH_3$), 24.96 ($CH(CH_3)(CH_3)$), 25.06 ($CH(CH_3)(CH_3)$), 25.75 (OCH_2CH_2), 27.42 ($CH(CH_3)_2$), 69.95 (OCH_2), 123.03 (aromatic C-4), 123.36 (aromatic C-3, C-5), 125.29 (p-$C_6H_5CH_3$), 128.22 (m-$C_6H_5CH_3$), 129.03 (o-$C_6H_5CH_3$), 137.86 ($H_3C-C_6H_5$), 142.56 (aromatic C-2, C-6), 147.85 (aromatic C-1). ^{29}Si NMR (99.36 MHz, $CDCl_3$, TMS): δ 3.78 ($Si(CH_3)_3$), −62.16 ($Si(OH)O_2$). IR (ν, cm^{-1}): 3242, 1605, 1576, 1318, 1257, 1246, 1182, 1107, 1042, 1024, 967, 947, 908, 865, 823, 802, 753, 727, 693, 599, 549, 464. MS (EI, 70 eV) [*m*/*e* (assignment, %)]: 162 (2,6-*i*-$Pr_2C_6H_3$, 100%), 177 (2,6-*i*-$Pr_2C_6H_3$-NH_2, 38%). Anal. Calcd for $\mathbf{2}\cdot C_7H_8$, $C_{83}H_{148}N_4O_{16}Si_8Zn_4$: C, 51.22; H, 7.61; N, 2.88. Found: C, 50.75; H, 7.68; N, 2.87.

Synthesis of 3 from 2. A solution of $ZnMe_2$ (1.6 mL of a 2 M solution in toluene, 6.1 mmol) was added to a suspension of **2** (1.5 g, 0.77 mmol) in THF/hexane (15 mL, 30 mL) at room temperature. After the evolution of methane gas ceased, the resulting clear solution was further stirred for 16 h at room temperature. The volatile components were removed, and the residue was dried for 6 h under vacuum. The remaining solid was washed with hexane (5 mL). Colorless crystals of **3** are obtained in toluene (5 mL) at 0 °C (1.27 g, 67%).

Synthesis of 4 from 2. A solution of MeLi (5.2 mL of a 1.6 M solution in diethyl ether, 6.1 mmol) was added to a suspension of **2** (4.0 g, 2.1 mmol) in THF/hexane (10 mL, 40 mL) at room temperature. After the evolution of methane gas ceased, the resulting clear solution was further stirred for 16 h at room temperature. To the resulting solution was added solid *N*,*N*,*N*′,*N*′-tetramethyl-l,4-phenylenediamine (L) (0.64 g, 3.9 mmol), and the solution was stirred for another 4 h. The solution was filtered and concentrated to 1/3 of its volume. Colorless crystals of **4** were obtained at room temperature (2.18 g, 45%).

Table 1. Crystal Data and Structure Refinement Details for $[(THF)Zn(O_2(OH)SiR)]_4$ ($\mathbf{2}\cdot C_7H_8$) (R = (2,6-*i*-$Pr_2C_6H_3$)N($SiMe_3$))

empirical formula	$C_{83}H_{148}N_4O_{16}Si_8Zn_4$
fw	1944.25
space group	$P2_1$
a (Å)	17.117(3)
b (Å)	16.692(5) Å
c (Å)	17.399(4)
α (deg)	90
β (deg)	91.45 (7)
γ (deg)	90
V (Å$^{3)}$	4970(2)
T (K)	200(2)
λ (Å)	0.710 73
Z	2
D_{calcd} (Mg m$^{-3)}$	1.299
μ (mm^{-1})	1.109
$R1$ [$I > 2\sigma(I)$]^a	0.0569, 0.1386
wR2 (all data)^a	0.1536, 0.1536

^{a} $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $wR2 = [\Sigma w(|F_o^2| - |F_c^2|)^2/\Sigma w|F_o|^2]^{1/2}$.

X-ray Structure Determination and Refinement for Compound 2. Data for the crystal structure of **2** were collected on a Stoe-Siemens four-circle diffractometer using Mo Kα radiation (λ = 0.710 73 Å). The structure was solved by direct methods (SHELXS-96)[13] and refined against F^2 using SHELXL-97.[14] All the heavy atoms were refined anisotropically. Hydrogen atoms were included using the riding model with U_{iso} tied to the U_{iso} of the parent atoms. A summary of cell parameters, data collection, and structure solution is given in Table 1.

Results and Discussion

The reaction of **1** with $ZnEt_2$, in 1:1 molar ratio, produced predominantly **2** by sequential formation of Si−O−Zn linkages, whereas the reaction of **1** and dimethylzinc forms not only **2** but also another product for which an additional resonance was found in silicon NMR spectroscopy at 71.8 ppm. Compound **2** is highly soluble in common organic solvents, such as benzene, toluene, diethyl ether, and THF. We have fully characterized **2** by means of analytical and spectroscopic techniques. Furthermore, the structure of **2**, the single crystals obtained in the former reaction, was confirmed unambiguously by the single-crystal X-ray diffraction studies.

The IR spectrum of **2** shows a broad band around 3300 cm^{-1} for the OH stretching frequencies of the silanol groups. The ^1H NMR spectrum of **2** displays the resonances of aryl, isopropyl, and methyl groups and broad resonances assigned to the coordinated THF molecules. The appearance of two different resonances for isopropyl groups is consistent with the crystal structure of **2** if the rotation of the aromatic groups about the C−N bond is restricted. The absence of resonances of the metal-bound ethyl groups in the region of near zero suggests that both ethyl groups have reacted with the silanetriol with the formation of **2**. However, we were not able to observe the resonances of free hydroxyls on each

---

(12) Winkhofer, N.; Voigt, A.; Dorn, H.; Roesky, H. W.; Steiner, A.; Stalke, D.; Reller, A. *Angew. Chem.* **1994**, *106*, 1414; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1352.

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

(14) Sheldrick, G. M. *SHELX-97, Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.

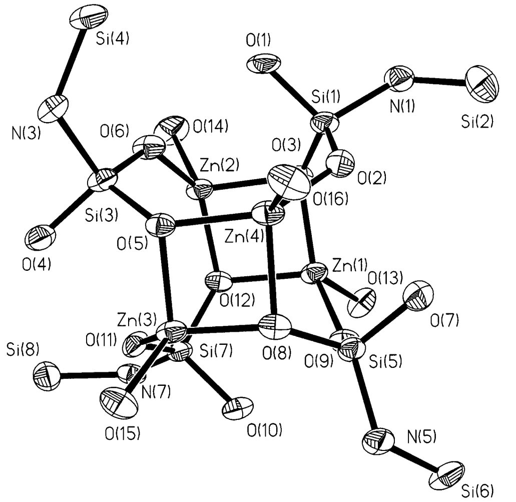


Figure 1. Core structure of **2** showing the drum polyhedron. The drawing shows 50% probability thermal ellipsoids.

silicon atom. The resonances of the SiMe$_3$ and Si(OH)O$_2$ groups were observed in the ^{29}Si NMR at 3.78 and −62.16 ppm, respectively. Moreover, the resonance due to Si(OH)-O$_2$ in ^{29}Si NMR is slightly shifted toward downfield compared to the observed value for **4** (−64.8 ppm) and it is also different from those of **3** (−60.87, −61.34).[10,11] By comparing the analytical and spectroscopic data, we were able to predict partially the structure of **2**. However, the formation of a drumlike structure was finally confirmed by the single-crystal X-ray diffraction studies.

Conversion of 2 to 3 and to 4. The formation of eight-(Zn$_2$Si$_2$O$_4$) and four-(Zn$_2$O$_2$) membered rings and the orientation of the OH groups around silicon atoms in **2** suggests that it could be reacted further to construct **3** and **4** that have been made previously from **1**.[10,11] Thus, 4 equiv of dimethylzinc reacts with **2** at room temperature to produce **3**. The fact that all of the spectroscopic and analytical data of this product were identical to those of **3**[11] strongly suggests that **2** could be an intermediate species in this reaction. Similarly, **4** was made from **2** with the addition of methyllithium in the presence of *N*,*N*,*N*′,*N*′-tetramethyl-l,4-phenylenediamine (L).

X-ray Crystal Structure of 2. The molecular structure of **2** is shown in Figure 1. Selected structural parameters are given in Table 2. The compound crystallizes in the monoclinic space group $P2_1$ with a molecule of toluene in the asymmetric unit. The molecule of **2** possesses a pseudo-4-fold (S_4) symmetry and consists of two eight-membered Zn$_2$Si$_2$O$_4$ units connected by four Zn−O bonds forming a drumlike structure. These two Zn$_2$Si$_2$O$_4$ rings are puckered and exist in a boat conformation. The four-membered Zn$_2$O$_2$ rings are almost planar, and the zinc atoms of one ring are in register with the oxygens of the second one.

The average Si−O bond length (1.61 Å) is slightly shorter than the values of the same in silantriols, whereas the Si−OH bond lengths (average 1.64 Å) are comparable with those of silanetriols.[15] There are two types of Zn−μ_3-O bond distances observed in the Zn$_2$O$_2$ rings that are also responsible for the eclipsed conformation. The bond lengths of the σ-bonded Zn−μ_3-O (Zn(1)−O(3) 1.950(7), Zn(2)−O(12) 1.938(7), Zn(3)−O(8) 1.939(8), and Zn(4)−O(5) 1.943(8)) are similar to the zinc siloxane compound reported values;[9c] however, these values are shorter than the coordinated ones (average 2.016(7) Å). The distances of coordinated Zn−μ_3-O bonds and the coordinated THF molecules are almost equal (see Table 2). The average Zn−μ_2-O (e.g. Zn(1)−O(9), Zn(2)−O(6), Zn(3)−O(11), and Zn(4)−O(2)) bond distance is 1.867(9) Å, which is shorter than the σ-bonded Zn−μ_3-O distance in the ring. The diagonal distances between the zinc atoms in Zn$_2$O$_2$ (Zn(1)−Zn(2) 2.8396(19) and Zn(3)−Zn(4) 2.850(3)) suggest that there is a weak Zn···Zn interaction.[9,11,16] The O−Zn−O bond angles within the Zn$_2$O$_2$ ring are close to 90° showing that the four-membered rings are almost perfect rectangles.

Table 2. Selected Bond Distance (Å) and Bond Angles (deg) of **2**

Si(1)−O(1)	1.625(8)	Si(1)−O(2)	1.596(8)
Si(1)−O(3)	1.585(9)	Si(3)−O(6)	1.603(7)
Si(3)−O(5)	1.633(8)	Si(3)−O(4)	1.647(9)
Zn(1)−O(9)	1.846(7)	Zn(1)−O(3)	1.950(7)
Zn(1)−O(12)	1.988(8)	Zn(1)−O(13)	2.048(7)
Zn(2)−O(6)	1.882(7)	Zn(2)−O(12)	1.938(7)
Zn(2)−O(3)	2.029(8)	Zn(2)−O(14)	2.053(8)
Zn(1)−Zn(2)	2.8396(19)	Zn(3)−Zn(4)	2.850(3)
O(3)−Si(1)−O(2)	109.1(4)	O(3)−Si(1)−O(1)	106.3(5)
O(2)−Si(1)−O(1)	113.5(4)	O(6)−Si(3)−O(5)	106.5(4)
O(6)−Si(3)−O(4)	114.6(4)	O(5)−Si(3)−O(4)	107.9(4)
O(3)−Zn(1)−O(12)	88.0(3)	O(9)−Zn(1)−O(13)	98.2(3)
O(3)−Zn(1)−O(13)	118.9(3)	O(12)−Zn(1)−O(13)	106.4(3)
O(6)−Zn(2)−O(12)	131.8(3)	O(6)−Zn(2)−O(14)	98.4(3)
O(6)−Zn(2)−O(3)	110.4(4)	O(12)−Zn(2)−O(3)	87.2(3)

Conclusion

In this paper, we have shown that changing the stoichiometric ratio of zinc alkyls with respect to the aminosilanetriol **1** leads to the formation of the new zinc siloxane compounds **2**−**4**. We have also shown that **2** can be an intermediate in the formation of **3** and **4**. The acidic protons in **2** are the reactive centers for further reactions with different metal alkyls.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft, the Göttinger Akademie der Wissenschaften, and the VW foundation.

Supporting Information Available: Single-crystal X-ray structural data for compound **2** (CIF format). This material is available free of charge via the Internet at http://pubs.acs.org.

IC020514U

---

(15) (a) Murugavel, R.; Chandrasekhar, V.; Voigt, A.; Noltemeyer, M.; Schmidt, H.-G.; Roesky, H. W. *Organometallics* **1995**, *14*, 5298. (b) Klemp, A.; Haptop, H.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G. *Inorg. Chem.* **1999**, *38*, 5832.

(16) For compounds having Zn···Zn interactions, see the following: (a) Elias, A. J.; Schmidt, H.-G.; Noltemeyer, M.; Roesky, H. W. *Organometallics* **1992**, *11*, 462. (b) Li, H.; Eddaoudi, M.; Groy, T. L.; Yaghi, O. M. *J. Am. Chem. Soc.* **1998**, *120*, 8571.