Syntheses and Molecular Structures of Metallasiloxanes Containing Zn_3O_4 and $Zn_6Si_6O_{10}$ Cores

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The trinuclear zinc siloxane $[(MeZn)_2Zn(OSiPh_3)_4]$ (**1**) and the first novel siloxane-bridged hexanuclear dimer $[\{Me(THF)Zn\}_2OZn(OSiR_2)(R^1)]_2$ (R = Ph, $R^1 = OSiR_2OSiR_2O$) (**2**) are accessible by Brønsted acid/base reaction of triorganosilanols with the zinc base $ZnMe_2$. Both compounds were characterised by NMR spectroscopy and a single-crystal X-ray structure analysis. The X-ray structures of the reported complexes are discussed.

Introduction

In recent years, a large variety of molecular metallasiloxanes (M-O-Si) have been synthesised through metallation of organosilanols.[1] These compounds have received considerable attention as versatile precursors for metal silicates[2] and doped metal oxides[3] or as molecular models for heterogeneous silica- and zeolite-supported catalytic systems.[4,5] We discovered recently that the thermolysis of molecular M-O-Si compounds with almost identical M−O and Si−O binding energies facilitates ambident decomposition pathways, affording elemental metal and/or metal oxide particles. The composition of the products can also be easily influenced by the nature of the substituents at the M and Si atoms and the reaction conditions. Thus, solid-to-solid and solid-to-vapour decomposition (CVD) of the tetranuclear zinc siloxane $[XZnOSiR_3]_4$ (X = Me, Et, I) or its polymeric analogue $[(Me_3SiO)_2Zn]_n$, affords nanocrystalline ZnO and/or Zn particles.[6]

Results and Discussion

In order to learn more about the influence of the degree of aggregation of the zinc siloxane precursors and the nature of their organic shell on the size and morphology of the produced Zn and/or ZnO particles, we have been interested in the synthesis of differently preorganised zinc siloxane aggregates. In this contribution, we describe the synthesis and characterisation of the sterically congested trinuclear zinc siloxane $[(MeZn)_2Zn(OSiR_3)_4]$ (**1**) which can be easily expanded to its hexanuclear dimer $[\{Me(THF)Zn\}_2OZn(OSiR_2)(OSiR_2OSiR_2O)]$ (**2**). The latter represents a novel type of metallasiloxane and is the first zinc polysiloxane. In accordance with recent studies, different zinc siloxane aggregates are accessible by Brønsted acid/base reaction of triorganosilanols R_3SiOH (R = Me, Et, *i*Pr) with the zinc bases ZnR_2 (R = Me, Et). Depending on the steric demand of the substituents this reaction furnishes dimeric, trimeric and tetrameric ZnO aggregates.[7,8]

Thus, the reaction of the sterically congested triphenylsilanol Ph_3SiOH with $ZnMe_2$ leads to the Zn_3O_4 aggregate **1** in 75% yield (Scheme 1). The crystal structure of **1** (Figure 1) consists of asymmetric units with a nonlinear array of three zinc atoms [Zn···Zn···Zn = 159.27(3)°] that are bridged by four triphenylsiloxy groups The spirocyclic zinc atom Zn(2) has a distorted tetrahedral geometry, whereas the two terminal zinc atoms (Zn1 and Zn3) are only trigonal-planar coordinated. The observed Zn_3O_4 core of the aggregate is in good agreement with that of the previously reported derivatives $[(MeZn)_2Zn(OSi\mathit{i}Pr_3)_4]$[7] and $[Me_3SiCH_2ZnOR]_2Zn]$ [R = (2,6-$\mathit{i}Pr_2$-C_6H_4)].[9] Remarkably, the Zn−O distances for the four-coordinate Zn(2) atom [average 1.949(3) Å] are shorter than those for the three-coordinate ones [average 1.981(3) Å] due to the greater partial positive charge at Zn(2). The inconspicuous Zn−C distances average 1.919(6) Å. While the dihedral angle between the two Zn_2O_2 planes of 86.9(1)° is close to the expected value of 90°, the endocyclic O(1)−Zn(2)−O(2) and O(3)−Zn(2)−O(4) angles are, at 84.1(1) and 86.0(1)° respectively, considerably distorted from the ideal tetrahedral value (109.5°). This large distortion is due to the strained four-membered Zn_2O_2 rings which, in turn, result in a corresponding expansion of the exocyclic O−Zn(2)−O angles [average 121.1(1)°]. To our surprise, the preference for the trinuclear structural motif of the Zn atoms in **1** is still preserved if the sterically congested Ph_3SiO groups are fully replaced by the less demanding Ph_2SiO_2 moieties.

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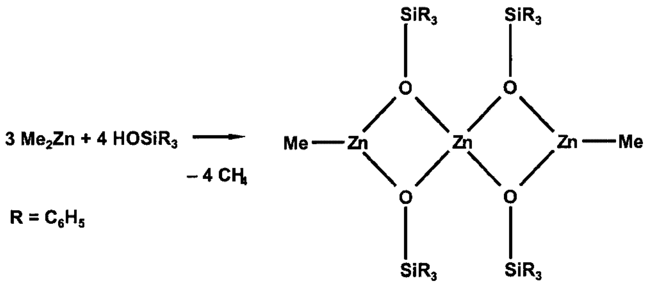

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Scheme 1

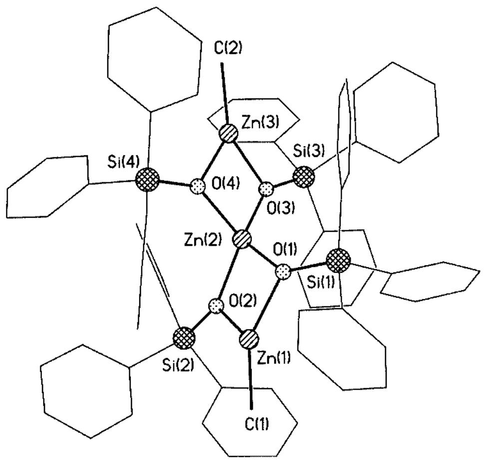


Figure 1. Molecular structure of **1**; hydrogen atoms omitted for clarity; selected distances (Å) and angles (°): Zn(2)−O(2) 1.940(3), Zn(2)−O(4) 1.949(3), Zn(2)−O(1) 1.952(3), Zn(2)−O(3) 1.957(3), Zn(1)−C(1) 1.918(5), Zn(1)−O(1) 1.954(3), Zn(1)−O(2) 2.000(3), Zn(3)−C(2) 1.919(6), Zn(3)−O(4) 1.962(3), Zn(3)−O(3) 2.011(3); O(2)−Zn(2)−O(1) 84.1(1), O(4)−Zn(2)−O(3) 86.1(1), Zn(3)−Zn(2)−Zn(1) 159.27(3), Zn(2)−O(1)−Zn(1) 96.6(1), O(4)−Zn(3)−O(3) 84.2(1), O(3)−Zn(2)−O(1) 124.4 (1), O(4)−Zn(2)−O(2) 119.6 (1), Zn(2)−O(2)−Zn(1) 95.5(1), Zn(2)−O(4)−Zn(3) 95.3(1), Zn(2)−O(3)−Zn(3) 93.5(1)

Thus, the reaction of $Ph_2Si(OH)_2$ with $ZnMe_2$ in THF leads to the hexanuclear $Zn_6Si_6O_{10}$ aggregate **2** in 52% yield (Scheme 2). Although the mechanism is still unknown, it seems likely that the initial steps involve the formation of a Zn_3O_4 core with terminal $OSi(Ph_2)OH$ functions.

Compound **2** crystallises in the monoclinic space group $P2_1/n$ with one half of the molecule in the asymmetric unit. The crystal structure of **2** (Figure 2) reveals a novel type of zinc siloxane in which two spirobicyclic Zn_3O_4 cores are linked together by two R_2Si-fragments.

Additionally, one periphery of each Zn_3O_4 core is bridged by an $Ph_2SiOSiPh_2$ moiety. The Zn atoms are tetrahedral and each of the Zn(2) and Zn(3) atoms bears one

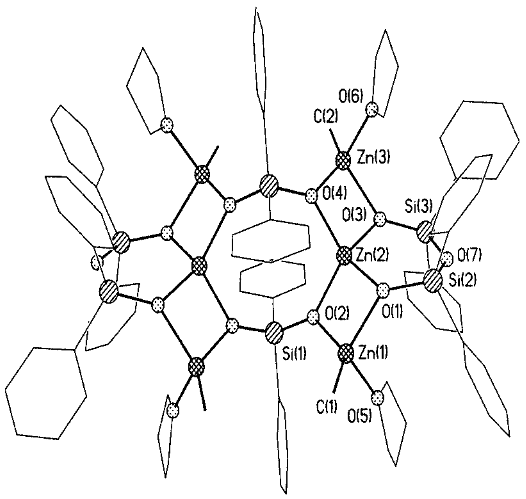
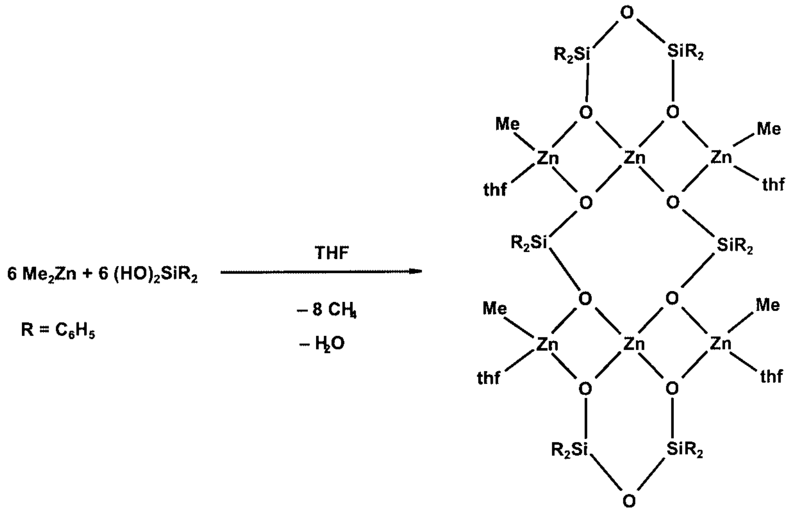


Figure 2. Molecular structure of **2**; hydrogen atoms omitted for clarity; selected distances (Å) and angles (°): Zn(2)−O(2) 1.943(2), Zn(2)−O(4) 1.947(2), Zn(2)−O(1) 1.973(2), Zn(2)−O(3) 1.983(2), Zn(1)−O(2) 2.022(2), Zn(1)−O(1) 2.026(2), Zn(3)−C(2) 1.962(3), Zn(3)−O(4) 2.003(2), Zn(3)−O(3) 2.046(2); O(2)−Zn(2)−O(1) 87.49(6), O(4)−Zn(2)−O(3) 88.08(6), Zn(3)−Zn(2)−Zn(1) 175.94(1), O(2)−Zn(1)−O(1) 83.99(6)



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Scheme 2

methyl and one THF ligand. The observed Zn_3O_4 core is practically identical to that in **1**. However, the three Zn atoms of the cores now adopt an almost linear arrangement [Zn···Zn···Zn = 175.94 (1)°]. The Zn−C distances [average 1.954 (5) Å] are longer than those in **1** due to the higher coordination number at the Zn atoms. Another striking structural feature of **2** is that the dihedral angle between the Zn(2)O_2Zn(3) and Zn(2)O_2(Zn1) planes is about 20° smaller than that in **1** [86.9(1)°]. However, the O−Zn−O and Zn−O−Zn angles are almost identical with these values in **1**. Similar to the situation in **1**, the Zn−O distances for the spiro-Zn(2) atom [average 1.962(2) Å] are conspicuously smaller than the corresponding values for Zn(1)−O and Zn(3)−O [average 2.069(2) Å].

Experimental Section

General Remarks: All manipulations were carried out under anaerobic conditions under dry argon using standard Schlenk techniques. Solvents were refluxed over an appropriate drying agent, and distilled and degassed prior to use. NMR spectra were recorded on a Bruker Avance250 spectrometer at ambient temperature operating at 250.1 MHz (^1H) or 63 MHz (^{13}C). Chemical shifts are reported relative to TMS at $\delta = 0.00$ ppm (^1H).

Preparation of [$(MeZn)_2Zn(OSiPh_3)_4$] (1): At −78 °C, a solution of $ZnMe_2$ (1.91 g, 20 mmol, 2 M solution in toluene) in toluene (ca. 50 mL) was slowly added to a solution of Ph_3SiOH (7.37 g, 26.7 mmol) in toluene (10 mL), resulting in the immediate evolution of methane. The solution was then allowed to warm to room temperature and all volatiles were removed in vacuo (10^{-3} Torr). Recrystallisation from toluene/hexane gave pure **1** as colourless crystals. Yield: 7.17 g (5.40 mmol, 81%); m.p. 221−223 °C (decomp.). ^1H NMR (C_6D_6): $\delta = -0.61$ (s, 6 H, ZnMe), 7.12−7.83 [m, 60 H, $(C_6H_5)_3Si$] ppm. ^{13}C NMR (C_6D_6): $\delta = -14.9$ (s, 2 C, ZnMe), 137.3−123.6 [m, 64 C, $(C_6H_5)_3Si$] ppm. $C_{74}H_{66}O_4Si_4Zn_3\cdot C_7H_8$ (1419.9): calcd. C 65.50, H 5.02; found C 65.30, H 5.00.

Preparation of [$\{Me(THF)Zn\}_2OZn(OSiR_2)(OSiR_2OSiR_2O)$] (2; R = Ph): Compound **2** was prepared in a similar manner as **1**, starting from $ZnMe_2$ (1.91 g, 20 mmol, 2 M solution in toluene) in toluene (ca. 50 mL) and a solution of $Ph_2Si(OH)_2$ (4.32 g, 20 mmol) in tetrahydrofuran (10 mL). Recrystallisation of the residue from tetrahydrofuran (10 mL) afforded colourless plates. Yield: 3.45 g (1.73 mmol, 52%) of a mixture of stereoisomers. ^1H NMR (C_6D_6): $\delta = -0.53$ to -1.11 (12 H, ZnMe), 7.02−8.08 [60 H, $(C_6H_5)_2Si$] ppm. ^{13}C NMR (C_6D_6): $\delta = -13.7$ to -15.3 (m, 4 C, ZnMe), 138.1−124.2 [m, 64 C, $(C_6H_5)_3Si$] ppm. $C_{92}H_{104}O_{14}Si_6Zn_6$ (1994.51): calcd. C 55.40, H 26.00; found C 55.2, H 25.95.

X-ray Crystallographic Study

1: $C_{74}H_{66}O_4Si_4Zn_3\cdot C_7H_8$, $M = 1419.9$, triclinic, space group $P\bar{1}$, $a = 13.202(7)$, $b = 13.402(8)$, $c = 21.69(1)$ Å, $\alpha = 97.175(12)°$, $\beta = 93.142(11)°$, $\gamma = 99.876(12)°$, $V = 3741(4)$ Å^3, $Z = 2$, $2\theta_{\max} = 59.1°$, 24158 measured reflections, 829 parameters, $\mu = 1.065$ mm^{-1}, $R1 = 0.0685$ for 6268 observed reflections [$I > 2\sigma(I)$], $wR2 = 0.1134$ for all reflections.

2: $C_{92}H_{104}O_{14}Si_6Zn_6$, $M = 1994.51$, monoclinic, space group $P2_1/n$, $a = 18.561(4)$, $b = 13.162(3)$, $c = 20.993(4)$ Å, $V = 4690(1)$ Å^3, $Z = 2$, $2\theta_{\max} = 50.28°$, 23990 measured reflections, 532 parameters, $\mu = 1.646$ mm^{-1}, $R1 = 0.0305$ for 6728 observed reflections [$I > 2\sigma(I)$], $wR2 = 0.0770$ for all reflections.

The intensity data were collected on a Bruker-axs-SMART 1000 diffractometer (Mo-K_α radiation, $\lambda = 0.71707$ Å, $T = 203$ K). Both structures were solved by direct methods and refined by full-matrix least-squares using SHELXTL-97.[10] The contribution of the disordered solvent in **1** to the structure factors was taken into account by back-Fourier transformation using PLATON/SQUEEZE.[11] All non-hydrogen atoms were refined using anisotropic thermal parameters; hydrogen atoms were included by use of a riding model and fixed isotropic thermal parameters.

CCDC-186433 (**1**) and -186434 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44−1223/336−033; E-mail: deposit@ccdc.cam.ac.uk].

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