Synthesis and Structure of Siloxy-Substituted ZnO Aggregates Having $(ZnO)_n$ (n = 2, 4) and Zn_3O_4 Cores

Matthias Driess,*[a] Klaus Merz,[a] and Stefan Rell[a]

Keywords: Clusters / Metal oxides / Siloxides / Zinc

Convenient syntheses and X-ray crystallographic characterizations of the first bis(trimethylsilyl)amido-, methyl-, and iodozinc triorganosiloxide aggregates **1**–**5** are described. They are accessible by the simple reaction of ZnR'_2 [R = Me, $N(SiMe_3)_2$] with the respective silanols R_3SiOH (R = Me, Et, *i*Pr), which affords the dimeric $[(Me_3Si)_2NZnOSiR_3]_2$ (**1a**: R = *i*Pr; **1b**: R = Et), trinuclear $[(MeZn)_2Zn(OSi\mathit{i}Pr_3)_4]$ (**2a**), $\{[(Me_3Si)_2NZn]_2Zn(OSiR_3)_4\}$ (**2b**: R = Et; **2c**: R = Me), and tetranuclear heterocubanes $[MeZnOSiR_3]_4$ (**3a**: R = Me; **3b**: R = Et), respectively. The latter were oxidized with four equivalents of elemental iodine to form the tetraiodo derivatives $[IZnOSiR_3]_4$ (**4a**: R = Me; **4b**: R = Et) in 82 and 88% yield, respectively. Due to the higher polarity of the Zn–I vs. Zn–C σ-bond, the Zn–O distances of the almost regular Zn_4O_4 core in **4a** are 2–6 pm shorter than those observed in the less Lewis-acidic cluster **3b**. However, the Zn–O distances in **3b** and **4a** are ca. 10–15 pm longer than those in **1a**, **2a**, and **2c**, due to different coordination numbers at Zn and the effects of ring strain. Remarkably, the iodo derivatives **4a**,**b** undergo dissociation in THF to give the respective dimeric THF solvates $[IZn(THF)OSiR_3]_2$ (**5a**: R = Me; **5b**: R = Et), whereas the Zn_4O_4 cores in **3a** and **3b** are retained even in aprotic polar solvents.

Introduction

Molecular single-source precursors for the formation of metal oxides such as metal alkoxides and siloxides[1] have attracted wide interest in the fields of material science and catalysis. While many fascinating applications have been developed in the series of homo- and heterometallic alkoxides and siloxides[1,2] relating to most s-, p-, d-, and f-block elements, the precursor chemistry of molecular zinc alkoxide aggregates[3] and related systems (siloxides, phosphonates)[4] has received much less attention. Remarkably, in contrast to molecular zinc thiolate/sulfide clusters, which consist of structural subunits of sphalerite with six-membered Zn_3S_3 rings comprised of alternating zinc and sulfur atoms,[5] zinc alkoxide aggregates possess single or edge-fused, four-membered Zn_2O_2 cores. This is evident from the rare examples of structurally characterized Zn_4O_4 heterocubanes, edge-shared Zn_7O_8 double-cubanes, and spirobicyclic Zn_3O_4 aggregates.[3] The formation of other types of aggregates or substitution of the exocyclic organic ligands at zinc without degradation of the Zn_xO_y framework seems very limited, due to the high polarity of the Zn−O bond. Since the degree of aggregation and reactivity of such clusters is strongly influenced by the steric and electronic properties of the substituents at oxygen, siloxy-substituted derivatives can be expected to be even more versatile building blocks than their alkoxide analogues due to the convenient leaving-group properties of silyl groups. Whereas only two types of siloxy-substituted ZnO aggregates have been described previously, 35 years ago by Schmidbaur et al.,[6] no information is yet available concerning the influence of the size of the triorganosilyl group at O or of the substituent at Zn on the degree of aggregation of molecular zinc siloxides. We report herein on the synthesis and structural characterization of the siloxy-substituted di-, tri-, and tetranuclear ZnO clusters **1**, **2**, and **3**, which represent potentially useful precursors for the synthesis of ZnO nanoparticles. Remarkably, the methyl groups at Zn in **3a**,**b** can easily be replaced by iodine atoms, ultimately leading to the respective tetraiodides **4a**,**b**, which are promising starting materials for the synthesis of other nonorgano-substituted (Zn−X) Zn_4O_4 heterocubanes.

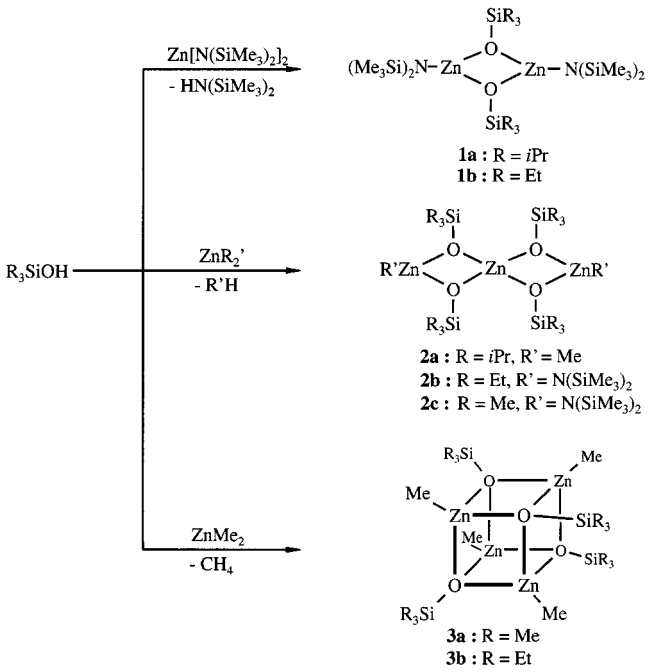
Results and Discussion

Different siloxy-substituted ZnO aggregates are accessible simply by the Brønsted acid/base reaction of triorganosilanols with dialkyl- and diamidozinc compounds. Thus, conversion of the triorganosilanols R_3SiOH (R = Me, Et, *i*Pr) with the zinc bases ZnR_2' [R′ = Me, $N(SiMe_3)_2$] furnishes, depending on the steric demand of the substituents, di-, tri-, and tetranuclear ZnO aggregates of types **1**−**3**. Reaction of the sterically congested silanol $\mathit{i}Pr_3SiOH$ with $ZnMe_2$ leads exclusively to the trinuclear, spirobicyclic Zn_3O_4 aggregate **2a** in 76% yield, while its analogous conversion with the bulky zinc diamide $Zn[N(SiMe_3)_2]_2$ affords only the dimer **1a** in 84% yield (Scheme 1). However, reaction of Et_3SiOH with $Zn[N(SiMe_3)_2]_2$ furnishes a 1:1 mixture of the dimeric and trinuclear species **1b** and **2b**, respectively. Apparently, the size of the silyl group has a stronger influence on the rate of deprotonation and the degree of

[a] Lehrstuhl für Anorganische Chemie I: Molekül- und Koordinationschemie, Ruhr-Universität Bochum, Universitätsstraße 150, 44780 Bochum, Germany
Fax: (internat.) + 49-(0)234/3214378
E-mail: matthias.driess@ac1.ruhr-uni-bochum.de

 © WILEY-VCH Verlag GmbH, D-69451 Weinheim, 2000 1434−1948/00/1212−2517 $ 17.50+.50/0

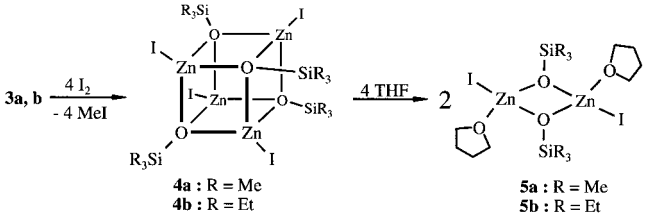
aggregation than the steric or electronic situation at the zinc center.



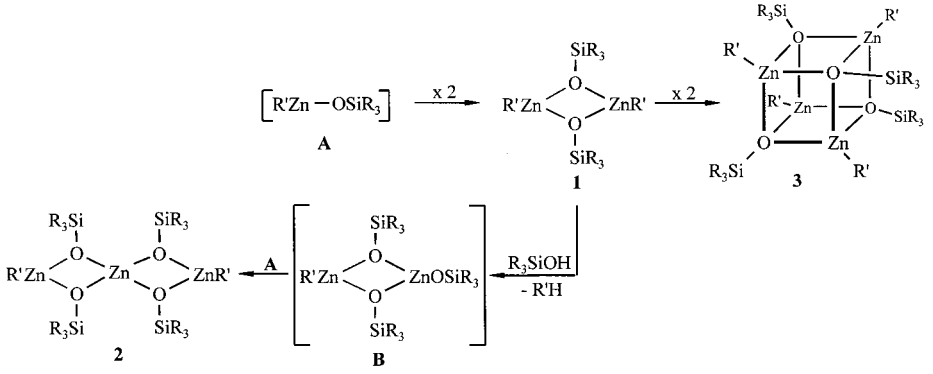
Scheme 1. Synthesis of **1**–**3**

Consequently, a higher degree of aggregation can be expected by employing sterically less congested silyl groups. This is confirmed by the reaction of R_3SiOH (R = Me, Et) with Me_2Zn, which leads to the tetranuclear heterocubanes **3a** and **3b**, respectively, in > 90% yield. Compound **3a** has already been prepared and structurally characterized by Schmidbaur et al.[6] The formation of tetrameric ZnO heterocubanes has also been observed for a few appropriate alkoxides, but in these cases the zinc atoms bore relatively bulky organo groups implying a relatively low reactivity of the cluster.[5] Although the mechanism of aggregation is still unknown, we propose that the initial step of the reaction of R_3SiOH with ZnR'_2 involves the formation of monomeric $R'ZnOSiR_3$ moieties **A**, which subsequently dimerize to a derivative of type **1** (Scheme 2).

$R'ZnOSiR_3$. Appropriate substitution favors dimerization of **1** to **3**, while additional Brønsted acid/base reaction (siloxylation) with one molecule R_3SiOH affords the polar, coordinatively unsaturated intermediate **B**. The latter can either undergo a rearrangement or association with **A** to form derivatives of type **2**. The siloxy derivatives **1**–**3** were found to be well soluble on warming in aliphatic and aromatic solvents, and their structures were also found to be retained in aprotic polar solvents such as ethers and tertiary amines. The relatively high stability of the Zn_4O_4 core in **3a** and **3b** permits oxidative exchange of the substituents at the zinc centers. While attempts to achieve Me/X exchange (X = halogen) at zinc on the intact Zn_4O_4 skeleton in **3a**,**b** with Ph_2PX as a potential halogenating agent failed,[7] we obtained the colorless, crystalline tetraiodo derivatives **4a** and **4b** in 88 and 82% yield, respectively, through direct iodination of **3a**,**b** with four molar equivalents of I_2 in toluene. This iodination was found to proceed in a stepwise manner, the rate of the reaction decreasing with increasing number of iodine atoms in the reaction intermediates, and complete conversion required about 48 h.



While **4b** is only sparingly soluble even in boiling toluene, **4a** dissolves in hexane and toluene at room temperature without dissociation. Because of the greater polarity of the terminal Zn–X bonds in the heterocubane core of **4a**,**b** (X = I) compared to those in **3a**,**b** (X = C), the Zn_4O_4 core in **4a**,**b** decomposes in aprotic polar solvents or in the presence of donor molecules, affording two molar equivalents of solvated Zn_2O_2 dimers. Thus, the dimers **5a** and **5b**



Scheme 2. Proposed mechanism for the formation of **1**–**3** via **A** and **B**

Apparently, the fate of **1** depends decisively on the steric demand of the substituents and the reactivity of the terminal Zn–X bond (X = C, N) toward R_3SiOH and are formed quantitatively in THF solution. The compositions of compounds **1**–**5** have been verified by correct combustion analyses, whereas mass spectrometric analyses (EI,

FAB) resulted only in the detection of fragment ions. Since most of the compounds discussed here give rise to relatively simple ^{1}H NMR spectra, their structures could only be unequivocally corroborated by single-crystal X-ray diffraction analysis, as discussed below.

Structural Descriptions

The dinuclear aggregate **1a** crystallizes in the monoclinic space group *C*2/*c* and consists of a planar Zn_2O_2 core (Figure 1). The coordination of the Zn and O centers is trigonal-planar with uniform Zn−O distances that resemble the values observed in other dimers.[5b] Due to the steric requirements of the iPr_3Si and amino groups, the $N(SiMe_3)_2$ groups at Zn cannot be oriented in a coplanar fashion in relation to the Zn_2O_2 plane. However, this configuration permits significant Zn−O π-interactions, which lower the high Zn−O σ-bond polarity (difference in Pauling electronegativities = 1.78).

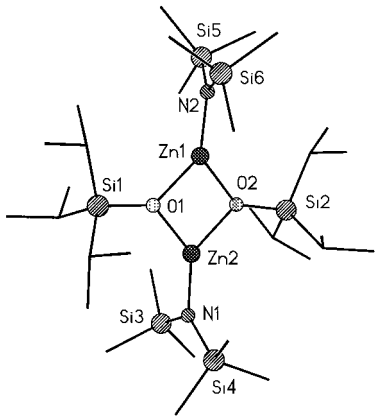


Figure 1. Solid-state structure of **1a**; H atoms are omitted for clarity

The average Zn−N distance of 1.871 Å is practically identical to values found for analogous dinuclear systems bearing terminal $N(SiMe_3)_2$ substituents,[7,8] but is significantly shorter than in the tris(amido) complex anion $Zn[N(SiMe_3)_2]_3^-$ (1.957 and 1.985 Å).[9] The topologically identical spirobicyclic Zn_3O_4 aggregates **2a** and **2c** crystallize in monoclinic (*C*2/*c*) and orthorhombic (*Pbcn*) space groups, respectively, and consist of an almost linear array of three Zn centers bridged by four siloxide ligands. The coordination of both the two terminal Zn and the O centers is trigonal-planar, whereas the central zinc atom has a distorted tetrahedral geometry (Figure 2 and Figure 3). Similar to the situation in **1a**, the amido groups at Zn in **2c** are almost perpendicularly oriented with respect to the Zn_2O_2 planes. Although the terminal and central Zn atoms have different coordination numbers, their respective Zn−O distances are almost uniform (Table 1), reflecting a relatively strong Zn−O σ-bond polarity within the Zn_3O_4 backbone.

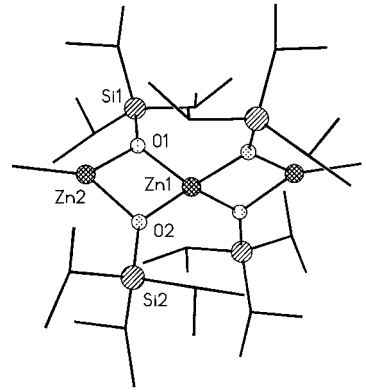


Figure 2. Molecular structure of **2a**; H atoms are omitted for clarity

In contrast, the Zn−O distances in the tetrameric ZnO aggregates **3b** and **4a**, which crystallize in monoclinic space groups (*C*2/*c* and $P2_1/n$, respectively) are, for steric reasons, ca. 10−15 pm longer than those in **1a**, **2a**, and **2c** (see Table 1). It is noteworthy that the Zn−O distances in the tetraiodo derivative **4a** are ca. 2−6 pm shorter than those in **3b**, probably because of the greater polarity of the Zn−I bond compared to the Zn−C bond. The heterocubane Zn_4O_4 cores in **3b** and **4a** (Figure 4 and Figure 5) are almost regular and therefore resemble very closely the structures observed for related Zn_4O_4 derivatives.[5b,6]

The Zn−I distances in **4a** are almost identical and are unremarkable, comparing well with the values observed for other iodozinc complexes.[7c,10] Slightly longer Zn−I distances, and concomitantly shorter endocyclic Zn−O1 distances are observed, as expected, in the THF solvate **5b**, which crystallizes in the orthorhombic space group *Pbca* (Figure 6). The terminal Zn−O2 distance, i.e. that between the zinc atom and the oxygen center of the THF ligand, is 10 pm longer than the endocyclic Zn−O1 distance, while the elongation of the Zn−I distance is caused by the stabilizing dative Zn−O(THF) bond. Apparently, the driving force behind the facile decomposition of heterocubanes **4a**,**b** in polar solvents can be interpreted in terms of coordination effects and the release of ring strain. Finally, it is worthy of note that the structures of the $Zn(OSiR_3)$ aggregates **1**−**4** show a striking similarity to those of the isoelectronic $Zn(NPR_3)$ clusters (phosphoraneimidinato complexes).[7] However, the Zn centers in the latter are much more electronically stabilized by π-donation from the N=P moiety and therefore, in contrast to **4a** and **4b**, the aggregates resist degradation even in donor solvents.

Experimental Section

General Remarks: All reactions were performed under anaerobic conditions using modified Schlenk techniques. Solvents were freshly distilled from Na and saturated with Ar prior to use. − ^{1}H NMR spectra were recorded at 250 MHz, ^{13}C NMR spectra at 63 MHz, and ^{29}Si NMR spectra at 50 MHz with samples in C_6D_6

Table 1. Selected bond lengths [Å] and angles [°] in **1a**, **2a**, **2c**, **3b**, **4a**, and **5b**

Zn_2O_2 (**1a**)			
Zn1−O1	1.962(1)	Zn1−N2	1.871(2)
Zn1−O2	1.943(1)	Zn2−N1	1.872(2)
Zn2−O2	1.950(1)	Si2−O2	1.665(1)
Zn2−O2	1.956(1)	Si2−O2	1.667(1)
N2−Zn1−O2	137.09(6)	Si1−O1−Zn2	131.93(8)
N2−Zn1−O1	138.22(6)	Si1−O1−Zn1	132.93(8)
O2−Zn1−O1	84.67(6)	Zn2−O1−Zn1	95.14(6)
Zn_3O_4 (**2a**)			
Zn1−O1	1.979(2)	Zn2−O1	1.968(2)
Zn1−O1A	1.979(2)	Zn2−O2	1.982(2)
Zn1−O2	1.966(2)	Zn−C	1.946(3)
Zn1−O2A	1.966(2)	Si1−O1	1.651(2)
O2−Zn1−O2A	130.9(1)	C−Zn2−O1	140.0(1)
O2−Zn1−O1	86.51(8)	C−Zn2−O2	133.6(1)
O2A−Zn1−O1	119.53(8)	O1−Zn2−O2	86.37(8)
O2−Zn1−O1A	119.52(8)	C−Zn2−Zn1	175.1(1)
Zn_3O_4 (**2c**)			
Zn1−O1	1.951(2)	Zn2−N1	1.855(3)
Zn1−O2	1.947(3)	Si1−O1	1.639(3)
Zn2−O1	1.933(3)	Si2−O2	1.636(3)
Zn2−O2	1.936(3)	Si3−N1	1.704(5)
O2−Zn1−O2A	1.228(2)	N1−Zn2−O1	136.8(2)
O2−Zn1−O1	85.3(1)	N1−Zn2−O2	137.0(2)
O2A−Zn1−O1	122.7(1)	O1−Zn2−O2	86.2(1)
O1−Zn1−O1A	122.6(2)	N1−Zn2−Zn1	179.8(2)
Zn_4O_4 (**3b**)			
Zn1−O1	2.104(4)	Zn1−C	1.959(6)
Zn1−O2	2.078(4)	Zn2−C	1.965(7)
Zn2−O1	2.085(4)	Si1−O1	1.675(4)
Zn2−O1	2.091(4)	Si2−O2	1.674(4)
C−Zn1−O2	127.8(3)	C−Zn2−O1	129.0(3)
C−Zn1−O2A	128.3(3)	C−Zn2−O2	130.3(3)
O2−Zn1−O1	85.9(2)	O1−Zn2−O2	86.1(2)
O2A−Zn1−O1	85.5(2)	O1A−Zn2−O2	85.8(2)
Zn_4O_4 (**4a**)			
Zn1−O1	87.0(5)	Zn2−O1	2.037(12)
Zn1−O2	86.7(5)	Zn2−O3	2.057(12)
Zn1−O3	126.6(3)	Zn2−O4	2.054(12)
Zn1−I1	128.9(3)	Zn2−I2	2.433(3)
O1−Zn1−O2	87.0(5)	O1−Zn2−O4	86.2(5)
O2−Zn1−O3	86.7(5)	O1−Zn2−O3	86.1(5)
O2−Zn1−I1	126.6(3)	O1−Zn2−I2	131.3(4)
O3 Zn1−I1	128.9(3)	O4−Zn2−I2	125.9(3)
Zn_2O_2·2THF (**5b**)			
Zn1−O1	1.945(6)	O1−Zn1−O2	105.1(3)
Zn1−O2	2043(5)	O1A−Zn1−O2	103.8(2)
Zn1−I1	2.498(1)	O1−Zn1−I1	126.4(1)
Si1−O1	1.658(6)	Si1−O1−Zn1A	133.2(3)

solution with a Bruker WP250 spectrometer; chemical shifts are quoted in δ values relative to $SiMe_4$ as an internal standard.

$[(Me_3Si)_2NZnOSi\mathit{i}Pr_3]_2$ (1a): A solution of $Zn[N(SiMe_3)_2]_2$ (Aldrich) (1.43 g, 3.71 mmol) in toluene (30 mL) was allowed to react with $\mathit{i}Pr_3SiOH$ (0.65 g, 3.71 mmol) at −78 °C. After stirring, the clear mixture for 6 h at room temperature, the volatile components were removed under reduced pressure (10^{-3} Torr, 40 °C) and the residue was redissolved by gently heating in a small volume of hexane. Colorless crystals of **1a** were deposited at room temperature. Yield: 1.24 g (1.55 mmol, 84%); m.p. 186−189 °C (decomp.). − ^{1}H NMR (C_6D_6): δ = 0.42 (s, 36 H, SiMe), 1.29 (sept, 6 H, C*H*Me_2), 1.35 (d, 36 H, CH*Me*$_2$). − ^{13}C NMR (C_6D_6): δ = 5.7 [q, 12 C, $SiMe_3$, ^1J(C,H) = 117 Hz], 16.3 [d, 6 C, *C*HMe_2, ^1J(C,H) = 116 Hz], 19.3 [q, 12 C, CH*Me*$_2$, ^1J(C,H) = 126 Hz]. − ^{29}Si NMR (C_6D_6): δ = −1.5 [dec, 4 Si, $SiMe_3$, ^2J(Si,H) = 3.8 Hz], 15.3 (m, 2 Si, Si*i*Pr_3). − $C_{30}H_{78}N_2O_2Si_6Zn_2$ (798.2): calcd. C 45.14, H 9.85; found C 44.98, H 9.83.

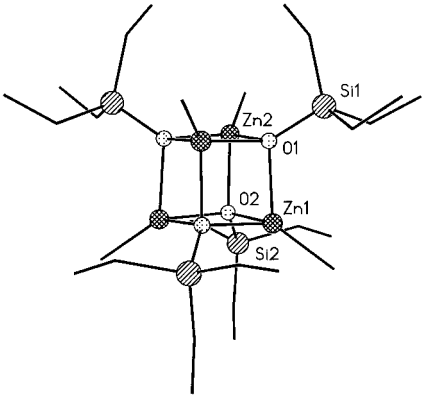


Figure 4. Molecular structure of **3b**; H atoms are omitted for clarity

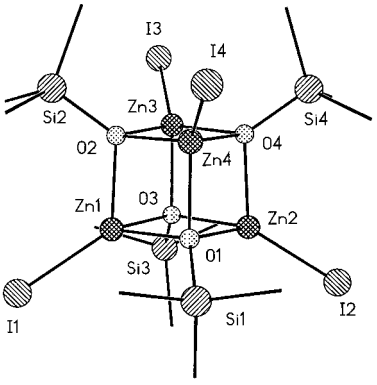


Figure 5. Solid-state structure of **4a**

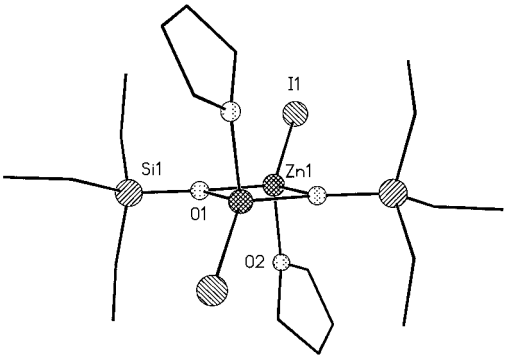


Figure 6. Molecular structure of **5b**; H atoms are omitted for clarity

$[(Me_3Si)_2NZnOSiEt_3]_2$ (1b), $\{[(Me_3Si)_2NZn]_2Zn(OSiEt_3)_4\}$ (2b): The product **1b** was prepared in a similar manner as **1a**. However, from common organic solvents, **1b** could only be crystallized in the form of a 1:1 mixture with **2b**. Reaction of a solution of zinc diamide (1.37 g, 3.55 mmol) in toluene (20 mL) with Et_3SiOH (0.47 g, 3.55 mmol) afforded colorless plates. Yield: 1.03 g; m.p. 167−170

Table 2. Details of the crystal structure determinations of **1a**, **2a**, **2c**, **3b**, **4a**, and **5b**

Compound	**1a**	**2a**	**2c**	**3b**	**4a**	**5b**
Crystal colour	transparent	transparent	transparent	transparent	transparent	transparent
Crystal size [mm]	0.1 × 0.2 × 0.1	0.2 × 0.2 × 0.2	0.3 × 0.1 × 0.1	0.2 × 0.3 × 0.3	0.1 × 0.1 × 0.1	0.2 × 0.2 × 0.2
Empirical formula	$C_{30}H_{78}N_2O_2Si_6Zn_2$	$C_{38}H_{90}O_4Si_4Zn_3$	$C_{24}H_{72}N_2O_4Si_8Zn_3$	$C_{28}H_{72}O_4Si_4Zn_4$	$C_{12}H_{36}I_4O_4Si_4Zn_4$	$C_{20}H_{46}I_2O_4Si_2Zn_2$
Formula mass	798.22	919.57	873.67	846.70	1125.96	791.28
Temperature [K]	203	203	203	203	203	203
Radiation (graphite-monochromated)	Mo-K_α	Mo-K_α	Mo-K_α	Mo-K_α	Mo-K_α	Mo-K_α
Wavelength [Å]	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system, space group	monoclinic, *C*2/*c*	monoclinic, *C*2/*c*	orthorhombic, *Pbcn*	monoclinic, *C*2/*c*	monoclinic, $P2_1/c$	orthorhombic, *Pbca*
Unit cell no. reflections	77	74	75	68	62	68
θ range [°]	3.45 to 19.40	3.85 to 19.20	3.55 to 18.65	4.10 to 19.50	4.05 to 20.05	4.05 to 18.95
a [Å]	30.8683(7)	21.200(5)	11.686(2)	21.419(7)	18.484(7)	14.360(6)
b [Å]	14.2321(3)	11.738(3)	17.920(3)	11.630(4)	10.982(8)	14.656(6)
c [Å]	20.5578(5)	22.367(4)	23.539(4)	20.149(7)	21.932(2)	15.006(6)
α [°]	90	90	90	90	90	90
β [°]	96.220(1)	115.330(1)	90	119.850(2)	111.91(5)	90
γ [°]	90	90	90	90	90	90
Volume [Å^3]	8978.3(4)	5031(2)	4929.2(15)	4353(3)	4130(5)	3158(2)
Z, $D_{calcd.}$ [Mg m^{-3}]	8, 1.181	4, 1.214	4, 1.177	4, 1.292	4, 1.936	4, 1.660
Abs. coeff. μ [mm^{-1}]	1.254	1.546	1.668	2.313	5.420	3.570
Diffractometer	Bruker axs SMART 1000	Bruker axs SMART 1000	Bruker axs SMART 1000	Bruker axs SMART 1000	Bruker axs SMART 1000	Bruker axs SMART 1000
Scan	ω-scan	ω-scan	ω-scan	ω-scan	ω-scan	ω-scan
F(000)	3456	1984	1856	1792	2280	1560
θ range for data collection [°]	1.58 to 34.04	2.01 to 25.00	1.73 to 25.19	2.07 to 27.50	1.91 to 25.23	2.41 to 25.00
Index range	$-48 \le h \le 37$ $-21 \le k \le 22$ $-32 \le l \le 31$	$0 \le h \le 22$ $0 \le k \le 13$ $-26 \le l \le 24$	$-13 \le h \le 13$ $-21 \le k \le 12$ $-28 \le l \le 27$	$0 \le h \le 17$ $0 \le k \le 15$ $-26 \le l \le 22$	$-22 \le h \le 14$ $-13 \le k \le 12$ $-23 \le l \le 26$	$-11 \le h \le 9$ $-17 \le k \le 3$ $-17 \le l \le 9$
Refl. collected/unique [R_{int}]	49725/17292 [0.0587]	4423/4295 [0.0601]	24024/4400 [0.0481]	4187/4057 [0.0598]	20856/7408 [0.1166]	4578/1946 [0.0743]
Refl. observed ([$I_0 > 2\sigma(I_0)$])	13670	3483	3285	1670	6155	1511
Data/restraints/parameters	17292/0/379	4295/0/223	4400/0/186	4057/3/183	7408/6/297	1946/0/137
Goodness-of-fit on F^2	1.115	0.975	1.030	0.745	1.069	1.051
Final *R*1, *wR*2 [$I > 2\sigma(I)$]	0.0482, 0.0990	0.0365, 0.0928	0.0451, 0.1226	0.0536, 0.1243	0.0674, 0.1684	0.0498, 0.1391
*R*1, *wR*2 (all data)	0.0715, 0.1117	0.0449, 0.0947	0.0643, 0.1411	0.1241. 0.1372	0.0780, 0.1790	0.0650, 0.1530
Extinction coefficient	–	0.00203	–	0.0003	0.0014	0.0028
Diff. peak and hole [e Å^{-3}]	0.963 and −1.230	0.547 and −0.940	0.672 and −0.470	0.392 and −0.545	1.908 and −1.924	0.651 and −0.846

°C (decomp.). The structure of this mixture was established by X-ray crystallography, which confirmed the presence of equimolar amounts of **1b** and **2b**. The moderate crystal quality did not permit a satisfactory refinement of the data.

[(MeZn)$_2$Zn(OSi*i*Pr$_3$)$_4$] (2a): At −78 °C, a solution of $ZnMe_2$ (1.44 g, 15.2 mmol, 2 M solution in toluene; Aldrich) in toluene (ca. 100 mL) was slowly treated with a solution of *i*Pr$_3$SiOH (3.52 g, 20.3 mmol) in toluene (10 mL), which resulted 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). Colorless plates were obtained after recrystallization of the residue from a small volume of hexane at 25 °C. Yield: 3.53 g (3.84 mmol, 76%); m.p. 211−214 °C (decomp.). − ^{1}H NMR (C_6D_6): δ = −0.05 (s, 6 H, ZnMe), 1.12 [sept, 12 H, C*H*Me$_2$, ^3J(H,H) = 6.8 Hz], 1.20 [d, 72 H, CH*Me*$_2$, ^3J(H,H) = 6.8 Hz]. − ^{13}C{1H} NMR (C_6D_6): δ = −11.9 (s, 2 C, ZnMe), 15.6 (s, 12 C, *C*HMe$_2$), 19.2 (s, 24 C, CH*Me*$_2$). − ^{29}Si{^{1}H} NMR (C_6D_6): δ = 14.9 (s). − $C_{38}H_{90}O_4Si_4Zn_3$ (919.6): calcd. C 49.63, H 9.86; found C 49.19, H 9.85.

{[(Me$_3$Si)$_2$NZn]$_2$Zn(OSiMe$_3$)$_4$} (2c): Product **2c** was prepared in a similar manner as **2a**, starting from Zn[N(SiMe$_3$)$_2$]$_2$ (1.01 g, 2.62 mmol) and Me$_3$SiOH (0.31 g, 3.49 mmol). Recrystallization of the residue from hexane (10 mL) afforded colorless cubes. Yield: 0.60 g (0.069 mmol, 79%); m.p. 218−222 °C (decomp.). − ^{1}H NMR (C_6D_6): δ = 0.31 (s, 36 H, OSiMe), 0.44 (s, 36 H, NSiMe), 1.27 (sept, 6 H, C*H*Me$_2$), 1.34 (d, 36 H, CH*Me*$_2$). − ^{13}C{^{1}H} NMR (C_6D_6): δ = 3.1 (s, 12 C, OSiMe$_3$), 5.7 (s, 12 C, NSiMe$_3$), 16.0 (s, 6 C, *C*HMe$_2$), 19.4 (s, 12 C, CH*Me*$_2$). − ^{29}Si{^{1}H} NMR (C_6D_6): δ = −1.5 (s, 4 Si, NSiMe$_3$), 19.6 (s, 4 Si, OSiMe$_3$). − $C_{24}H_{72}N_2O_4Si_8Zn_3$ (873.6): calcd. C 32.99, H 8.30; found C 32.34, H 8.28.

[MeZnOSiMe$_3$]$_4$ (3a): This compound was prepared and characterized according to a literature procedure.[6]

[MeZnOSiEt$_3$]$_4$ (3b): At −78 °C, a solution of $ZnMe_2$ (0.90 g, 11.11 mmol, 2 M solution in toluene; Aldrich) in toluene (ca. 80 mL) was treated with Et$_3$SiOH (1.46 g, 11.11 mmol). After methane evolution had ceased, the clear solution was concentrated to dryness in vacuo. Recrystallization of the residue from hexane afforded colorless plates. Yield: 2.23 g (2.63 mmol, 95%). − ^{1}H NMR (C_6D_6): δ = 0.01 (s, 12 H, ZnMe), 0.96 [q, 24 H, C*H*$_2$Me, ^3J(H,H) = 7 Hz], 1.08 [t, 36 H, CH$_2$*Me*, ^3J(H,H) = 7 Hz]. − ^{13}C{^{1}H} NMR (C_6D_6): δ = −8.30 (s, 4 C, ZnMe), 7.97 (s, 12 C, CH$_2$*Me*), 8.70 (s, 12 C, *C*H$_2$Me). − ^{29}Si{^{1}H} NMR (C_6D_6): δ = 23.8 (s). − $C_{28}H_{72}O_4Si_4Zn_4$ (846.7): calcd. C 39.71, H 8.57; found C 39.11, H 8.50.

[IZnOSiMe$_3$]$_4$ (4a): A solution of **3a** (1.37 g, 2.02 mmol) was treated with I_2 (4.90 g, 8.08 mmol) at room temperature. The violet color of the mixture slowly disappeared in the course of about 48 h. Evaporation of all volatile components in vacuo (10^{-3} Torr) afforded a solid residue, which was redissolved by gently heating in a small volume of hexane. The product **4a** crystallized in the form of colorless cubes. Yield: 2.00 g (1.70 mmol, 88%). – ^{1}H NMR (C_6D_6): δ = 0.62 (s, SiMe). – ^{13}C NMR (C_6D_6): δ = 4.20 [q, SiMe, ^1J(C,H) = 119 Hz]. – ^{29}Si{^{1}H} NMR (C_6D_6): δ = 37.7 (s). – $C_{12}H_{36}I_4O_4Si_4Zn_4$ (1126): calcd. C 12.80, H 3.22; found C 12.47, H 3.19.

[IZnOSiEt$_3$]$_4$ (4b): Derivative **4b** was prepared in a similar manner as **4a**, starting from **3b** (1.01 g, 1.19 mmol) and I_2 (1.21 g, 4.76 mmol). Recrystallization of the residue from hot benzene afforded colorless cubes. Yield: 1.15 g (0.97 mmol, 82%). – ^{1}H NMR (C_6D_6): δ = 0.91 [q, C*H*$_2$Me, ^3J(H,H) = 7 Hz], 1.01 [t, CH$_2$*Me*, ^3J(H,H) = 7 Hz]. – ^{13}C{^{1}H} NMR (C_6D_6): δ = 7.97 (s, CH$_2$*Me*), 8.70 (s, *C*H$_2$Me). – ^{29}Si{^{1}H} NMR (C_6D_6): δ = 23.2 (s). – $C_{24}H_{60}I_4O_4Si_4Zn_4$ (1294): calcd. C 22.27, H 4.67; found C 22.04, H 4.61.

[IZn(THF)OSiMe$_3$]$_2$ (5a) and [IZn(THF)OSiEt$_3$]$_2$ (5b): The heterocubanes **4a** (1.00 g, 0.88 mmol) and **4b** (1.10 g, 0.93 mmol) were dissolved in THF at room temperature. Complete evaporation of the solvent in vacuo (10^{-3} Torr) and recrystallization of the residue from hexane afforded colorless cubes in quantitative yield. – **5a:** ^{1}H NMR (C_6D_6): δ = 0.65 (s, 18 H, SiMe), 1.32 (m, 8 H, THF), 3.50 (m, 8 H, THF). – ^{29}Si{^{1}H} NMR (C_6D_6): δ = 36.7 (s). – $C_{14}H_{34}I_2O_4Si_2Zn_2$ (707.1): calcd. C 23.78, H 4.84; found C 23.23, H 4.80. – **5b:** ^{1}H NMR (C_6D_6): δ = 0.99 [q, 12 H, C*H*$_2$Me, ^3J(H,H) = 7 Hz], 1.01 [t, 18 H, CH$_2$*Me*, ^3J(H,H) = 7 Hz], 1.28 (m, 8 H, THF), 3.44 (m, 8 H, THF). – ^{29}Si{1H} NMR (C_6D_6): δ = 23.7 (s). – $C_{20}H_{46}O_4I_2Si_2Zn_2$ (791.3): calcd. C 30.35, H 5.86; found C 30.11, H 5.84.

X-ray Structure Determinations: Experimental details relating to the X-ray crystal structure determinations of **1a**, **2a**, **2c**, **3b**, **4a**, and **5b** are listed in Table 2. The intensities were measured with a Bruker-axs-SMART 1000 diffractometer. The structures were solved by direct methods (SHELXS-97). Refinements were carried out using the SHELXL-97 package. All nonhydrogen atoms were refined with anisotropic temperature factors. The hydrogen atoms were placed in calculated positions and refined isotropically in riding mode. All refinements were made by full-matrix least-squares methods on F^2. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-143075 (**1a**), -143076 (**2c**), -143077 (**4a**), -143078 (**2a**), -143079 (**5b**), and -143080 (**3b**). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

We thank the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the Ministerium für Wissenschaft, Schule, und Weiterbildung, Nordrhein-Westfalen (Germany), for support.

[1] [1a] K. G. Coulton, L. G. Hubert-Pfalzgraf, *Chem. Rev.* **1990**, *90*, 969. –[1b] C. D. Chandler, C. Roger, M. J. Hampden-Smith, *Chem. Rev.* **1993**, *93*, 1205. –[1c] D. J. Teff, J. C. Huffman, K. G. Coulton, *J. Am. Chem. Soc.* **1996**, *118*, 4030. –[1d] P. O'Brien, *Precursors for Electronic Materials* in *Inorganic Materials* (Eds.: D. W. Bruce, D. O'Hare), Wiley, New York, **1996**, p. 525.

[2] [2a] K. W. Terry, T. D. Tilley, *Chem. Mater.* **1991**, *3*, 1001. –[2b] K. W. Terry, K. Su, T. D. Tilley, A. L. Rheingold, *Polyhedron* **1998**, *5–6*, 891.

[3] [3a] H. M. M. Shearer, C. B. Spencer, *Chem. Commun.* **1966**, 194. –[3b] H. M. M. Shearer, C. B. Spencer, *Acta Crystallogr., Sect. B* **1980**, *B36*, 2046. –[3c] M. L. Ziegler, J. Weiss, *Angew. Chem.* **1970**, *82*, 931. –[3d] J. Boersma, A. L. Spek, J. G. Noltes, *J. Organomet. Chem.* **1974**, *81*, 7. –[3e] M. Ishimori, T. Hagiwara, T. Tsuruta, Y. Kai, N. Yasuoka, N. Kasai, *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1165.

[4] [4a] T. D. Tilley, K. Su, M. J. Sailor, *J. Am. Chem. Soc.* **1996**, *118*, 3459. –[4b] M. G. Walawalkar, H. W. Roesky, *Acc. Chem. Res.* **1999**, *32*, 117. –[4c] C. G. Lugmair, T. D. Tilley, *Inorg. Chem.* **1998**, *37*, 6304.

[5] [5a] I. G. Dance, A. Choy, M. L. Scudder, *J. Am. Chem. Soc.* **1984**, *106*, 6285. –[5b] M. M. Olmstead, P. P. Power, S. C. Shoner, *J. Am. Chem. Soc.* **1991**, *113*, 3379.

[6] [6a] F. Schindler, H. Schmidbaur, U. Krüger, *Angew. Chem.* **1965**, *77*, 865. –[6b] F. Schindler, H. Schmidbaur, *Angew. Chem.* **1967**, *79*, 697.

[7] [7a] M. Krieger, R. O. Gould, B. Neumüller, K. Harms, K. Dehnicke, *Z. Anorg. Allg. Chem.* **1998**, *624*, 1434. –[7b] M. Driess, K. Merz, S. Rell, unpublished. –[7c] S. Abram, U. Abram, R. Meyer zu Köck, K. Dehnicke, *Z. Anorg. Allg. Chem.* **1996**, *622*, 867.

[8] S. C. Goel, M. Y. Chiang, W. F. Buhro, *Inorg. Chem.* **1990**, *29*, 4646.

[9] M. A. Putzer, B. Neumüller, K. Dehnicke, *Z. Anorg. Allg. Chem.* **1997**, *623*, 539.

[10] [10a] B. Müller, H. Vahrenkamp, *Eur. J. Inorg. Chem.* **1999**, 129. –[10b] G. Sawitzki, H. G. von Schnering, *Chem. Ber.* **1974**, *107*, 3266.

Received April 17, 2000
[I00147]