

Organozinc Siloxide-Hydrazide Aggregates $[(\text{RZn})_4(\text{NHNMe}_2)_x(\text{OSiMe}_3)_{(4-x)}]$

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Dedicated to Professor Wolfgang Jeitschko on the occasion of his 70th birthday

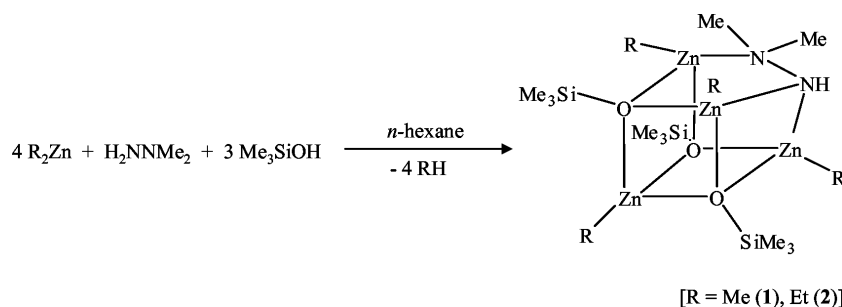
The reaction of dialkylzinc compounds R_2Zn ($\text{R} = \text{Me}, \text{Et}$) with *N,N*-dimethylhydrazine and trimethylsilanol in a 4:2:2 ratio leads to the formation of tetra(alkylzinc) tris-siloxide mono-hydrazide aggregates, $[(\text{RZn})_4(\text{NHNMe}_2)(\text{OSiMe}_3)_3]$ [$\text{R} = \text{Me}$ (**1**) and Et (**2**)]. These compounds are aggregates of mirror symmetry, containing the novel $\text{Zn}_4\text{N}_2\text{O}_3$ core. Both compounds have been characterised by ^1H , ^{13}C and ^{29}Si NMR and IR spectroscopy, by mass spectrometry and by elemental analysis, and **2** also by X-ray crystallography. The structure can be derived from a heterocubane, in which one anionic vertex is replaced by an NHNMe_2 group contributing two N atoms to the core constitution. By applying a ratio of hydrazine:silanol of 2:1 in a reaction with R_2Zn ($\text{R} = \text{Me}, \text{Et}, i\text{Pr}$), compounds of the general formula $[(\text{RZn})_4(\text{NHNMe}_2)_2(\text{OSiMe}_3)_2]$ [$\text{R} = \text{Me}$ (**3**), Et (**4**), $i\text{Pr}$ (**5**)] are obtained. These aggregates contain a $\text{Zn}_4\text{N}_4\text{O}_2$ core. Upon employing a hydrazine:silanol ratio of 5:1 in a reaction with diisopropyl zinc, the compound $[(i\text{PrZn})_4(\text{NHNMe}_2)_3(\text{OSiMe}_3)]$ results, containing a $\text{Zn}_4\text{N}_6\text{O}$ unit. Compounds **3–6** have been characterised by ^1H , ^{13}C and ^{29}Si NMR and IR spectroscopy, by mass spectrometry and by elemental analysis. The topologic relationship between the pure hydrazides $[(\text{RZn})_4(\text{NHNMe}_2)_4]$, the mixed aggregates $[(\text{RZn})_4(\text{NHNMe}_2)_3(\text{OR}')]_x$, $[(\text{RZn})_4(\text{NHNMe}_2)_2(\text{OR}')_2]$ and $[(\text{RZn})_4(\text{NHNMe}_2)_3(\text{OR}')_3]$ and the pure alkoxides $[(\text{RZn})_4(\text{OR}')_4]$ is discussed.

Key words: Siloxidehydrazide, Zinc, Cage Compounds, Organometallic Chemistry, Trimethylsilanol

Introduction

Organometallic alkoxides [1] and amides [2] are important classes of reagents. Their structures show an extreme wealth of different aggregation motifs. As a subgroup of anionic nitrogen ligands, the hydrazides are particularly interesting, as they offer two directly linked nitrogen binding sites. Hydrazides in general are ligands which – compared to amides – have reduced carbon contents. The lability of the N-N bond leads to high energy densities of the resulting hydrazides. Both features make hydrazides useful as molecular precursors for nitride materials, an area which has been investigated in some detail with the aim of generating aluminium and gallium nitride films [3]. Many more investigations in metal hydrazides were performed simply for the sake of exploring the manifold aggregation behaviour of hydrazides of Al and Ga and the bind-

ing modes of the different hydrazide ligands towards such metal centres [4]. This area has recently been reviewed [5] and finds its parallels in the chemistry of hydroxylamide anions in the coordination sphere of Al and Ga, which was investigated by our group [6]. The hydrazide chemistry of zinc, the neighbour element of gallium in the Periodic Table, was – apart experiments leading to the only known zinc hydrazide $[\text{Zn}(\text{N}_2\text{H}_3)_2]$ [7] – untouched, until our two recent studies of the compounds $[(\text{RZn})_4(\text{NHNMe}_2)_4]$ [8, 9]. These are the sole products of the reactions of dialkylzinc solutions (ZnR_2 , $\text{R} = \text{Me}, \text{Et}, i\text{Pr}$) with *N,N*-dimethylhydrazine. These hydrazides adopt unsymmetrical cage structures. They react with water and alcohols, whereby the parent hydrazine is regenerated and aggregates with various compositions of the general formula $[(\text{RZn})_4(\text{NHNMe}_2)_{4-x}(\text{OR}')_x]$ are formed [8, 9]. The common motif for all



Scheme 1.

compounds is always that of tetranuclear cage compounds.

Related to the zinc alkoxides are the siloxides of zinc, first prepared by Schmidbaur and co-workers [10]. Recent reports on the chemistry of zinc siloxides and alkoxides and by Driess, Fischer and coworkers, has shown the great potential of these compounds as molecular sources for zinc oxide materials [11]. Depending on the thermolysis conditions the formation of either zinc oxide or zinc metal can be achieved [12]. We are interested in the possibility of realizing organometallic hydrazides/alkoxides of zinc in defined mixed aggregates with tuneable Zn:O:N ratios. These compounds are not only interesting in their own right as novel cluster compounds with Zn/O/N cores, but could potentially be used for the generation of nitrogen containing zinc oxide by thermolysis procedures. ZnO is an important wide band gap semiconductor, which can be tuned into a *p*-semiconductor by incorporation of nitrogen [13]. This is an interesting target material for electronic applications for which so far no straightforward synthesis exists. The first step in this direction is the exploration of pathways to precursors with various Zn/O/N stoichiometries. For this reason we report here on the synthesis and characterisation of the first organozinc siloxide hydrazides.

Results and Discussion

Tetra(alkylzinc) tris-siloxide mono-hydrazides

In an one-pot synthesis protocol two equivalents of dialkylzinc solutions R_2Zn (R = Me, Et) were reacted with one equivalent of *N,N*-dimethylhydrazine followed by addition of one equivalent of trimethylsilanol in a toluene/hexane solvent. This resulted in the formation of siloxide-hydrazide aggregates of the composition $[(\text{RZn})_4(\text{NHNMe}_2)(\text{OSiMe}_3)_3]$ [R = Me (**1**), Et (**2**)] in moderate yields (Scheme 1). The reactions worked well for dimethyl- and diethylzinc, but un-

der the same conditions the reaction with $i\text{Pr}_2\text{Zn}$ leads to $[(i\text{PrZn})_4(\text{NHNMe}_2)_2(\text{OSiMe}_3)_2]$ with a different siloxide:hydrazide ratio of 2:2 (the product is discussed in more detail below). Compounds **1** and **2** are soluble in common hydrocarbon solvents and ethers and can easily be purified by crystallization. The compounds are obtained in micro-crystalline form, and only for **2** the growth of single crystals of suitable size and quality for structure determination by X-ray diffraction was successful. Compounds **1** and **2** melt at 205–206 °C and 238–239 °C, respectively.

The mass spectra of **1** and **2** gave strong evidence for the presence of aggregates containing four Zn atoms, as the highest masses found were those corresponding to the molecular ions diminished by the masses of the alkyl groups bonded to the Zn atoms. The IR spectra proved the presence of the NH functions in both compounds. The ^1H and ^{13}C NMR spectra in solution indicated the presence of molecular mirror symmetry for the aggregates.

In the ^1H NMR spectra of both, **1** and **2**, the protons of the OSiMe_3 groups lying on the mirror plane give singlet signals with a relative intensity corresponding to nine protons, while the other two symmetry related OSiMe_3 groups give resonances double as high in intensity. Three different resonances for the alkyl groups at the zinc atoms are observed in an intensity ratio of 1:2:1, as one zinc atom is part of one four-membered and two five-membered rings, while two zinc atoms are part of one five-membered and two four-membered rings and the fourth zinc atom is part of three four-membered rings. Furthermore, the molecular symmetry is also reflected by the ^{13}C and ^{29}Si NMR spectra. The ^{29}Si NMR spectra contain two signals for compound **1** at 16.98 and 19.67 ppm and two for **2** at 17.29 and 19.87 ppm, in both cases with an intensity ratio of approximately 1:2.

A single crystal X-ray diffraction experiment of **2** confirmed the spectroscopic data. The compound crys-

Table 1. Selected bond lengths (Å) and angles (°) for [(EtZn)₄(NHNMe₂)(OSiMe₃)₃] (**2**) as determined by X-ray crystallography.

Zn(1)-O(3)	2.063(2)	Zn(1)-O(2)	2.065(2)
Zn(1)-N(1)	2.114(2)	Zn(2)-O(2)	2.128(2)
Zn(2)-O(4)	2.128(2)	Zn(2)-N(2)	2.029(2)
Zn(4)-O(2)	2.105(2)	Zn(4)-O(3)	2.095(2)
Zn(4)-O(4)	2.010(2)	N(1)-N(2)	1.462(3)
Si(2)-O(2)	1.656(2)	Zn(1)-C(13)	1.961(4)
O(3)-Zn(1)-O(2)	85.1(1)	O(2)-Zn(1)-N(1)	95.2(1)
O(3)-Zn(1)-N(1)	96.3(2)	N(2)-N(1)-Zn(1)	104.9(2)
Zn(2)-N(2)-Zn(3)	97.2(1)	N(1)-N(2)-Zn(2)	113.5(2)
N(1)-N(2)-Zn(3)	114.0(2)	Zn(1)-O(2)-Zn(2)	106.7(1)
Zn(1)-O(2)-Zn(4)	93.5(1)	Zn(2)-O(2)-Zn(4)	92.8(1)
O(2)-Zn(2)-O(4)	83.9(1)	N(2)-Zn(2)-O(4)	85.9(1)
N(2)-Zn(2)-O(2)	93.8(1)	Zn(2)-O(4)-Zn(3)	90.8(1)
Zn(2)-O(4)-Zn(4)	95.5(1)	Zn(3)-O(4)-Zn(4)	95.7(1)
O(2)-Zn(4)-O(3)	83.3(1)	O(2)-Zn(4)-O(4)	87.4(1)
O(3)-Zn(4)-O(4)	86.7(1)	Si(2)-O(2)-Zn(1)	119.7(1)

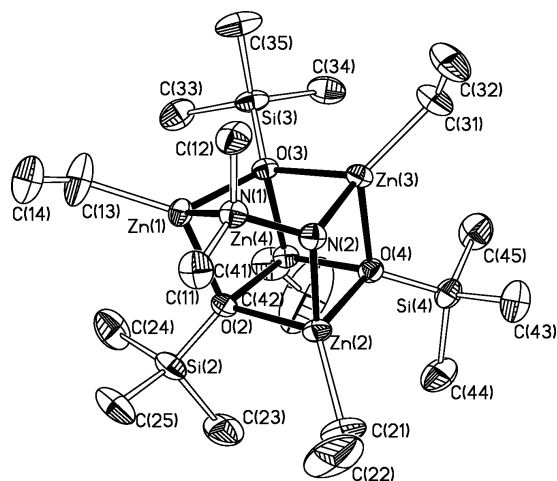


Fig. 1. Molecular structure of [(EtZn)₄(NHNMe₂)(OSiMe₃)₃] (**2**) as determined by X-ray crystallography. Hydrogen atoms are omitted for clarity. The displacement ellipsoids are drawn at the 50% level.

tallises in the triclinic system, space group $P\bar{1}$. The molecular geometry is shown in Fig. 1 and Table 1 provides selected geometric parameters.

The molecules in the solid state approach closely the expected mirror symmetry deduced from the NMR data in solution. All zinc, oxygen, nitrogen, silicon and carbon atoms in **2** have the coordination number four. The zinc atoms span a topological tetrahedron, the four faces of which are capped by three siloxy groups (*via* the oxygen atom) and by one hydrazide group *via* its N-N unit. The cages of **2** are composed of two five-membered Zn₂N₂O rings, three four-membered Zn₂O₂ rings and one four-membered Zn₂ON ring.

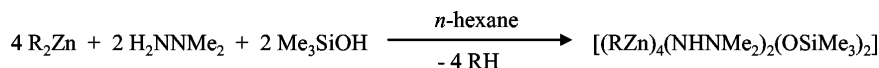
The description as a heterocubane with one single atom anionic vertex replaced by a biatomic N₂ unit of an NHNMe₂ group is a good basis for a discussion of the structure. The atom Zn(4) on the opposite side to the hydrazide unit has angles within the cluster of less than 90° as expected for the cationic part in a heterocubane, and O(4) is surrounded by angles somewhat wider than 90°. The distortion of a hypothetical heterocubane structure is most pronounced for O(2), which is surrounded by two angles only a few degrees larger than 90°, but one, Zn(1)-O(2)-Zn(2), which is substantially wider at 106.7(1)°. The anionic centre N(2) adopts a distorted tetrahedral coordination geometry with the two angles involving N(1) being wider than the tetrahedral angle and the angle Zn(2)-N(2)-Zn(3) compressed to 97.2(1)°. Despite being incorporated into the cage, the N-N bond adopts a typical value of 1.462(3) Å. Surprisingly, the dative bond N(1)-Zn(1) [2.114(2) Å] is shorter than several of the Zn-O bonds [*e. g.* Zn(2)-O(2) 2.128(2) Å]. Generally there is a relatively wide range of Zn-O bond lengths within the cage structure with values from 2.010(2) Å [Zn(4)-O(4)] to 2.136(2) Å [Zn(3)-O(4)], whereas the two non-dative Zn-N bonds are comparatively short at 2.019(2) and 2.029(2) Å.

Tris(alkylzinc) bis-siloxide bis-hydrazides

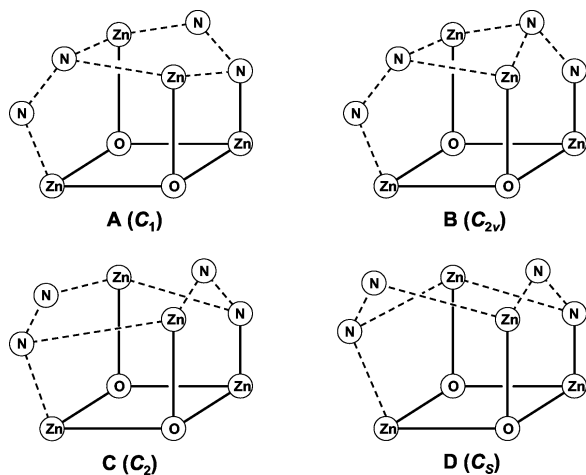
The reaction of two equivalents of R₂Zn (R = Me, Et, *i*Pr) with two equivalents of *N,N*-dimethylhydrazine followed by addition of one equivalent of trimethylsilanol in an one-pot reaction resulted in the formation of aggregates of the formula [(RZn)₄(NHNMe₂)₂(OSiMe₃)₂] [R = Me (**3**), Et (**4**), *i*Pr (**5**)] (Scheme 2). As we discussed above, compound **5** was also obtained when the ratio of hydrazine to silanol was 1 : 1. Due to the bulkiness of the isopropyl group at the zinc atom, the incorporation of a third trimethylsiloxy group into the aggregate with four Zn atoms is more difficult than the incorporation of a comparatively slim hydrazide unit. This has been visualized by simple force field calculations.

Compounds **3**, **4** and **5** are soluble in common hydrocarbon solvents and in ethers. As **1** and **2**, the compounds precipitate in a micro-crystalline form from their *n*-hexane solutions upon cooling for several days to -26 °C. Despite many attempts, single crystalline materials of a quality suitable for structure elucidation could not be obtained.

The composition of compounds **3**, **4** and **5** follows from their elemental analyses, the integration ratios of

[R = Me (**3**), Et (**4**), *i*Pr (**5**)]

Scheme 2.



Scheme 3. The possible four different structural isomers for $\text{Zn}_4\text{N}_4\text{O}_2$ core units in the compounds $[(\text{RZn})_4(\text{NHNMe}_2)_2(\text{OR}')_2]$. Only Zn, O and N atoms are shown for clarity. N atoms with twofold connectivity represent NMe_2 groups, those with threefold connectivity represent NH groups.

the signals in the ^1H NMR spectra and the fact that the mass spectra always show as highest observable mass the value corresponding to the molecular ion of the compositions shown in Scheme 2 diminished by the mass of the respective alkyl groups bound to zinc. IR spectra prove the presence of NH functions.

In the ^1H NMR spectrum of **3**, the protons of the methyl group at zinc show four singlets and the same number of singlets is observed for the methyl groups bound to the nitrogen atoms. Accordingly, each of the methyl groups gives rise to a different signal in the ^{13}C NMR spectra. In the ^{29}Si NMR spectrum of **3** two peaks of the same intensity are observed at 16.87 and 19.33 ppm. All this leads to the conclusion that the cage compound **3** has no molecular symmetry (C_1). The analogous situation can be concluded for the compounds **4** and **5**.

Of the four possible isomers for a $\text{Zn}(\text{N}_2)_2\text{O}_2$ cluster shown in Scheme 3, we can therefore conclude that

only constitution A (Scheme 3) is consistent with the spectroscopic data described above.

Tetra(isopropylzinc) mono-siloxide tris-hydrazide

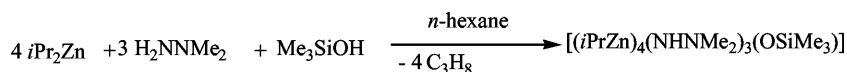
The reaction of two equivalents of $i\text{Pr}_2\text{Zn}$ with five equivalents of *N,N*-dimethylhydrazine and one equivalent of trimethylsilanol in a one-pot reaction led to the formation of $[(i\text{PrZn})_4(\text{NHNMe}_2)_3(\text{OSiMe}_3)]$ (**6**) (Scheme 4). The compound precipitated in microcrystalline form upon storage of *n*-hexane solutions in a -26°C freezer for a few days.

Compound **6** was identified by elemental analysis and spectroscopic methods. The mass spectrum run in EI mode shows a highest mass of $m/z = 583$ corresponding to the mass of the molecular ion diminished by that of an isopropyl group, a trimethylsilyl group and one hydrogen atom. The IR spectrum of **6** shows bands at 3169 and 3279 cm^{-1} corresponding to the N-H stretching modes.

In the ^1H NMR spectrum four sets of doublets were observed for the methyl protons of the isopropyl groups attached to the zinc atoms, while the corresponding septets of the methine protons overlap with one another. The N-H protons lead to one broad resonance at 1.80 ppm and the nitrogen bound methyl groups cause three resolved resonances at 1.95, 2.26 and 2.27 ppm. The higher dispersion of the ^{13}C NMR experiment is more straightforward to assign and contains one single resonance at 4.33 ppm (SiMe_3), four resonances for the methine groups between 11.26 and 13.24 ppm, four resonances between 25.27 and 25.95 ppm for the methyl units in the isopropyl groups and three resonances for the NMe_2 groups between 53.04 and 54.77 ppm. The proton decoupled ^{29}Si NMR spectrum contains one single peak at 17.84 ppm.

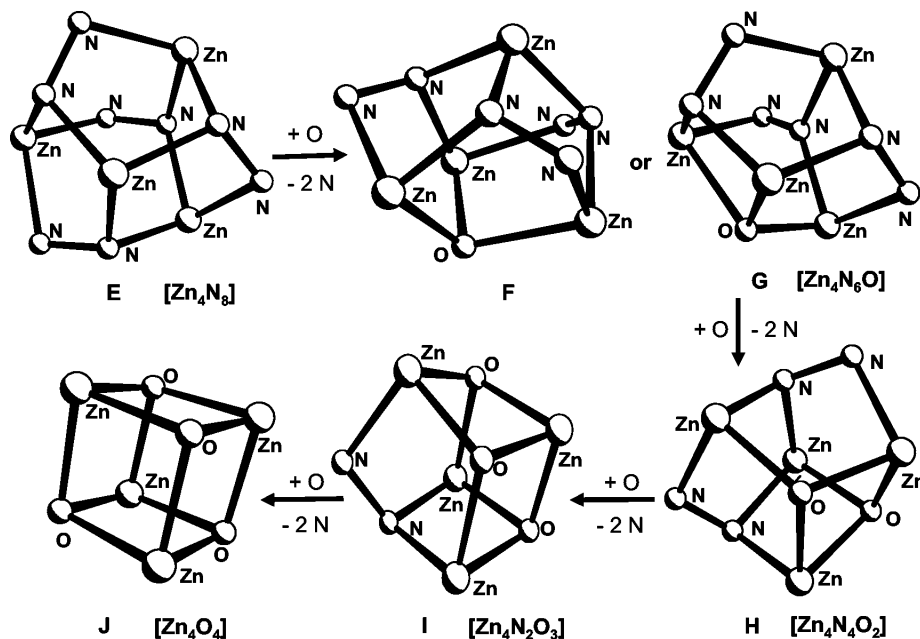
Topology relations between tetra-nuclear zinc hydrazide and alkoxide aggregates

Scheme 5 is the schematic representation of the transformation of the cluster cage Zn_4N_8 to $\text{Zn}_4\text{N}_6\text{O}$ to



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Scheme 4.



Scheme 5. Schematic representation of the formal transformation of cages from Zn_4N_8 (E) to Zn_4O_4 (J) by successive replacement of hydrazide units in $[(\text{RZn})_4(\text{NHNMe}_2)_4]$ by alkoxide/siloxide groups. Only the cage atoms are shown.

$\text{Zn}_4\text{N}_4\text{O}_2$ to $\text{Zn}_4\text{N}_2\text{O}_3$ to Zn_4O_4 by successive replacement of N_2 units (hydrazides) by an O unit (alkoxide/siloxide). In our previous work, we discussed the cage structures of Zn_4N_8 , $\text{Zn}_4\text{N}_6\text{O}$ and $\text{Zn}_4\text{N}_4\text{O}_2$. The Zn_4N_8 cage consists of two six-membered rings and four five-membered rings (shown as E). A $\text{Zn}_4\text{N}_6\text{O}$ cage can adopt two types of aggregation motifs. In one experimentally verified structure, it consists six five-membered rings (shown as F) and in another case a structure with one six-membered, one four-membered and four five-membered rings (shown as G) was found [9].

The $\text{Zn}_4\text{N}_4\text{O}_2$ cage consists of four five-membered and two four-membered rings (shown as H). The $\text{Zn}_4\text{N}_2\text{O}_3$ cage structure discussed for compound **6** in this paper consists of two five-membered and four four-membered rings (shown as I). The hydrazine-free Zn_4O_4 cage consists of a symmetrical heterocubane type structure (shown as J) [11].

The common structural motif of all these compounds is thus a tetrahedron of zinc atoms, with the four faces capped by three bonds to either siloxide/alkoxide groups or hydrazide units. However, of the possible isomeric forms of the Zn_4N_8 , $\text{Zn}_4\text{N}_6\text{O}$ and $\text{Zn}_4\text{N}_4\text{O}_2$ cages only those depicted in Scheme 5 have been experimentally realised.

Experimental Section

General considerations: All manipulations of air-sensitive compounds were carried out under a dry nitrogen atmosphere with standard Schlenk and high-vacuum techniques using double manifolds or a glovebox operated under argon. Solvents were purified and dried by standard methods immediately prior to use. *N,N*-Dimethylhydrazine was purchased from Aldrich Chemical Company and was dried by distillation over CaH_2 under nitrogen atmosphere. Diisopropylzinc was synthesized according to a literature procedure [14]. ^1H and ^{13}C NMR spectra were recorded on a Bruker ARX 400 spectrometer. ^1H and ^{13}C assignments were confirmed when necessary with the use of two-dimensional ^1H – ^1H and ^{13}C – ^1H correlation NMR experiments. All spectra were referenced internally to residual protiosolvent (^1H) or solvent (^{13}C) resonances. Chemical shifts are quoted in ppm and coupling constants in Hz. IR spectra were measured with a Bruker IFS (103 V) using KBr pellets prepared in the glovebox.

$[(\text{MeZn})_4(\text{NHNMe}_2)(\text{OSiMe}_3)_3]$ (**1**): Me_2Zn (10.0 ml of a 2.0 M solution in toluene; 20.0 mmol) was added dropwise via a syringe to a stirred solution of H_2NNMe_2 (0.80 ml, 10.4 mmol) in *n*-hexane (20 ml) at 0 °C. Then Me_3SiOH (1.06 ml, 10.0 mmol) was added slowly. The reaction mixture was gradually warmed to r. t. and stirred for 4 h. The solvents were removed under reduced pressure and the resulting residue was dissolved in *n*-hexane and filtered. The clear,

colourless filtrate was stored at -26°C to afford colourless micro-crystals. Yield: 54% (1.75 g, 2.70 mmol), m. p. $205-206^{\circ}\text{C}$. ^1H NMR (300 MHz, CDCl_3): $\delta = -0.75$ [s, 3 H; ZnCH_3], -0.73 [s, 3 H; ZnCH_3], -0.58 [s, 6 H; ZnCH_3], 0.13 [s, 18 H; $\text{OSi}(\text{CH}_3)_3$], 0.18 [s, 9 H; $\text{OSi}(\text{CH}_3)_3$], 2.44 [s, 1 H; NH], 2.55 ppm [m, 6 H; NMe_2]. ^{13}C $\{^1\text{H}\}$ NMR (75 MHz, CDCl_3): $\delta = -12.23, -12.19, -11.47$ [ZnCH_3], $2.63, 2.85, 3.36$ [$\text{OSi}(\text{CH}_3)_3$], 53.77 ppm [NMe_2]. ^{29}Si $\{^1\text{H}\}$ NMR (79.5 MHz, DEPT135, C_6D_6) $\delta = 16.98, 19.67$ ppm [OSiMe_3]. – EI-MS [m/z (%): 633 (11), [$\text{M}^+ - \text{CH}_3$]; 493 (100), [$\text{M}^+ - \text{MeZnNHNMe}_2$]. – IR [KBr, cm^{-1}]: 3151 (N–H). – $\text{C}_{15}\text{H}_{46}\text{N}_2\text{O}_3\text{Si}_3\text{Zn}_4$: calcd. C 27.79, H 7.15, N 4.32; found C 27.59, H 7.20, N 4.29.

$[(\text{EtZn})_4(\text{NHNMe}_2)(\text{OSiMe}_3)_3]$ (2): The experimental procedure was the same as for compound 1, but Et_2Zn (10.0 ml of a 2.0 M solution in *n*-hexane; 20.0 mmol) was used instead of Me_2Zn . An *n*-hexane solution of compound 2 was stored at -26°C for several days to afford colourless plate-like crystals. Yield: 63% (2.22 g, 3.15 mmol), m. p. $238-239^{\circ}\text{C}$. ^1H NMR (400.1 MHz, C_6D_6): $\delta = 0.27$ [s, 9 H; $\text{OSi}(\text{CH}_3)_3$], 0.29 [s, 18 H; $\text{OSi}(\text{CH}_3)_3$], 0.44 [q, $^3J_{\text{H,H}} = 8.1$ Hz, 2 H; ZnCH_2CH_3], 0.51 [q, $^3J_{\text{H,H}} = 8.1$ Hz, 4 H; ZnCH_2CH_3], 0.63 [q, $^3J_{\text{H,H}} = 8.1$ Hz, 2 H; ZnCH_2CH_3], 1.34 [t, $^3J_{\text{H,H}} = 8.1$ Hz, 3 H; ZnCH_2CH_3], 1.46 [t, $^3J_{\text{H,H}} = 8.1$ Hz, 6 H; ZnCH_2CH_3], 1.56 [t, $^3J_{\text{H,H}} = 8.1$ Hz, 3 H; ZnCH_2CH_3], 1.95 [s, 1 H; NH], 2.00 ppm [s, 6 H; NMe_2]. ^{13}C $\{^1\text{H}\}$ NMR (100.6 MHz, C_6D_6): $\delta = 1.37, 2.87, 2.96$ [ZnCH_2CH_3], $3.29, 3.53$ [$\text{OSi}(\text{CH}_3)_3$], $13.40, 13.45, 13.82$ [ZnCH_2CH_3], 53.30 ppm [NMe_2]. ^{29}Si $\{^1\text{H}\}$ NMR (79.5 MHz, DEPT135, C_6D_6) $\delta = 17.29, 19.87$ ppm [OSiMe_3]. – EI-MS [m/z (%): 675 (23), [$\text{M}^+ - \text{C}_2\text{H}_5$]; 615 (72), [$\text{M}^+ - \text{C}_3\text{H}_9\text{OSi}$]. – IR [KBr, cm^{-1}]: 3174 (N–H). – $\text{C}_{19}\text{H}_{54}\text{N}_2\text{O}_3\text{Si}_3\text{Zn}_4$: calcd. C 32.39, H 7.73, N 3.98; found C 32.10, H 7.56, N 4.15.

$[(\text{MeZn})_4(\text{NHNMe}_2)_2(\text{OSiMe}_3)_2]$ (3): Me_2Zn (10.00 ml of a 2.0 M solution in toluene; 20.0 mmol) was added dropwise via a syringe to a stirred solution of H_2NNMe_2 (1.55 ml, 20.24 mmol) in *n*-hexane (20 ml) at 0°C . Me_3SiOH (1.06 ml, 10.0 mmol) was added slowly and the reaction mixture was gradually warmed to r. t. and stirred for 4 h. The solvents were removed under reduced pressure and the resulting residue was dissolved in *n*-hexane and filtered. The clear, colourless filtrate was stored at -26°C to afford micro-crystals of 3. Yield: 57% (1.76 g, 2.85 mmol), m. p. $135-136^{\circ}\text{C}$. ^1H NMR (400.1 MHz, C_6D_6): $\delta = -0.56$ [s, 3 H; ZnCH_3], -0.45 [s, 3 H; ZnCH_3], -0.39 [s, 3 H; ZnCH_3], -0.24 [s, 3 H; ZnCH_3], 0.35 [s, 9 H; $\text{OSi}(\text{CH}_3)_3$], 0.39 [s, 9 H; $\text{OSi}(\text{CH}_3)_3$], 1.41 [s, 1 H; NH], 1.63 [s, 3 H; NMe_2], 1.82 [s, 1 H; NH], 2.03 [s, 3 H; NMe_2], 2.14 [s, 3 H; NMe_2], 2.15 ppm [s, 3 H; NMe_2]. ^{13}C $\{^1\text{H}\}$ NMR (100.6 MHz, C_6D_6): $\delta = -13.17, -12.94, -10.84, -9.39$ [ZnCH_3], $3.42, 4.01$ [$\text{OSi}(\text{CH}_3)_3$], $52.44, 52.67, 53.33, 53.36$ ppm [NMe_2]. ^{29}Si $\{^1\text{H}\}$ NMR (79.5 MHz, DEPT135, C_6D_6) $\delta = 16.87,$

19.33 ppm [OSiMe_3]. – EI-MS [m/z (%): 603 (38), [$\text{M}^+ - \text{CH}_3$]; 433 (100), [$\text{M}^+ - \text{MeZnOSiMe}_3 - \text{Me}$]. – IR [KBr, cm^{-1}]: 3186 (N–H). – $\text{C}_{14}\text{H}_{44}\text{N}_4\text{O}_2\text{Si}_2\text{Zn}_4$: calcd. C 27.20, H 7.17, N 9.06; found C 26.92, H 6.93, N 8.95.

$[(\text{EtZn})_4(\text{NHNMe}_2)_2(\text{OSiMe}_3)_2]$ (4): The experimental procedure was the same as for 3, but Et_2Zn (10.00 ml of a 2.0 M solution in *n*-hexane; 20.0 mmol) was used instead of Me_2Zn . An *n*-hexane solution of compound 4 was stored at -26°C for several days to afford colourless micro-crystals. Yield: 52% (1.75 g, 2.59 mmol), m. p. $220-222^{\circ}\text{C}$. ^1H NMR (400.1 MHz, C_6D_6): $\delta = 0.23, 0.27, 0.29, 0.32, 0.34$ [s, 18 H; $\text{OSi}(\text{CH}_3)_3$], $0.39-0.65$ [m, 8 H; ZnCH_2CH_3], $1.34-1.58$ [m, 12 H; ZnCH_2CH_3], 1.75 [s, 2 H; NH], $1.97-2.29$ ppm [m, 12 H; NMe_2]. ^{13}C $\{^1\text{H}\}$ NMR (100.6 MHz, C_6D_6): $\delta = 1.38, 2.06, 2.62, 2.87$ [ZnCH_2CH_3], $3.31, 3.89, 4.14$ [$\text{OSi}(\text{CH}_3)_3$], $13.65, 13.96, 14.04, 14.12$ [ZnCH_2CH_3], $53.10, 53.22, 53.75, 53.87$ ppm [NMe_2]. ^{29}Si $\{^1\text{H}\}$ NMR (79.5 MHz, DEPT135, C_6D_6) $\delta = 16.45, 18.86$ ppm [OSiMe_3]. – EI-MS [m/z (%): 657 (29), [$\text{M}^+ - \text{C}_2\text{H}_5$]; 597 (65), [$\text{M}^+ - \text{C}_3\text{H}_9\text{OSi}$]. – IR [KBr, cm^{-1}]: 3177 (N–H). – $\text{C}_{18}\text{H}_{52}\text{N}_4\text{O}_2\text{Si}_2\text{Zn}_4$: calcd. C 32.06, H 7.77, N 8.31; found C 31.85, H 7.52, N 8.28.

$[(\text{iPrZn})_4(\text{NHNMe}_2)_2(\text{OSiMe}_3)_2]$ (5): iPr_2Zn (8.00 ml of a 2.5 M solution in diethylether; 20.0 mmol) was added dropwise via a syringe to a stirred solution of H_2NNMe_2 (1.55 ml, 20.2 mmol) in *n*-hexane (20 ml) at 0°C . Me_3SiOH (1.06 ml, 10.0 mmol) was added slowly and the reaction mixture was gradually warmed to r. t. and stirred for 4 h. The solvents were removed under reduced pressure and the resulting residue was dissolved in *n*-hexane and filtered. The clear, colourless filtrate was stored at -26°C to afford colourless micro-crystals of 5. Yield: 66% (2.41 g, 3.30 mmol), m. p. $192-193^{\circ}\text{C}$. ^1H NMR (400.1 MHz, C_6D_6): $\delta = 0.28-0.42$ [m, 18 H; $\text{OSi}(\text{CH}_3)_3$], $0.59-0.75$ [m, 2 H; $\text{ZnCH}(\text{CH}_3)_2$], $0.83-0.95$ [m, 2 H; $\text{ZnCH}(\text{CH}_3)_2$], $1.40-1.60$ [m, 24 H; $\text{ZnCH}(\text{CH}_3)_2$], $1.72-2.36$ ppm [m, 14 H; NH , NMe_2]. ^{13}C $\{^1\text{H}\}$ NMR (100.6 MHz, C_6D_6): $\delta = 3.73, 4.28$ [$\text{OSi}(\text{CH}_3)_3$], $13.36, 13.74, 13.79, 14.69$ [$\text{ZnCH}(\text{CH}_3)_2$], $25.21, 25.27, 25.44, 25.54, 25.58, 25.80$ [$\text{ZnCH}(\text{CH}_3)_2$], $53.89, 53.95, 54.18, 54.62$ ppm [NMe_2]. ^{29}Si $\{^1\text{H}\}$ NMR (79.5 MHz, DEPT135, C_6D_6) $\delta = 15.99, 18.61$ ppm [OSiMe_3]. – EI-MS [m/z (%): 687 (5), [$\text{M}^+ - \text{C}_3\text{H}_7$]; 613 (65), [$\text{M}^+ - \text{C}_3\text{H}_7 - \text{SiMe}_3$]; 555 (100), [$\text{M}^+ - \text{C}_3\text{H}_7 - \text{SiMe}_3 - \text{NHNMe}_2 - \text{H}$]; IR [KBr, cm^{-1}]: 3186 (N–H). – $\text{C}_{22}\text{H}_{60}\text{N}_4\text{O}_2\text{Si}_2\text{Zn}_4$: calcd. C 36.17, H 8.28, N 7.67; found C 35.89, H 8.35, N 7.42.

$[(\text{iPrZn})_4(\text{NHNMe}_2)_3(\text{OSiMe}_3)]$ (6): iPr_2Zn (8.00 ml of a 2.5 M solution in diethylether; 20.0 mmol) was added dropwise via syringe to a stirred solution of H_2NNMe_2 (3.83 ml, 50.03 mmol) in *n*-hexane (20 ml) at 0°C . Me_3SiOH (1.06 ml, 10.0 mmol) was added slowly and the reaction mixture was gradually warmed to r. t. and stirred for 4 h. The solvents were removed under reduced pressure and the result-

ing residue was dissolved in *n*-hexane and filtered. The clear, colourless filtrate was stored at $-26\text{ }^{\circ}\text{C}$ to afford colourless micro-crystals of **6**. Yield: 52% (1.82 g, 2.60 mmol), m.p. $123\text{--}124\text{ }^{\circ}\text{C}$. – ^1H NMR (400.1 MHz, C_6D_6): δ = 0.30 [s, 9 H; $\text{OSi}(\text{CH}_3)_3$], 0.67 [sept, $^3J_{\text{H,H}} = 7.8\text{ Hz}$, 4 H; $\text{ZnCH}(\text{CH}_3)_2$], 1.42 [d, $^3J_{\text{H,H}} = 7.6\text{ Hz}$, 3 H; $\text{ZnCH}(\text{CH}_3)_2$], 1.49 [d, $^3J_{\text{H,H}} = 7.6\text{ Hz}$, 9 H; $\text{ZnCH}(\text{CH}_3)_2$], 1.51 [d, $^3J_{\text{H,H}} = 7.6\text{ Hz}$, 9 H; $\text{ZnCH}(\text{CH}_3)_2$], 1.63 [d, $^3J_{\text{H,H}} = 7.8\text{ Hz}$, 3 H; $\text{ZnCH}(\text{CH}_3)_2$], 1.80 [broad s, 3 H; NH], 1.95 [s, 9 H; NMe_2], 2.26, 2.27 ppm [s, 9 H; NMe_2]. – ^{13}C $\{^1\text{H}\}$ NMR (100.6 MHz, C_6D_6): δ = 4.33 [$\text{OSi}(\text{CH}_3)_3$], 11.26, 11.69, 11.88, 13.24 [$\text{ZnCH}(\text{CH}_3)_2$], 25.27, 25.33, 25.42, 25.50, 25.95 [$\text{ZnCH}(\text{CH}_3)_2$], 53.04, 54.12, 54.77 ppm [NMe_2]. – ^{29}Si $\{^1\text{H}\}$ NMR (79.5 MHz, DEPT135, C_6D_6) δ = 17.84 ppm [OSiMe_3]. – EI-MS [m/z (%): 583 (23), [$\text{M}^+ - \text{C}_3\text{H}_7 - \text{SiMe}_3 - \text{H}$]; 525 (96), [$\text{M}^+ - \text{C}_3\text{H}_7 - \text{OSiMe}_3 - \text{H}$]. – IR [KBr, cm^{-1}]: 3169, 3279 (N–H). – $\text{C}_{21}\text{H}_{58}\text{N}_6\text{OSiZn}_4$: calcd. C 36.01, H 8.35, N 12.00; found C 35.88, H 8.42, N 11.97.

Crystal structure determination. A Nonius Kappa-CCD X-ray diffractometer was used to collect the scattering intensities for the single crystal of **2**. Crystals were selected and prepared under perfluoropolyether and mounted in a drop of it onto the tip of a glass fibre on the goniometer head of the diffractometer. The structures were solved by direct methods and refined with the full-matrix least

squares procedure (SHELXTL) [15] against F^2 . Formula $\text{C}_{19}\text{H}_{54}\text{N}_2\text{O}_3\text{Si}_3\text{Zn}_4$ M_r 704.39, crystal size $0.40 \times 0.30 \times 0.30\text{ mm}$, crystal system triclinic, space group $P\bar{1}$, $a = 9.422(1)$, $b = 10.473(1)$, $c = 18.885(1)\text{ \AA}$, $\alpha = 91.61(1)$, $\beta = 104.16(1)$, $\gamma = 112.17(1)^{\circ}$, $V = 1658.2(3)\text{ \AA}^3$, $T = 198(2)\text{ K}$, $Z = 2$, $\rho_{\text{calc}} = 1.41\text{ g cm}^{-3}$, $\lambda = 0.71073\text{ \AA}$, $\mu = 2.99\text{ mm}^{-1}$. 18953 scattering intensities were collected of which 7881 were independent and 6085 met the observed criterion. $R_{\text{int}} = 0.059$, $R_1 = 0.038$, $wR_2 = 0.088$ for $i > 2\sigma(i)$, and $R_1 = 0.057$, $wR_2 = 0.095$ for all data. $\Delta\rho_{\text{fin}} = 0.55/-0.67\text{ e\AA}^{-3}$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been forwarded to the Cambridge Crystallographic Data Centre as supplementary publication. The deposition number is CCDC number 601602. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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