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Facile synthesis and structural variation of novel heterobimetallic alkali metal–zinc-alkoxide and -siloxide clusters†

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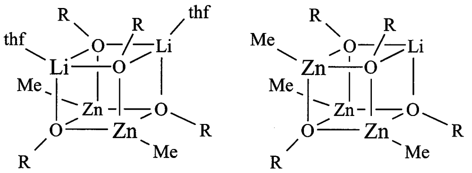
The novel alkali metal zinc-alkoxide and the first -siloxide aggregates $[(thf)M(MeZn)(O^tBu)_2]_2$ **1a** (M = Li), **1b** (M = Na), $[(thf)_2K(MeZn)(OSiMe_3)_2]_2$ **2** and $[(tmeda)KZn(OSiMe_3)_3]_2$ **3** are easily accessible from the reaction of Me_2Zn with MOR (molar ratio 1 : 1; M = Li, Na, K; R = ^{t}Bu, $SiMe_3$) in boiling thf and tmeda, respectively. While **1a**, **1b** and **2** possess distorted $M_2Zn_2O_4$ heterocubane frameworks, compound **3** consists of a $K_2Zn_2O_6$ core of a strongly distorted, face-fused double-heterocubane with two missing corners. In contrast, heating a mixture of Me_2Zn and KO^tBu in the molar ratio of 1 : 1 in toluene affords the donor solvent-free K–Zn–O cluster $[K(MeZn)_3(O^tBu)_4]$ **4** which crystallizes as a polymer of strongly distorted $[KZn_3O_4]$ heterocubanes *via* intermolecular agostic K ··· MeZn interactions. The formation of the clusters may be rationalized in terms of alkali metal ion- and donor solvent-dependent ligand exchange reactions of methyl(alkoxide)- and methyl(siloxide)-zincates as initial products. Some of the initial products have been detected by means of electro spray ionisation (ESI) mass spectrometry.

Introduction

The rich structural variety of discrete metal–oxygen clusters is of importance for the development of new multi-component materials and catalysts based on metal oxides.[1] Especially the development of novel single-source precursors which allow the synthesis of size- and shape-selected, homo- and hetero-metal oxide particles is one of the actual challenges in inorganic chemistry with regard to material science. Volatile organometallic oxide presursors offer several advantages for the synthesis of nano-scaled metal oxides in different environments because they can be used in chemical-vapour-synthesis (CVS), in solution (non-hydrolytic and hydrolytic sol–gel-synthesis) or in solid state synthesis (synthesis of nanoscaled solids). We are currently using organozinc-alkoxide[2] and -siloxide clusters[3] as molecular models and volatile multiple precursors for nano-scaled ZnO, Zn and ortho-zinc silicate (Zn_2SiO_4) particles.[4] ZnO is one of the most important substrates in heterogeneous catalysis (*e.g.*, industrial methanol synthesis[5]) but its (micro)-structure–reactivity relationship is not yet well understood even after more than 30 years of intensive research. We have shown that organozinc siloxide clusters[3] can be used as remarkable versatile precursors for the synthesis of highly active nanocrystalline ZnO and heterometal ZnO supports for the conversion of CO_2 and H_2 into methanol and H_2O.[5] Remarkably, alkali metal ion-modified ZnO supports show uncommonly strong one- and two-electron donor properties and are unusual super-basic heterogeneous catalysts.[6] Since the catalytic activity of ZnO supports can be drastically enhanced in the presence of several promotor components (*e.g.*, Cu particles, alkali metal ions, *etc.*) it is furthermore highly desirable to gain access to appropriate single-source precursors for such multi-component ZnO substrates which are far less developed or hitherto unknown. Therefore we are also currently focusing on the synthesis of structurally defined heterometal zinc-alkoxide and -siloxide clusters as molecular single-source presursors for alkali metal-modified ZnO systems. We learned that the structural chemistry of seemingly simple mixed alkali metal zinc alkoxides is only scarcely developed, although they have a long tradition as reactive species in both organic and inorganic synthesis. For example, it is well known that dialkylzinc compounds can be highly activated as alkyl transfer reagents towards unsaturated organic substrates in the presence of alkali metal alkoxides,[7] and diorganozinc compounds react with CO to give acyloins but only in the presence of alkali metal alkoxides as promotors.[8]

A survey of the literature on alkali metal zincates shows that the structural chemistry is mostly devoted to lithium tri-organo- and tetraorgano-zincates,[9] while little is known about alkoxyzincates.[10] Recently, remarkable one-pot syntheses of mixed organo-alkoxyzincates have been reported by reactions of $ZnMe_2$ with secondary amines or amidine ligands and Li^tBu in the presence of molecular oxygen but this method seems rather limited to lithium derivatives.[11,12] The latter method gave access to the structurally characterized Li–Zn–O clusters $[((thf)Li)_2(MeZn)_2(O^tBu)_4]$ **A** and $[Li(MeZn)_3(O^tBu)_4]$ **B** having a heterocubane core. Related bimetallic organozinc siloxides with larger cluster frameworks have also been reported.[13,14]



A R = ^{t}Bu **B**

While previous investigations on the reaction of diorganozinc compounds (R_2Zn) with alkali metal alkoxides (MOR′) in benzene were reported to give only organozincates with R_2Zn : MOR′ ratios of 1 : 1 or 2 : 1,[15] we have found that ligand exchange reactions between dimethylzinc and alkali metal-alkoxides and -siloxides can also lead to a variety of novel heterobimetallic ZnO clusters. We present here a simple and productive method for the synthesis of novel alkali metal–methylzinc-alkoxide and -siloxide clusters, starting from dimethylzinc and the respective alkali metal salts in coordinating and non-coordinating solvents at elevated temperature.

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† Electronic supplementary information (ESI) available: the ESI spectra of the reaction mixtures ^{t}BuOLi + $ZnMe_2$, Me_3SiOK + $ZnMe_2$ and ^{t}BuOK + $ZnMe_2$. See http://www.rsc.org/suppdata/dt/b3/b302585c/

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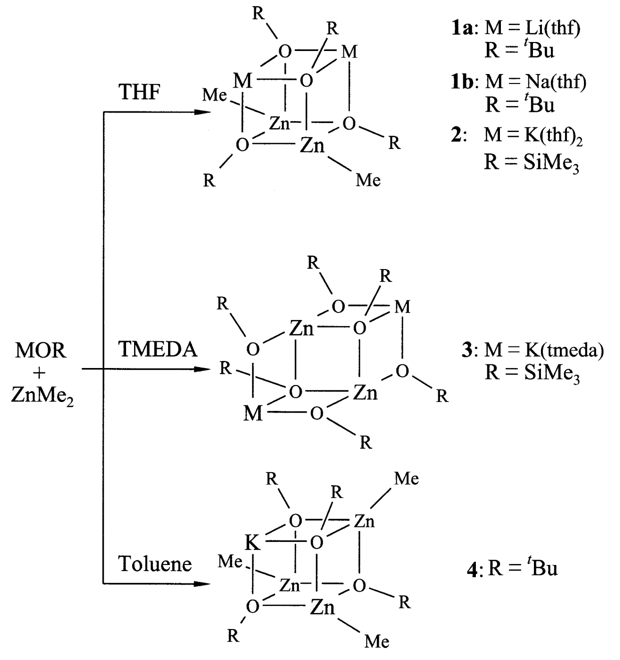
Results and discussion

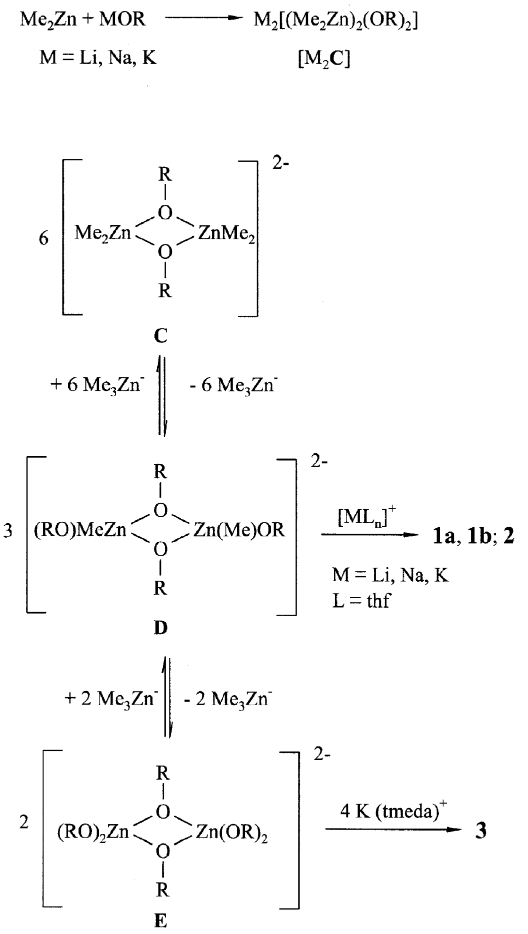
Reaction of a mixture of the respective alkali metal *tert*-butoxides and trimethylsiloxides with ZnMe$_2$ in the molar ratio of 1 : 1 in thf, tmeda or toluene affords the bimetallic M–Zn–O clusters **1a** (M = Li), **1b** (M = Na), **2**, **3**, and **4** (M = K), respectively, which were isolated in the form of colorless crystals in 62–74% yield (Scheme 1).



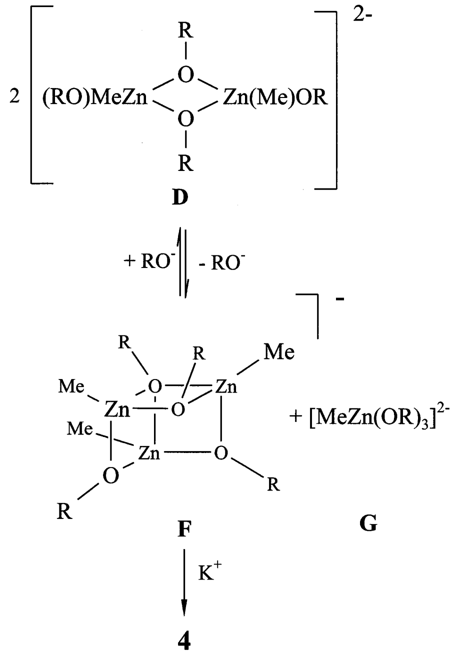
Scheme 1 Reagents and conditions to synthesize the compounds **1a**, **1b**, **2**, **3**, and **4**.

Since the driving force for the formation of the mixed aggregates is attributed to ligand exchange and effective solvation of the alkali metal ions during formation of different contact ion pairs, one can expect that the polarity and donor ability of the solvent have a large influence on the nature of the products. Surprisingly, replacement of thf by tmeda affords neither the structural analogue of **1a**, **1b** nor that of **2**. Instead the reaction of a thf/tmeda solution of KO^{t}Bu with ZnMe$_2$ affords a solution from which the crystalline compound **3** deposits. This signals that the donor ability of the solvent plays a major role during the required ligand exchange processes. Although the mechanism is still unknown, it is reasonable to assume that the initial step of the reaction of MOR with ZnMe$_2$ occurs *via* several multinuclear zincate species as outlined in Scheme 2. Previous results by Richey *et al.* suggested that the dimeric zincate species **C** is one of the initial products.[15] Our attempts to detect **C** and the other anionic intermediates **D, E** and **F** (Schemes 2 and 3) in reaction mixtures were only of partial success. We applied ESI (electro spray ionisation) mass spectrometry for the detection of negatively charged intermediates in the reaction mixtures. Thus, reaction mixtures for the synthesis of **1a** contain mostly the cluster anion {[**C** + Li$^+$ + (LiO^{t}Bu)$_2$ + 4 thf]} (see ESI†). The formation of **C** is also evident by detection of [**C** + K$^+$] in the mixture for the synthesis of **2**. Additionally, the spectrum for the synthesis of **2** shows the anion [**D** + K$^+$] besides other not as yet identified anions (see ESI†).

However, alkali metal-coordinated or “free” **E** could not be detected by ESI mass spectrometry of reaction mixtures in the synthesis of **3**. Apparently, coordination of **D** to thf-solvated Li and K ions readily leads to **1a**, **1b**, **2**, while coordination of **E** to tmeda-solvated potassium ions furnishes **3**. The formation of **4** can be simply explained on the basis of another equilibrium where **D** dismutates, under liberation of OR$^-$, to the pseudo-cubic chelate ligand **F** and **G** as depicted in Scheme 3. While **G** could not be detected, the mixed anion [(MeZn)$_3$(O^{t}Bu)$_4$]$^-$ (**F**) is visible in ESI mass spectrometry from reaction mixtures in the synthesis of **4**.



Scheme 2 Proposed mechanism for the formation of **1a**, **1b**, **2**, and **3** *via* **C**, **D**, and **E**.



Scheme 3 Proposed mechanism for the formation of **4** *via* **D**, **F**, and **G**.

Due to fast ligand exchange processes at ambient temperature on the NMR time scale and the scarce solubility of the zincates below room temperature, neither ^{1}H nor ^{13}C NMR spectroscopic measurements were appropriate for the assignment of the products in the reaction mixtures. Therefore the structural characterization of **1a**, **1b**, **2**, **3** and **4** is based on single-crystal X-ray diffraction.

The lithium salt **1a** is identical with **A** and adopts a pseudo-cubane structure which has already been reported.[16] X-Ray analysis of the sodium analogue **1b** revealed the presence of the isostructural $Na_2Zn_2O_4$ cubane core but due to the moderate crystal quality the structural model could not be refined accurately. In the case of the siloxide cluster **2** the molecular structure consists of a pseudo-cubic $K_2Zn_2O_4$ cluster core where each potassium ion bears two thf ligands (Fig. 1). Apparently, the large potassium ion radius and the presence of the thf donor molecules affects a remarkably strong distortion of the hetero-cubane core. The nearly planar Zn_2O_2-moiety reveals mean Zn–O distances of 2.033(4) and 2.063(4) Å, which are slightly shorter than the values observed in $[MeZn(OSiEt_3)]_4$ (Zn–O average 2.089(4) Å) and related systems.[3c,17] However, the Zn1–O3 and Zn2–O4 distances in **2** are even shorter (averaged 1.995(3) and 1.984(3) Å) due to the higher negative partial charge of the O3 and O4 atoms. In contrast to the almost planar Zn_2O_2 partial structure, the four-membered K_2O_2 moiety is puckered with a dihedral angle between the two KO_2 planes of 36.6°. In line with that, the endocyclic O–K–OZn angles (average 69°) deviate from the ideal value of 90° for a cubic system.

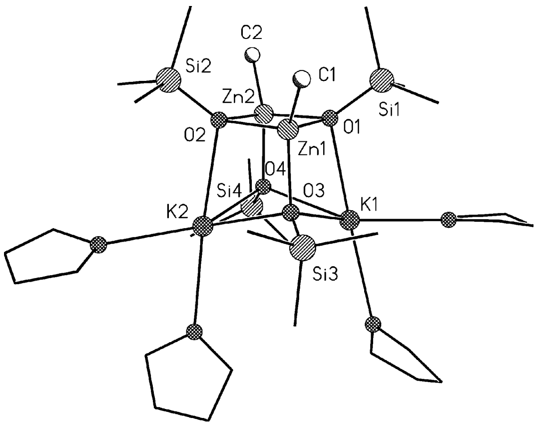


Fig. 1 Molecular structure of the $K_2Zn_2O_4$ heterocubane $[(thf)_2K(MeZn)(OSiMe_3)_2]_2$ **2**; hydrogen atoms omitted for clarity. Selected distances [Å] and angles [°]: Zn(1)–O(1) 2.033(4), Zn(1)–O(2) 2.063(4), Zn(2)–O(1) 2.061(4), Zn(2)–O(2) 2.081(4), Zn(1)–O(3) 1.995(3), Zn(2)–O(4) 1.984(3), K(1)–O(1) 2.682(4), K(1)–O(4) 2.692(4), K(1)–O(3) 2.716(3), K(2)–O(3) 2.672(4), K(2)–O(2) 2.696(4), K(2)–O(4) 2.698(4); O(1)–K(1)–O(4) 68.5(1), O(1)–K(1)–O(3) 68.7(1), O(4)–K(2)–O(2) 70.1(1), O(2)–K(2)–O(4) 69.9(1).

X-Ray structure analysis of $[(tmeda)KZn(OSiMe_3)_3]_2$ **3** revealed a centrosymmetric structure of a novel hetero-bimetallic alkali metal zincate cluster framework. As shown in Fig. 2, the crystal is composed of units which formally are dimers of mixed K(tmeda)OR/Zn(OR)$_2$ aggregates (R = SiMe$_3$) in which all metal centers share bridging $OSiMe_3$ groups. The molecular structure of the mixed $K_2Zn_2O_6$ cluster core consists of a strongly distorted face-fused double heterocubane with two missing corners. The planar Zn_2O_2 moiety has uniform Zn–O distances which resemble the values observed for related Zn_2O_2 dimers.[3c,17] While each Zn atom exhibits a slightly distorted tetrahedral ligand surrounding, the K ions are five-fold-coordinated.

The structural analysis of **4** revealed that the heterocubane cluster crystallizes as a toluene solvate and is polymeric. The framework-constituents of the new heterobimetallic polymer are strongly distorted cubes of KZn_3O_4 units (Fig. 3). In contrast to the previously reported crystal structure analysis of $LiZn_3O_4$ **B**,[11] the metal centers in the KZn_3O_4 core can be refined with 100% occupancy. The result of the refinement of **4** shows significant differences in M–O bond lengths and angles. The average Zn–O and K–O distances of 2.055(7) and 2.687(7) Å as well as the intramolecular Zn ··· Zn (3.050(2) Å) and Zn ··· K (3.575(3) Å) distances reflect a strong distortion of the pseudo-cubic KZn_3O_4 core. Similar to **2** and **3**, the O–K–O angles are strongly distorted (66.4(2), 67.3(2) and 67.6(2)°) and differ from the expected value of 90° for an ideal cube. Interestingly, the KZn_3O_4 cubes in **4** are connected to a zig-zag polymer *via* agostic intermolecular K ··· H_3CZn coordination (K ··· H–C interactions) of the coordinatively unsaturated potassium ion with one close Me group of an adjacent cluster (Fig. 3b). The K1 ··· C2a–Zn2a angle of the bridge is nearly linear (174.0(6)°) and the intermolecular K1 ··· C2a distance (3.20(1) Å) indicates K ··· H–C interactions. The respective K ··· H distances (hydrogen atoms of Zn–Me could not be located) were calculated to range from 2.9 to 3.1 Å. There is no sign of significant coordinating interactions between the toluene molecules in the voids of the crystal and the potassium ion.

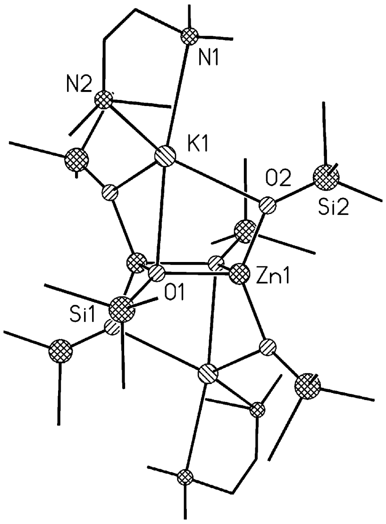


Fig. 2 Molecular structure of dimeric tmeda solvate $[(tmeda)KZn(OSiMe_3)_3]_2$ **3**; hydrogen atoms omitted for clarity. Selected distances [Å] and angles [°]: Zn(1)–O(1) 2.025(2), Zn(1)–O(2) 1.889(3), K(1)–O(1) 2.807(4), K(1)–O(2) 2.698(4); O(1)–Zn(1)–O(2) 104.5(1), Zn(1)–O(1)–Zn(1) 94.0(1), O(2)–K(1)–O(1) 68.44(8).

Conclusion

We have shown that the ligand exchange reactions between dimethylzinc and alkali metal *tert*-butoxides and trimethylsiloxides in coordinating (thf, tmeda) or non-coordinating solvents (toluene) offer a simple and efficient access to novel mixed alkali metal–zinc-alkoxide and -siloxide clusters. Apparently the coordination ability of the solvent molecules towards the alkali metal ions has a more delicate influence on ligand exchange and formation of higher mixed aggregates than previously proposed by Richey *et al.* and Wheatley *et al.*[11,12] Further work is necessary to elucidate the mechanism for the nucleation process and to probe whether one could also use this method to synthesize other molecular heterobimetallic transition-metal/zinc oxo clusters.

Experimental

Methods and materials

General remarks. All manipulations were carried out under anaerobic conditions in dry argon using standard Schlenk techniques. Solvents were refluxed over an appropriate drying agent, and distilled and degassed prior to use. All other chemical reagents were used as received from Aldrich or Lancaster

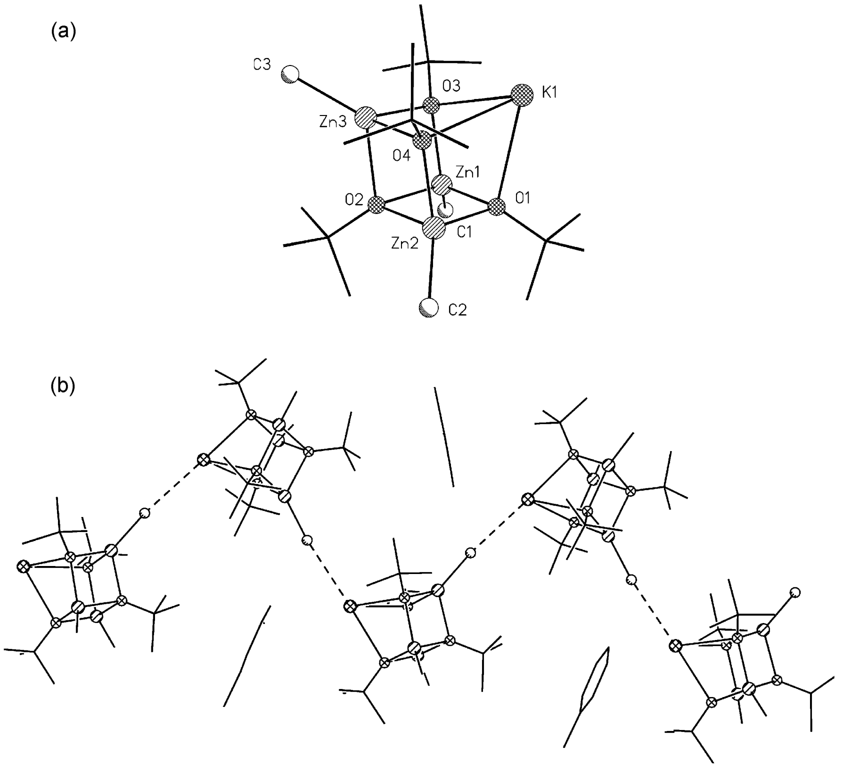


Fig. 3 a) Molecular structure of **4**·C_7H_8 and b) crystal packing of the polymeric [K(MeZnO^{t}Bu)$_4$]·C_7H_8 (**4**·C_7H_8); hydrogen atoms have been omitted for clarity. Selected distances [Å] and angles [°]:.Zn(1)–O(1) 2.055(7), Zn(1)–O(2) 2.093(7), Zn(1)–O(3) 2.015(7), Zn(2)–O(1) 2.017(7), Zn(2)–O(2) 2.087(7), Zn(2)–O(4) 2.005(7), Zn(3)–O(2) 2.104(7), Zn(3)–O(3) 2.047(7), Zn(3)–O(4) 2.036(7), K(1)–O(1) 2.696(7), K(1)–O(3) 2.667(7), K(1)–O(4) 2.698(7), Zn(2)–C(2) 2.00(1), K(1) ··· C(2a) 3.20(1); O(1)–K(1)–O(4) 66.4(2), O(1)–K(1)–O(3) 67.3(2), O(3)–K(1)–O(4) 67.6(2).

without further purification. NMR spectra were recorded on a Bruker Avance250 spectrometer at ambient temperature operating at 250.1 MHz (^{1}H). Chemical shifts are referenced to $SiMe_4$ at 0.00 ppm (^{1}H). ESI mass spectra were measured on a Bruker Daltonik Esquire 3000 plus (4 kV spray voltages) in negative mode, controlled by Esquirecontrol 5.0.

Synthesis and characterization. *[(thf)M(MeZn)(O^{t}Bu)$_2$]$_2$ **1a**: M = Li; **1b**: M = Na.* A solution of $ZnMe_2$ (1.44 g, 15.2 mmol, 2 M solution in toluene (Aldrich)) at −78 °C in *ca.* 100 ml thf was slowly treated with (15.2 mmol) MO^{t}Bu in 10 ml thf. After being allowed to warm to room temperature the mixture was refluxed for 1 h. At room temperature all volatile components were removed *in vacuo* (10^{-3} Torr). Colorless plates were isolated after recrystallization of the residue from a little toluene at −25 °C.

1a: M = Li. Yield: 3.43 g (5.63 mmol, 74%); the compound was characterized according to the literature procedure.[16]

1b: M = Na. Yield: 3.25 g (5.17 mmol, 68%); mp = 183–188 °C (decomp.). ^{1}H NMR (C_6D_6): δ = 3.61 (m, 8H; thf), 1.79 (m, 8H; thf), 1.22 (s, 18H; ^{t}Bu), 1.17 (s, 18H; ^{t}Bu), −0.75 (s, 6H; ZnMe); $C_{26}H_{48}Na_2O_2Zn_2$ (643.5): calc. C 48.53, H 9.09; found C 48.01, H 9.06%.

*[(thf)$_2$K(MeZn)(OSiMe$_3$)$_2$]$_2$ **2**.* A solution of $ZnMe_2$ (1.44 g, 15.2 mmol, 2 M solution in toluene (Aldrich)) was added at −78 °C to a solution of 1.95 g (15.2 mmol) $KOSiMe_3$ in 100 ml thf and stirred at this temperature for 1 h. After being allowed to warm to room temperature the mixture was refluxed for 2 h. After removal of the solvent and other volatile components *in vacuo* (10^{-3} Torr), the resulting residue was taken up in *ca.* 20 ml toluene. The desired product crystallizes at −25 °C after several days in the form of colorless needles. Yield: 5.09 g (5.78 mmol, 76%); mp = 181–185 °C (decomp.). ^{1}H NMR (C_6D_6): δ = 3.63 (m, 16H; thf), 1.80 (m, 16 H; thf), 0.62 (s, 18 H; $SiMe_3$), 0.61 (s, 18 H; $SiMe_3$), −0.71 (s, 6 H; ZnMe). $C_{30}H_{72}O_8K_2Si_4Zn_2$ (882.2): calc. C 40.84, H 8.13; found C 39.62, H 8.10%.

*[(tmeda)KZn(OSiMe$_3$)$_3$]$_2$ **3**.* A solution of $ZnMe_2$ (1.44 g, 15.2 mmol, 2 solution in toluene (Aldrich)) was added at −78 °C to a solution of 1.95 g (15.2 mmol) $KOSiMe_3$ in 80 ml thf and 20 ml tmeda and stirred at this temperature for 1 . After being allowed to warm to room temperature the mixture was refluxed for 1 h. At room temperature all volatiles were removed *in vacuo* (10^{-3} Torr). Colorless crystals were isolated after recrystallization of the residue from a little thf at −25 °C. Yield: 4.51 g (4.71 mmol, 62%); mp = 178–182 °C (decomp.). ^{1}H NMR (C_6D_6): δ = 2.2 (s, 8 H; tmeda), 2.4 (s, 24 H; tmeda), 0.60 (s, 36 H; $SiMe_3$), 0.58 (s, 18H; $SiMe_3$). $C_{30}H_{68}N_4O_6K_2Si_6Zn_2$ (958.36): calc. C 37.60, H 7.15; found C 37.15, H 7.12%.

*[K(MeZn)$_3$(O^{t}Bu)$_4$]·C$_7$H$_8$ **4**·C$_7$H$_8$.* A solution of $ZnMe_2$ (1.44 g, 15.2 mmol, 2 M solution in toluene (Aldrich)) at −78 °C in *ca.* 100 ml toluene was slowly treated with 1.70 g (15.2 mmol) KO^{t}Bu in 100 ml toluene. The reaction mixture was allowed to warm to room temperature within 8 h and then stirred for 1 d at 70 °C. The solvent was removed under reduced pressure affording a solid residue. The latter was redissolved in *ca.* 20 ml toluene from which the desired product crystallizes in a few days in the form of colorless crystals. Yield: 2.19 g (3.29 mmol, 65%); mp > 330 °C (decomp.). ^{1}H NMR (C_6D_6): δ = 7.12–7.83 (m, 8 H), 1.25 (s, 9 H; ^{t}BuOK), 1.27 (s, 27 H; ^{t}BuOZn), −0.61 (s, 3H; MeZn). $C_{26}H_{53}O_4KZn_3$ (664.89): calc. C 46.96, H 8.03; found C 46.51, H 7.99%.

X-Ray crystallography

The intensities were measured with a Bruker-axs-SMART diffractometer (Mo$_{K\alpha}$ radiation, λ = 0.71707 Å, ω-scan, T = 213 K), the structures were solved by direct methods.[18] Refinements were carried out with the SHELXL-97 package.[19] All non hydrogen 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 on F^2. For **3**, the tmeda solvent molecule and one of the two independent trimethylsilyl groups was found to be disordered and therefore modeled in two equally-occupied orientations. The contribution of the disordered thf solvent molecules in **3** to the structure factors was taken into account by back-Fourier transformation using PLATON/SQUEEZE.[20]

Compound 2. Orthorhombic, space group $Pna2_1$, formula: $C_{30}H_{74}K_2O_8Si_4Zn_2$, $a = 24.379(4)$, $b = 13.394(3)$, $c = 15.094(3)$ Å, $V = 4929(2)$ Å^3, $Z = 4$, μ(Mo-K$_\alpha$) = 1.28 mm^{-1}, 416 parameters, 26363 reflections measured, 8568 unique ($R_{\text{int}} = 0.0484$), 6255 independent reflections ($I > 2\sigma(I)$), $R1 = 0.0446$ (observed reflections), $wR2 = 0.1095$ (all data).

Compound 3. Orthorhombic, space group $Pnnm$, formula: $C_{30}H_{86}K_2N_4O_6Si_6Zn_2$, $a = 19.208(7)$, $b = 10.995(4)$, $c = 13.369(5)$ Å, $V = 2823(2)$ Å^3, $Z = 2$, μ(Mo-K$_\alpha$) = 1.16 mm^{-1}, 191 parameters, 14611 reflections measured, 2595 unique, ($R_{\text{int}} = 0.0632$), 1767 independent reflections ($I > 2\sigma(I)$), $R1 = 0.0534$ (observed reflections), $wR2 = 0.1545$ (all data).

Compound 4. Orthorhombic, space group $P2_12_12_1$, formula: $C_{26}H_{53}KO_4Zn_3$, $a = 10.748(5)$, $b = 13.214(6)$, $c = 23.706(9)$ Å, $V = 3367(2)$ Å^3, $Z = 4$, μ(Mo-K$_\alpha$) = 2.27 mm^{-1}, 295 parameters, 7099 reflections measured, 4215 unique, ($R_{\text{int}} = 0.0941$), 3067 independent reflections ($I > 2\sigma(I)$), $R1 = 0.0625$ (observed reflections), $wR2 = 0.1259$ (all data).

CCDC reference numbers 205578–205580.

See http://www.rsc.org/suppdata/dt/b3/b302585c/ for crystallographic data in CIF or other electronic format.

Acknowledgements

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