

X-Ray Crystal Structure of a Heterobimetallic Al-Zn-Oxide Complex

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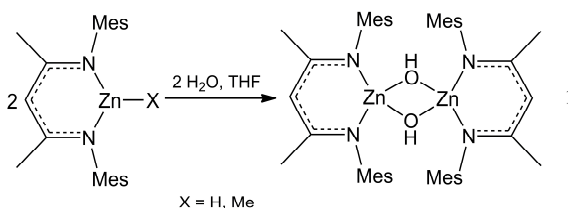
OH/R (R = H, Me, *i*-Bu) exchange was observed in reactions of [MesnacnacZn(μ -OH)]₂ (**1**) with metal complexes L_nMR, whereas DippnacnacAl(Me)OH reacts with MesnacnacZnH with elimination of H₂ and formation of the heterobimetallic Al-Zn-oxide complex MesnacnacZnOAl(Me)Dippnacnac **2**.

Heterobimetallic oxides have received growing interest due to their potential to serve as precursors in materials sciences, i.e. the synthesis of spinels M^{II}Al₂O₄,[1] and catalysis.[2] They are expected to show new reactivity patterns and physical properties due to cooperative effects,[3] which are typical for biological systems such as proteins and which can not be achieved in monometallic systems,[4] and may also serve as a model for the fixation of catalysts on oxide surfaces.[5] Consequently, new synthetic strategies for well-defined heterometallic complexes containing metal centers with entirely different chemical properties were developed. Oxo-bridged Al-O-M complexes (M = Ti, Zr, Hf) were obtained from reactions of metal hydroxides such as DippnacnacAl(Me)OH with alkyl-substituted metal complexes, i.e. group 4 metallocene and half-metallocene complexes.[6] They exhibit high catalytic activities in olefin polymerization reactions.[7] These studies have been consequently extended to other main group and transition metal and lanthanide complexes,[8] proving its general applicability. In contrast, heterobimetallic complexes with group 12 and group 13 metals are unknown. This is surprising since bimetallic Zn complexes are *living single-site catalysts* for the ring-opening polymerization (ROP) of lactide[9] and the epoxides/CO₂ copolymerization,[10] whereas bimetallic Ca/Zn complexes catalyze epoxide/anhydride/CO₂ terpolymerization[11] and epoxide/CO₂ copolymerization reactions, respectively.[12]

Due to our general interest in organozinc complexes LZnX (L = [HC{C(Me)N(2,4,6-Me₃C₆H₂)₂}]₂, X = H, R, OR),[13] we began to study the synthesis molecular zinc hydroxides and report herein on the synthesis of a molecular zinc hydroxide LZnOH **1**, which we assumed to be a valuable precursor for heterobimetallic oxide complexes, and its reactions with methyl-substituted main group and transition metal complexes. In addition, the synthesis and X-ray crystal structure of the μ -O-bridged complex LZn- μ -O-Al(Me)L' **2** (L' = [HC{C(Me)N(2,6-*i*-Pr₂C₆H₃)₂}]₂) is reported.

LZnOH **1** was obtained from reactions of LZnMe or LZnH with one equivalent of water in THF (scheme 1). The ¹H NMR spectrum of **1** showed a singlet at -0.20 ppm (OH group). Pulsed gradient spin echo (PGSE) diffusion measurements of **1** in benzene-d₆ (T = 25 °C) yielded a hydrodynamic radius of 5.90(1)

Å, which is larger than those reported for monomeric LZnH (5.2(1) Å),[14] LZnH (4.96(25) Å),[13b] and LZnMe (4.65(23) Å) in toluene-d₈,[13a] indicating **1** to be dimeric in solution.



Scheme 1 Synthesis of **1** via hydrolysis of the zinc methyl / hydride complexes

1 shows a strong IR absorption [ν (O-H)] at 3667 cm⁻¹, which corresponds well with values reported for a pyrazolylborate zinc hydroxide (3611 cm⁻¹)[15] and dimeric zinc hydroxides such as [(Me₂PhSi)₃CZnOH]₂ (3680 cm⁻¹)[16] and NHC-Zn(OMes)OH (3680 cm⁻¹; NHC = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene),[17] whereas the absorption band observed for [(Me₃Si)₂CHZn]₂(μ -OH){ μ -N(CH₂py)₂} (3312 cm⁻¹)[18] is shifted to a smaller wave number.

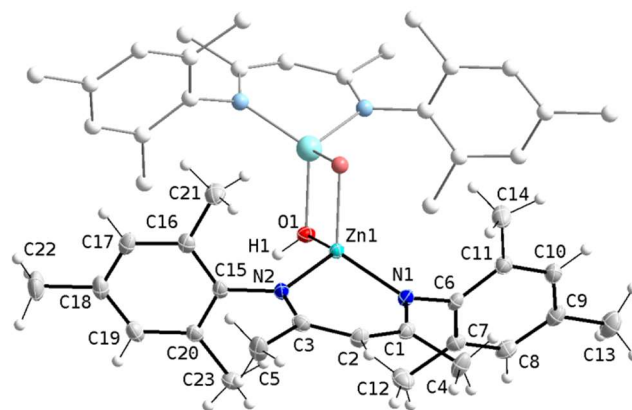
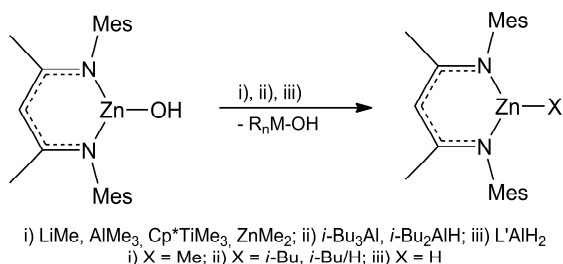


Fig. 1 Solid state structure of **1** (light part generated via inversion); non-H-atoms shown as thermal ellipsoids at 50 % probability levels (others at arbitrary radii); H atoms partially omitted for clarity.

1 crystallizes in the triclinic space group *P*-1 with one molecule in the unit cell as a hydroxide-bridged centrosymmetric dimer (figure 1). The Zn-O bond lengths in **1** are almost identical (Zn1-O1 1.9623(10); Zn1-O1A 1.9890(11) Å) as was previously observed for zinc hydroxides,[10c,16,17,19,20] whereas terminal OH groups show shorter Zn-O bond lengths (1.85 - 1.90 Å).[21] The C₃N₂Zn ring in **1** is planar (0.109 Å r.m.s. deviation from

mean plane, 0.0368 for mean plane of C and N-atoms) with the Zn atoms slightly out of the mean plane of the C- and N-atoms (0.4218(17) Å). C-C, C-N and Zn-N bond lengths within the rings are almost identical compared to the starting complexes L₂ZnH and L₂ZnMe.[13]

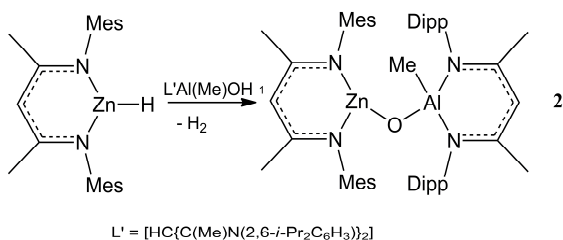
1 was reacted with Me-substituted complexes of main group (LiMe, AlMe₃) and transition metals (ZnMe₂, Cp*TiMe₃). Surprisingly, no gas evolution but only the formation of LZnMe via *hydroxide/methyl exchange* reaction occurred. This reaction pattern remarkably contrasts that observed for 1,4-dioxane stabilized EtZnOH, which was found to react with AlMe₃ with methane/ethane evolution.[23] Moreover, when **1** was reacted with Al(*i*-Bu)₃ and L'AlH₂, the formation of LZn(*i*-Bu) and LZnH, respectively, was unambiguously proved by ¹H NMR spectroscopy,[22] while the reaction of **1** with *i*-Bu₂AlH yielded a mixture of LZnH and LZn(*i*-Bu) in a 5:1 molar ratio according to ¹H NMR spectroscopic studies (scheme 2).



Scheme 2 Reactions of **1** with metal alkyl and hydride complexes

Obviously, the Brønsted acidity of the Zn-OH group in **1** is less pronounced compared to that of L'Al(Me)OH, L'Ga(Me)OH, L'GeOH, Cp₂Zr(Me)OH and [L'Sr(thf)-μ-OH]₂, respectively. Our studies demonstrate the distinguished *nucleophilicity* of Zn-OH, which is generally accepted for hydrolytic zinc enzymes. Nevertheless, it is remarkable that a Zn-OH unit was transformed into a Zn-alkyl and even a Zn-H unit by reaction with a metal alkyl or a metal hydride complex such as L'AlH₂.

In an attempt to prove the general accessibility of bimetallic zinc oxides, we reacted L'Al(Me)OH with LZnH (scheme 3). The reaction proceeded with H₂-evolution and formation of LZn-μ-O-Al(Me)L' **2** in almost quantitative yield. An analogous reaction with LZnMe proceeded much slower, giving **2** in less yield, demonstrating LZnH to be the more reactive species.



Scheme 3 Synthesis of **2**

In situ monitoring of the reaction with LZnH by ¹H NMR spectroscopy showed steadily decreasing Zn-H and Al-OH resonances. The resonances due to the three organic substituents (L, L', Me) in **2** itself show the expected 1:1:1 relative intensity. We also reacted L'Al(Me)OH with L'ZnH, but L'ZnH was found to be less reactive than LZnH, yielding L'Zn-μ-O-Al(Me)L' in

low yield together with several by-products.[24] These findings indicate a kinetically controlled reaction pathway, with the less effectively shielded zinc hydride complex LZnH being more reactive than L'ZnH and LZn-Me.

2 crystallizes in the monoclinic space group *P*2₁/*n* (figure 2). The Zn atom adopts a distorted trigonal planar coordination sphere with Zn1 deviating 0.0208(16) Å from the N₃/N₄/O1 plane. The N-Zn-O angles are slightly larger than 120° (128.28(12)°, 132.88(11)°). Zn1 is off the mean plane of the C₃N₂ central part of the ligand (0.230(4) Å) as was observed in **1**. The Al atom is distorted tetrahedrally coordinated and Al1 deviates from the mean plane of the C₃N₂ unit by 0.413(3) Å. The Zn-O bond length (1.782(2) Å) is elongated compared to the Al-O bond length (1.686(2) Å) due to the different covalent radii of Zn and Al. Analogous structural trends were observed for Zn-N (1.950(3), 1.960(3) Å) and Al-N bond lengths (1.938(3), 1.918(2) Å). The N-Al-N bond angle (95.05(11)°) is slightly smaller compared to the N-Zn-N bond angle (98.80(12)°). The C-C-C backbone angles of the β-diketiminato ligands were found to be slightly smaller for the Al heterocycle (127.4(3)°) compared to the Zn heterocycle (130.9(4)°). The Al-O-Zn bond angle of 144.78(15)° is within the range of 141-176° observed for oxo-bridged bimetallic complexes of the general type Al-O-TM (TM = transition metal).[25]

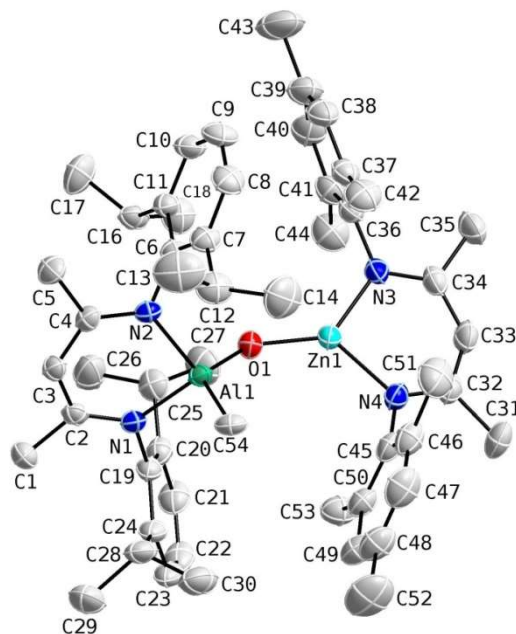


Fig. 2 Solid state structure of **2**; H atoms are omitted for clarity, thermal ellipsoids at 30 % probability levels.

The catalytic activity of **2** towards CO₂/cyclohexene oxide (CHO) copolymerization was investigated in neat CHO with 10 bar CO₂ at 50 °C and a monomer/catalyst ratio of 1000/1. For comparison, the catalytic activities of LZnH and L'Al(Me)OH were tested as well, but both showed no catalytic activity. This is not surprising for LZnH, since β-diketiminato zinc complexes with methyl-substituents at the 2,6-aryl positions were reported to be inactive in CO₂/CHO copolymerization reactions.[10a,c] In stoichiometric NMR-scale reactions, L'Al(Me)OH also showed no reaction with CHO up to 100 °C, whereas the reaction with CO₂ (1 atm) occurred with decomposition of L'Al(Me)OH and

considerable formation of L'H. This is probably due to initial formation of the intermediate L'Al(Me)CO₃H, containing an acidic H-atom that readily protonates the β-diketiminato ligand with subsequent formation of L'H and Al(Me)CO₃. A comparable reactivity is known for the calcium complex [L'CaOH]₂, also yielding L'H and CaCO₃.^[26] Unfortunately, LZnOAl(Me)L' **2** showed no increased catalytic activity compared to LZnH and L'Al(Me)OH. To investigate this inactivity in more detail, reactions of **2** with CO₂ and CHO were tested in NMR-scale experiments in deuterated benzene. **2** showed no reaction with CHO within the temperature range of 20 – 100 °C, whereas the reaction with 1 atm CO₂ resulted in a clean conversion of **2** into a product with a completely new set of ¹H NMR signals, indicating that incorporation of CO₂ is feasible. The characterization of this new complex is currently under investigation.

Conclusions

LZnOH **1**, which was prepared by controlled hydrolysis of LZnX (X = H, Me) with water in THF solution, reacts with alkyl- and hydride-substituted main group and transition metal complexes with OH/Y exchange reactions (Y = H, Me, *i*-Bu) and subsequent formation of LZnY, whereas the more Brønsted acidic L'Al(Me)OH reacts with LZnH with formation of the bimetallic complex L'Al(Me)OZnL **2**.

Notes and references

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† Electronic Supplementary Information (ESI) available: Full details on the experimental procedures and characterization of **1**, and **2** including single crystal X-ray diffraction, reactivity studies of [MesnacnacZnOH]₂ towards MeLi, AlMe₃, Al(*i*-Bu)₃, HAl(*i*-Bu)₂, Cp*TiMe₃, ZnMe₂ and DippnacnacAlH₂ and preliminary experiments on the CO₂/CHO copolymerization of **2**. See DOI: 10.1039/b000000x/

‡ CCDC 804558 (**1**) and 804557 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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