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## COMMUNICATION

## X-Ray crystal structure of a heterobimetallic Al-Zn-oxide complex<sup>†</sup>

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OH/R (R = H, Me, *i*-Bu) exchange was observed in reactions of [MesnacnacZn( $\mu$ -OH)]<sub>2</sub> (1) with metal complexes L<sub>n</sub>MR, whereas DippnacnacAl(Me)OH reacts with MesnacnacZnH with elimination of H<sub>2</sub> 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  $\hat{M}^{II}Al_2O_4$ ,<sup>1</sup> and catalysis.<sup>2</sup> They are expected to show new reactivity patterns and physical properties due to cooperative effects,<sup>3</sup> which are typical for biological systems such as proteins and which can not be achieved in monometallic systems,<sup>4</sup> and may also serve as a model for the fixation of catalysts on oxide surfaces.<sup>5</sup> Consequently, new synthetic strategies for well-defined heterobimetallic 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.<sup>6</sup> 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,<sup>8</sup> proving their 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 lactides9 and the epoxide/CO2 copolymerization,<sup>10</sup> whereas bimetallic Ca/Zn complexes catalyze epoxide/anhydride/CO<sub>2</sub> terpolymerization<sup>11</sup> and epoxide/CO<sub>2</sub> copolymerization reactions, respectively.<sup>12</sup>

Due to our general interest in organozinc complexes LZnX  $(L = [HC{C(Me)N(2,4,6-Me_3C_6H_2)}_2], X = H, R, OR)$ <sup>13</sup> we began to study the synthesis of 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 alkyl-substituted main group and transition metal complexes. In addition, the synthesis and X-ray crystal structure of the  $\mu$ -O-bridged complex LZn- $\mu$ -O-Al(Me)L' 2 (L' = [HC{C(Me)N(2,6-*i*-Pr\_2C\_6H\_3)}\_2]) is reported.

LZnOH 1 was obtained from reactions of LZnMe or LZnH with one equivalent of water in THF (Scheme 1). The <sup>1</sup>H NMR spectrum of 1 showed a singlet at -0.20 ppm (OH group). Pulsed gradient spin echo (PGSE) diffusion measurements of 1 in benzene-d<sub>6</sub> (T = 25 °C) yielded a hydrodynamic radius of 5.90(1) Å, which is larger than those reported for monomeric L'ZnH (5.2(1) Å),<sup>14</sup> LZnH (4.96(25) Å),<sup>13b</sup> and LZnMe (4.65(23) Å) in toluene-d<sub>8</sub>,<sup>13a</sup> indicating 1 to be dimeric in solution.

**1** shows a strong IR absorption  $[\nu(O-H)]$  at 3667 cm<sup>-1</sup>, which corresponds well with values reported for a pyrazolylborate zinc hydroxide (3611 cm<sup>-1</sup>)<sup>15</sup> and dimeric zinc hydroxides such as  $[(Me_2PhSi)_3CZnOH]_2$  (3680 cm<sup>-1</sup>)<sup>16</sup> and NHC–Zn(OMes)OH (3680 cm<sup>-1</sup>; NHC = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene),<sup>17</sup> whereas the absorption band observed for  $[{(Me_3Si)_2CHZn}_2(\mu-OH){\mu-N(CH_2py)_2}]$  (3312 cm<sup>-1</sup>)<sup>18</sup> is shifted to a smaller wave number.

**1** crystallizes in the triclinic space group  $P\bar{1}$  with one molecule in the unit cell as a hydroxide-bridged centrosymmetric dimer (Fig. 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, <sup>10c,16,17,19,20</sup> whereas terminal OH groups show shorter Zn–O bond lengths (1.85–1.90 Å).<sup>21</sup> The C<sub>3</sub>N<sub>2</sub>Zn ring in **1** is planar (0.109 Å rms 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 ring are almost identical compared to the starting complexes LZnH and LZnMe.<sup>13</sup>

1 was reacted with Me-substituted complexes of main group (LiMe, AlMe\_3) and transition metals ( $ZnMe_2$ ,  $Cp*TiMe_3$ ).



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

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<sup>†</sup> 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]<sub>2</sub> towards MeLi, AlMe<sub>3</sub>, Al(*i*-Bu)<sub>3</sub>, HAl(*i*-Bu)<sub>2</sub>, Cp\*TiMe<sub>3</sub>, ZnMe<sub>2</sub> and DippnacnacAlH<sub>2</sub> and preliminary experiments on the CO<sub>2</sub>/CHO copolymerization of 2. CCDC 804558 (1) and 804557 (2). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0cc05599a





**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.

Surprisingly, no gas evolution but only the formation of LZnMe *via* a *hydroxide/methyl exchange* reaction occurred. This reaction pattern remarkably contrasts that observed for 1,4-dioxane stabilized EtZnOH, which was found to react with AlMe<sub>3</sub> with methane/ethane evolution.<sup>23</sup> Moreover, when 1 was reacted with Al(*i*-Bu)<sub>3</sub> and L'AlH<sub>2</sub>, the formation of LZn(*i*-Bu) and LZnH, respectively, was unambiguously proved by <sup>1</sup>H NMR spectroscopy,<sup>22</sup> while the reaction of 1 with *i*-Bu<sub>2</sub>AlH yielded a mixture of LZnH and LZn(*i*-Bu) in a 5 : 1 molar ratio according to <sup>1</sup>H NMR spectroscopic studies (Scheme 2).

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, Cp<sub>2</sub>Zr(Me)OH and [L'Sr(thf)–µ-OH]<sub>2</sub>, 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'AlH<sub>2</sub>.

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 H<sub>2</sub>-evolution and formation of



i) LiMe, AIMe<sub>3.</sub> Cp\*TiMe<sub>3.</sub> ZnMe<sub>2</sub>; ii) *i*-Bu<sub>3</sub>AI, *i*-Bu<sub>2</sub>AIH; iii) L'AIH<sub>2</sub> i) X = Me; ii) X = *i*-Bu, *i*-Bu/H; iii) X = H

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



 $LZn-\mu$ -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.

In situ monitoring of the reaction with LZnH by <sup>1</sup>H 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– $\mu$ -O–Al(Me)L' in low yield together with several by-products.<sup>24</sup> 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  $P2_1/n$  (Fig. 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°  $(128.28(12)^{\circ}, 132.88(11)^{\circ})$ . Zn1 is off the mean plane of the  $C_3N_2$  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  $C_3N_2$  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  $(98.80(12)^{\circ})$ . The C-C-C backbone angles of the β-diketiminato ligands were found to be slightly smaller for the Al heterocycle  $(127.4(3)^{\circ})$  compared to the Zn heterocycle  $(130.9(4)^{\circ})$ . 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  $CO_2$ /cyclohexene oxide (CHO) copolymerization was investigated in neat CHO with 10 bar CO<sub>2</sub> 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  $\beta$ -diketiminate zinc complexes with methyl-substituents at the 2,6-aryl positions were reported to be inactive in CO<sub>2</sub>/CHO copolymerization reactions.<sup>10a,c</sup> In stoichiometric NMR-scale reactions, L'Al(Me)OH also showed no reaction with CHO up to 100 °C, whereas the reaction with CO<sub>2</sub> (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)CO<sub>3</sub>H, containing an acidic H-atom that readily protonates the β-diketiminato ligand with subsequent formation of L'H and Al(Me)CO<sub>3</sub>. A comparable reactivity is known for the calcium complex [L'CaOH]<sub>2</sub>, also yielding L'H and  $CaCO_3$ <sup>26</sup> 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 CO<sub>2</sub> 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 CO<sub>2</sub> resulted in a clean conversion of 2 into a product with a completely new set of <sup>1</sup>H NMR signals, indicating that incorporation of CO<sub>2</sub> is feasible. The characterization of this new complex is currently under investigation.

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 by OH/Y exchange reactions (Y = H, Me, *i*-Bu) and subsequently forms LZnY, whereas the more Brønsted acidic L'Al(Me)OH reacts with LZnH to form the bimetallic complex L'Al(Me)OZnL 2.

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