

# Synthesis, structural characterization, and reactivity of the ethyl substituted aluminum hydroxide and catalytic properties of its derivative

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Received 25 June 2007; received in revised form 25 August 2007; accepted 26 August 2007

Available online 4 September 2007

Dedicated in memoriam to Professor F. Albert Cotton

## Abstract

The ethyl substituted aluminum hydroxide  $\text{LAlEt(OH)}$  (**2**;  $\text{L} = \text{HC}[\text{C}(\text{Me})\text{N}(\text{Ar})]_2$ ;  $\text{Ar} = 2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3$ ) was prepared by the hydrolysis of  $\text{LAlEt(Cl)}$  (**1**) in the presence of a N-heterocyclic carbene. The reaction of **2** with  $\text{Cp}_2\text{ZrMe}_2$  in toluene afforded  $\text{LAlEt}(\mu\text{-O})\text{ZrMeCp}_2$  (**3**) by evolution of methane, while the reaction of **2** with  $\text{Cp}_3\text{M}$  in THF led to the intermolecular elimination of  $\text{HCp}$  and formation of  $\text{LAlEt}(\mu\text{-O})\text{M}(\text{THF})\text{Cp}_2$  ( $\text{M} = \text{Yb}$ , **4**;  $\text{Er}$ , **5**;  $\text{Dy}$ , **6**;  $\text{Y}$ , **7**). Compounds **2** and **3** were characterized by single X-ray structural analysis. Compound **2** crystallizes in the orthorhombic space group  $P2_12_12_1$ , while compound **3** crystallizes in space group  $Pnma$ . In both cases, the displacement of the Al and the  $\gamma\text{-C}$  atom out of the NCCN plane is observed in a boat conformation, but with converse direction. Furthermore, compound **3** was used as catalyst for ethylene polymerization.

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**Keywords:** Aluminum hydroxide; Heterobimetallic oxide;  $\beta$ -Diketiminato ligand; Lanthanide; Polymerization

## 1. Introduction

Well-defined heterobimetallic oxides have attracted extensive attention to acquire structurally unusual materials or potentially good catalysts [1,2]. So far, various approaches were proposed both in chemistry and material science [3], among which an elaborate strategy via organometallic hydroxides distinguished itself to be a facile route to form the  $\text{M-O-M}'$  unit in compounds without bridging OR or OAr arrangements. Especially in the course of design and synthesis of single-site homogeneous catalysts containing  $\text{Al-O-M}'$  ( $\text{M}' = \text{Zr}, \text{Ti}, \text{Ln}$ ) moiety, our labora-

tory developed the unprecedented aluminum monohydroxide with a terminal OH group,  $\text{LAlMe(OH)}$  [4], supported by the sterically hindered  $\beta$ -diketiminato ligand ( $\text{L} = \text{HC}[\text{C}(\text{Me})\text{N}(\text{Ar})]_2$ ,  $\text{Ar} = 2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3$ ).  $\text{LAlMe(OH)}$  turned out to be a suitable synthon to successfully prepare a series of new compounds  $\text{LAlMe}(\mu\text{-O})\text{ZrRCp}_2$  ( $\text{R} = \text{Me}, \text{Cl}$ ) and  $\text{LAlMe}(\mu\text{-O})\text{Ln}(\text{THF})\text{Cp}_2$  ( $\text{Ln} = \text{Yb}, \text{Er}, \text{Dy}$ ) with well-defined structures and noticeable catalytic activity [4,5]. Recent ab initio calculations showed that in the  $\text{M-O-M}'$  system the oxygen is responsible for the depletion of the electron density at the metal centers [2,6]. Furthermore, our interest was intrigued by varying the group R on the aluminum site to extend the perspective of  $\text{LAlR(OH)}$ . In this regard, we report on the preparation and structural characterization of ethyl substituted aluminum hydroxide

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LAIEt(OH) (**2**). The reactivity of this OH group was examined by the reactions with  $\text{Cp}_2\text{ZrMe}_2$  and  $\text{Cp}_3\text{M}$  ( $\text{M} = \text{Yb}$ , Er, Dy, Y) to form the desired oxo bridged heterobimetallic oxides. The catalytic activity of the zirconium derivative LAIEt( $\mu\text{-O}$ )ZrMeCp<sub>2</sub> (**3**) was preliminarily investigated in ethylene polymerization.

## 2. Results and discussion

### 2.1. Synthesis of LAIEt(Cl) (**1**) and LAIEt(OH) (**2**)

Compound **1** was obtained in high yield by the reaction of  $\text{LLi} \cdot \text{OEt}_2$  with 1 equiv. of  $\text{EtAlCl}_2$  in toluene (Scheme 1). Subsequent hydrolysis of compound **1** was carried out with 1 equiv. of  $\text{H}_2\text{O}$  in the presence of 1,3-diiisopropyl-4,5-dimethylimidazol-2-ylidene (abbreviated as :C) as a HCl acceptor [7] in toluene at 0 °C to afford compound **2** as a white solid. Compound  $[\text{H}:\text{C}]^+\text{Cl}^-$  is nearly insoluble in toluene and can be removed by filtration.

The composition of both compounds was confirmed by analytical and spectroscopic methods. The  $^1\text{H}$  NMR spectrum of **1** shows one quartet ( $\delta -0.04$  ppm) and one triplet ( $\delta 0.80$  ppm) corresponding to methylene and methyl proton resonances of the ethyl group on aluminum, while in the  $^{13}\text{C}$  NMR spectrum the resonances of these groups are assigned to  $\delta -1.0$  and 8.5 ppm. In contrast, in the  $^1\text{H}$  NMR spectrum of **2** the methylene and methyl proton resonances of the ethyl group on aluminum show upfield shifts ( $\delta -0.23$  and 0.71 ppm) relative to those of **1**, whereas the corresponding  $^{13}\text{C}$  NMR resonances are shifted apart ( $\delta -2.4$  and 9.2 ppm). The singlet ( $\delta 0.63$  ppm) in the  $^1\text{H}$  NMR spectrum of **2** is assigned to the OH proton resonance, while for LAIME(OH) this resonance was observed at  $\delta 0.53$  ppm [4]. This downfield shift is probably due to the electronic effect of the substituent changing from methyl to ethyl on aluminum. In the IR spectrum of **2**, the OH stretching frequency is found at  $3729\text{ cm}^{-1}$ . The mass spectrum of **2** indicates the mono-

meric composition with  $m/z$  (%) 473 (24)  $[\text{M}^+ - \text{OH}]$  and 461 (100)  $[\text{M}^+ - \text{Et}]$ .

### 2.2. Synthesis of LAIEt( $\mu\text{-O}$ )ZrMeCp<sub>2</sub> (**3**)

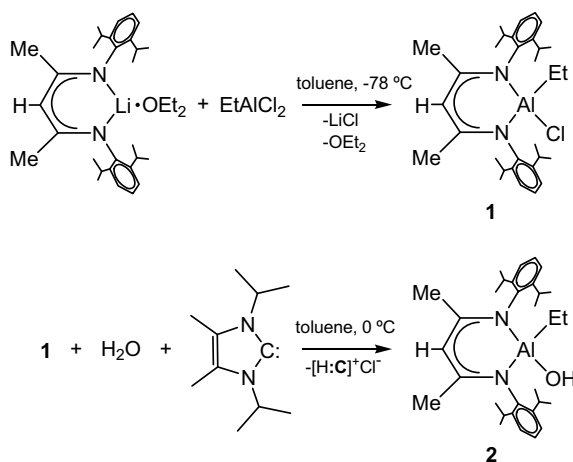
Reaction of **2** with 1 equiv. of  $\text{Cp}_2\text{ZrMe}_2$  in toluene at 100 °C afforded the  $\mu\text{-O}$  bridged LAIEt( $\mu\text{-O}$ )ZrMeCp<sub>2</sub> (**3**) (Scheme 2) accompanied by methane evolution.

The mass spectrum of **3** exhibits a peak at  $m/z$  (%) 709 (88) representing the fragment  $[\text{M}^+ - \text{Me}]$ . In the  $^{13}\text{C}$  NMR spectrum of **3** the characteristic Cp resonances appear at  $\delta 109.9$  ppm. The  $^1\text{H}$  NMR spectrum displays the Cp resonances as singlet ( $\delta 5.30$  ppm). At high field, one singlet ( $\delta -0.32$  ppm) is assigned to the Me protons of ZrMe, while one quartet ( $\delta -0.14$  ppm) and one triplet ( $\delta 1.14$  ppm) are attributed to the methylene and methyl proton resonances of the AlEt group. No hydroxyl proton resonance is observed in the expectable range, which is consistent with the absence of any OH absorption in the range  $3600\text{--}3800\text{ cm}^{-1}$  in the IR spectrum [4].

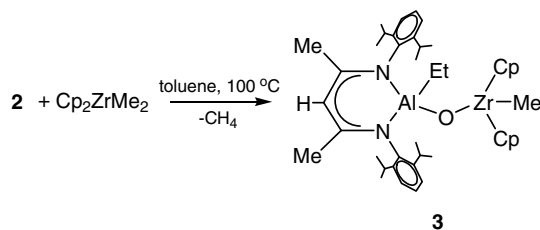
### 2.3. Synthesis of LAIEt( $\mu\text{-O}$ )M(THF)Cp<sub>2</sub> ( $\text{M} = \text{Yb}$ , **4**; Er, **5**; Dy, **6**; Y, **7**)

In contrast to the previous elimination of  $\text{CH}_4$ , the reaction of compound **2** with 1 equiv. of  $\text{Cp}_3\text{M}$  in THF at room temperature resulted in an intermolecular elimination of HCp to render the yttrium and rare earth metal derivatives LAIEt( $\mu\text{-O}$ )M(THF)Cp<sub>2</sub> ( $\text{M} = \text{Yb}$ , **4**; Er, **5**; Dy, **6**; Y, **7**) (Scheme 3).

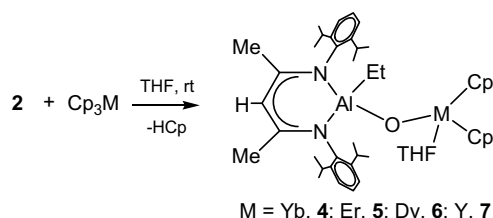
The melting points of **4**, **6**, and **7** are in the range from 208 to 210 °C, and for **5** it is 235 °C. In an average they are 40 °C lower compared to those of the corresponding methyl analogues [5], which could be attributed to the different alkyl group on aluminum. IR spectra of **4**, **5**, **6**, and **7**



Scheme 1.



Scheme 2.



Scheme 3.

are free of any OH absorption in the reasonable range. The mass spectra of **4**, **5**, and **6** exhibit the most intense peak  $[M^+ - \text{THF} - \text{Et}]$  with isotopic pattern, followed by  $[M^+ - \text{THF} - \text{Et} - \text{Cp}]$ . In the mass spectrum of **7**, the base peak is assigned to the fragment  $[M^+ - \text{Et} - \text{Y}(\text{THF})\text{Cp}_2]$ .

Because of the paramagnetic properties of the three lanthanide elements, it is not meaningful to describe the detailed NMR spectra of **4**, **5**, and **6** in solution, whereas the data of the yttrium analogue  $\text{LAlEt}(\mu\text{-O})\text{Y}(\text{THF})\text{Cp}_2$  (**7**) could be helpful for characterizing these systems. In the  $^{13}\text{C}$  NMR spectrum of **7** the Cp resonances are found at  $\delta$  110.0 ppm. In the  $^1\text{H}$  NMR spectrum, the Cp resonances appear as singlet ( $\delta$  5.85 ppm), while one quartet ( $\delta$  0.40 ppm) and one triplet ( $\delta$  1.60 ppm) are assigned to the methylene and methyl proton resonances of the AlEt group. Two broad resonances ( $\delta$  1.34 and 3.08 ppm) correspond to those of the protons of the coordinated THF. The absence of a hydroxyl proton resonance additionally confirms the formation of **7** by intermolecular elimination of HCP. It is worth mentioning that all  $^1\text{H}$  and  $^{13}\text{C}$  resonances of the substituents on the metal centers of **7** exhibit a downfield shift when compared with those of **3**, which may be related to the change of the chemical environment.

#### 2.4. X-ray structural analysis of $\text{LAlEt}(\text{OH})$ (**2**) and $\text{LAlEt}(\mu\text{-O})\text{ZrMeCp}_2$ (**3**)

Keeping the THF solution of **2** at  $4^\circ\text{C}$  overnight resulted in colorless X-ray quality crystals. The structure of **2** is depicted in Fig. 1. Compound **2** crystallizes in the orthorhombic space group  $P2_12_12_1$  and shows a mononuclear composition with an aluminum center in a distorted tetrahedral geometry coordinated to the chelating  $\beta$ -diketiminato ligand, an ethyl, and an OH group. Selected bond lengths and angles are listed in Table 2. On the one hand the  $\text{N}(1)\text{-Al-N}(2)$  angle ( $95.32(8)^\circ$ ) is even smaller than that of  $\text{LAlMe}(\text{OH})$  ( $96.3(1)^\circ$ ) [4], on the other the Al–O bond length ( $1.7409(17)\text{ \AA}$ ) is slightly longer than those of  $\text{LAlMe}(\text{OH})$  ( $1.731(3)\text{ \AA}$ ) and  $\text{LAl}(\text{OH})_2$  ( $1.695(15)$ ,

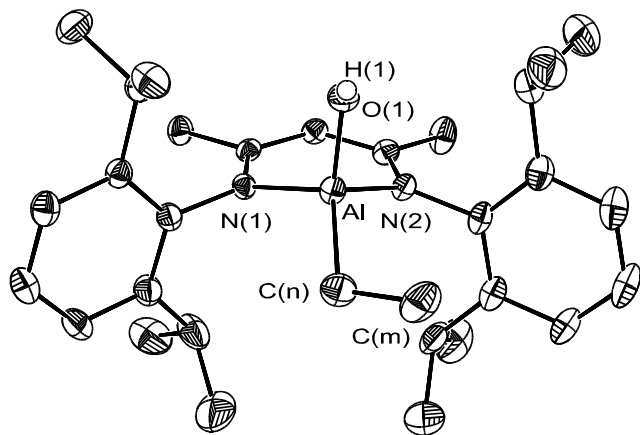


Fig. 1. Molecular structure of **2**. Thermal ellipsoids are drawn at the 50% level, and the hydrogen atoms of the ligand and the two THF molecules are omitted for clarity.

$1.711(16)\text{ \AA}$ ) [8], and comparable to the terminal ones of  $[\text{LAl}(\text{OH})_2(\mu\text{-O})]$  ( $1.738(3)$ ,  $1.741(3)\text{ \AA}$ ) [9].

Compound **3** crystallizes in the orthorhombic space group  $Pnma$  (Fig. 2). Table 1 shows the crystal data and structure refinement for compounds  $\mathbf{2} \cdot (\text{THF})_2$  and **3**. The ethyl group on Al and the methyl group on Zr are located in the same Al–O–Zr plane and stay away from each other in a *trans* conformation. The Al–O bond length ( $1.7285(10)\text{ \AA}$ ) falls in between those of  $\text{LAlMe}(\mu\text{-O})\text{ZrMeCp}_2$  ( $1.711(2)\text{ \AA}$ ) [4] and of **2** ( $1.7409(17)\text{ \AA}$ ), while the Al–C distance ( $1.9688(14)\text{ \AA}$ ) is comparable to that of **2** ( $1.965(3)\text{ \AA}$ ). The Zr–O bond separation ( $1.9424(10)\text{ \AA}$ ) is slightly longer than that of  $\text{LAlMe}(\mu\text{-O})\text{ZrMeCp}_2$  ( $1.929(2)\text{ \AA}$ ) [4], because of more steric repulsion by the ethyl group compared to its methyl counterpart. The Al–O–Zr angle ( $144.41(6)^\circ$ ) is obviously narrower than that of  $\text{LAlMe}(\mu\text{-O})\text{ZrMeCp}_2$  ( $158.2(1)^\circ$ ) [4]. Selected bond distances and bond lengths for compounds **2** and **3** are shown in Table 2.

In both cases, the Al and  $\gamma\text{-C}$  atoms are arranged out of the NCCN plane to exhibit a boat conformation as shown in the simplified side view of **2** and **3** (Fig. 3). Interestingly, the direction of this arrangement turns upside down when a more bulky substituent than a proton is attached to the oxygen atom, while the angles of  $\text{N}(1)\text{-Al-N}(2)$  and  $\text{N-Al-C}$  remain almost the same. This property of the ligand ensures both stability and flexibility in such a system.

#### 2.5. Ethylene polymerization studies

Table 3 summarizes the polymerization results of catalyst **3**. All polymeric materials were isolated as white powders. Under comparable polymerization conditions, the methylalumoxane (MAO)/**3** catalyst system shows lower activity compared to that of MAO/ $\text{LAlMe}(\mu\text{-O})\text{ZrMeCp}_2$

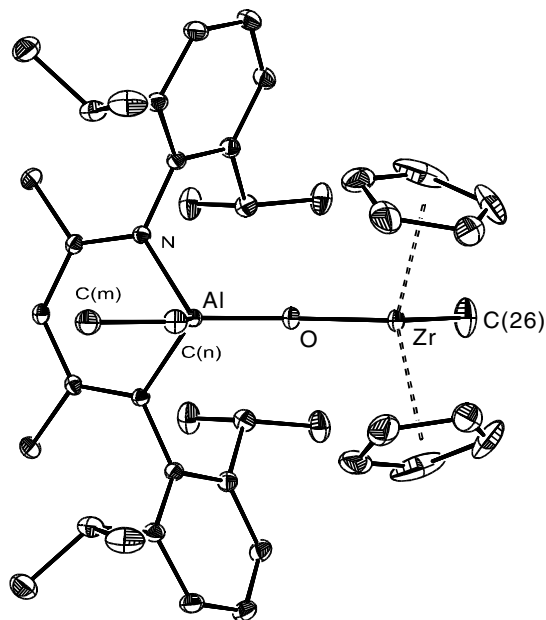


Fig. 2. Molecular structure of **3**. Hydrogen atoms are omitted for clarity.

Table 1  
Crystal data and structure refinement for compounds **2**·(THF)<sub>2</sub> and **3**

	<b>2</b> ·(THF) <sub>2</sub>	<b>3</b>
Formula	C <sub>39</sub> H <sub>63</sub> AlN <sub>2</sub> O <sub>3</sub>	C <sub>42</sub> H <sub>59</sub> AlN <sub>2</sub> OZr
fw	634.89	726.11
<i>T</i> (K)	133(2)	100(2)
Crystal system	Orthorhombic	Orthorhombic
Space group	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	<i>Pnma</i>
$\lambda$ (Å)	0.71073	0.71073
<i>a</i> (Å)	9.4622(9)	18.8469(17)
<i>b</i> (Å)	15.1590(15)	19.6279(17)
<i>c</i> (Å)	26.479(3)	10.2628(9)
<i>V</i> (Å <sup>3</sup> )	3798.0(6)	3796.5(6)
<i>Z</i>	4	4
$\rho_{\text{calc}}$ (g/cm <sup>3</sup> )	1.110	1.270
$\mu$ (mm <sup>-1</sup> )	0.090	0.347
Crystal size (mm)	0.40 × 0.30 × 0.25	0.27 × 0.27 × 0.12
$\theta$ Range for data collection (°)	1.54–28.70	2.08–33.73
Index ranges	−12 ≤ <i>h</i> ≤ 12, −20 ≤ <i>k</i> ≤ 20, −35 ≤ <i>l</i> ≤ 35	−29 ≤ <i>h</i> ≤ 29, −30 ≤ <i>k</i> ≤ 30, −15 ≤ <i>l</i> ≤ 16
Reflections collected	44236	128071
Independent reflections [ <i>R</i> <sub>int</sub> ]	9787 [0.0414]	7767 [0.0398]
Data/restr./param.	9787/137/421	7767/4/240
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.059	1.040
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	0.0561, 0.1462	0.0286, 0.0734
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (all data)	0.0817, 0.1656	0.0358, 0.0781
Largest differences in peak/hole (e Å <sup>-3</sup> )	0.569/−0.450	0.772/−0.461

Table 2  
Selected bond distances (Å) and angles (°) for compounds **2** and **3**

	<b>2</b>	<b>3</b>
Al–O	1.7409(17)	1.7285(10)
Al–N(1)	1.9047(18)	1.9213(8)
Al–N(2)	1.9147(19)	1.9213(8)
Al–C	1.965(3)	1.9688(14)
C(m)–C(n) <sup>a</sup>	1.533(4)	1.528(2)
Zr–O		1.9424(10)
Zr–X <sub>Cp</sub>		2.267
O–Al–N(1)	109.42(8)	112.68(3)
O–Al–N(2)	105.80(9)	112.68(3)
N(1)–Al–N(2)	95.32(8)	96.59(5)
O–Al–C	115.70(11)	109.34(5)
N(1)–Al–C	113.60(10)	112.58(3)
N(2)–Al–C	114.95(10)	112.58(3)
C(m)–C(n)–Al <sup>a</sup>	115.04(19)	121.35(10)
Al–O–Zr		144.41(6)
X <sub>Cp1</sub> –Zr–X <sub>Cp2</sub>		127.73

<sup>a</sup> C(m) and C(n) stand for the methyl and methylene carbon of AlEt group.

[4]. However, the MAO activated compound **3** still exhibits good catalytic activity for the polymerization of ethylene. Fig. 4 visualizes the MAO/3 ratios dependence activity, which reveals a gradual increase in the activity with the MAO/3 till to 400, followed by a slow decrease as the MAO/3 ratio is raised further.

## 2.6. Polymer properties

DSC measurements show that the melting points (*T*<sub>m</sub>) of the polyethylene produced by MAO activated **3** are in the

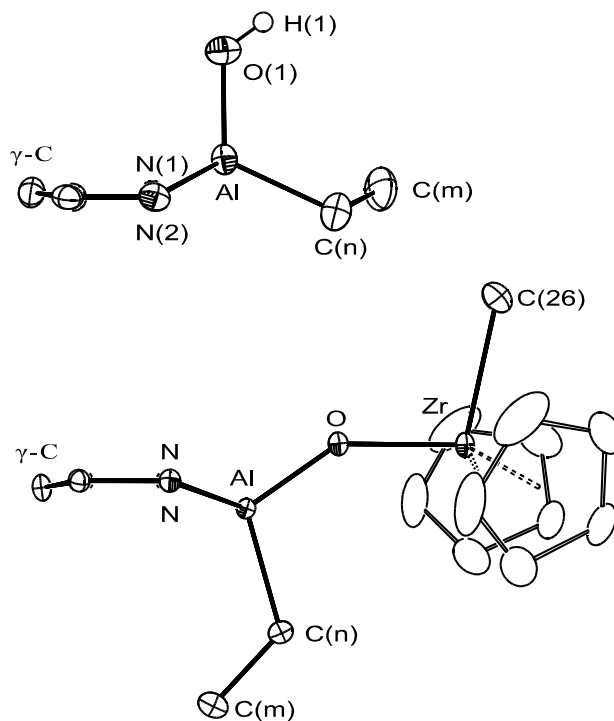


Fig. 3. Side view of compounds **2** and **3**. Only selected atoms are included for clarity.

range of 119–127 °C, somewhat lower than the typical range for the linear polyethylene. The <sup>13</sup>C NMR data exhibit a resonance ( $\delta$  29.81 ppm) corresponding to the backbone carbon of the linear polyethylene.

Table 3  
Ethylene polymerization for compound **3** (12.4  $\mu\text{mol}$ ) in 100 mL of toluene under 1 atm ethylene pressure at 25 °C

Catalyst	MAO/ <b>3</b>	<i>t</i> (min)	PE (g)	Activity ( $10^5$ g PE/mol cat h)	<i>T<sub>m</sub></i> (°C)
<b>3</b>	200	30	0.31	0.50	123
<b>3</b>	300	30	0.75	1.20	127
<b>3</b>	400	30	1.21	1.95	121
<b>3</b>	600	30	1.01	1.61	119

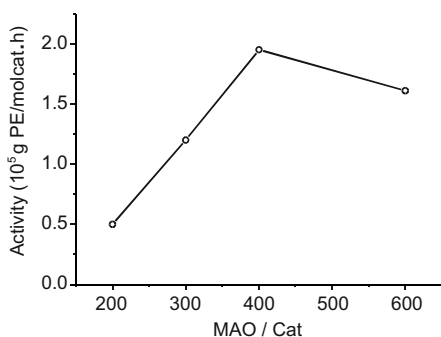


Fig. 4. Activity against MAO to catalyst ratio of **3**.

### 3. Conclusion

A novel ethyl substituted aluminum hydroxide LAIEt(OH) (**2**) was synthesized by controlled hydrolysis of LAIEt(Cl) (**1**) and characterized analytically and spectroscopically. In subsequent reactions, the proton of the OH group exhibited an expected reactivity by intermolecular elimination of  $\text{CH}_4$  and  $\text{HCp}$ , respectively, to afford  $\mu\text{-O}$  bridged heterobimetallic compounds LAIEt( $\mu\text{-O}$ )ZrMeCp<sub>2</sub> (**3**) and LAIEt( $\mu\text{-O}$ )M(THF)Cp<sub>2</sub> (M = Yb, **4**; Er, **5**; Dy, **6**; Y, **7**). Compound **3** exhibits good catalytic activity in ethylene polymerization. Currently, we are aiming at the variation of R in LAIR(OH) to explore further M–O–M' precursor with new properties and applications.

### 4. Experimental

#### 4.1. General procedures

All manipulations were carried out under an atmosphere of purified nitrogen using standard Schlenk techniques. The samples for analytical measurements as well as for reactions were manipulated in a glove box. The solvents were purified and dried using conventional procedures, and were freshly distilled under nitrogen, and degassed prior to use. Cp<sub>2</sub>ZrMe<sub>2</sub> and EtAlCl<sub>2</sub> were purchased from Aldrich. LLi·OEt<sub>2</sub> [10], Cp<sub>3</sub>M [11], and 1,3-diiisopropyl-4,5-dimethylimidazol-2-ylidene [12] were prepared as described in the literature.

#### 4.2. Synthesis of LAIEt(Cl) (**1**)

EtAlCl<sub>2</sub> (11.2 mL, 1.8 M in *n*-hexane, 20 mmol) was added drop by drop at –78 °C to LLi·OEt<sub>2</sub> (9.97 g,

20 mmol) in toluene (100 mL). The mixture was allowed to warm to room temperature and stirred for 12 h. After filtration the filtrate was concentrated (20 mL) and kept at 4 °C to afford colorless crystals. X-ray quality crystals were grown from toluene. Yield 8.05 g (79%).

M.p. 153–155 °C. <sup>1</sup>H NMR (300.13 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  –0.04 (q,  $J$  = 8.0 Hz, 2H, AlCH<sub>2</sub>CH<sub>3</sub>), 0.80 (t,  $J$  = 8.0 Hz, 3H, AlCH<sub>2</sub>CH<sub>3</sub>), 1.00 (d,  $J$  = 6.8 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.19 (d,  $J$  = 6.8 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.30 (d,  $J$  = 6.8 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.48 (d,  $J$  = 6.6 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.55 (s, 6H, CMe), 3.21 (sept,  $J$  = 6.8 Hz, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 3.76 (sept,  $J$  = 6.8 Hz, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 4.96 (s, 1H,  $\gamma$ -CH), 7.04–7.15 (m, Ar) ppm. <sup>13</sup>C NMR (75.5 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  170.7 (CN), 146.0, 143.3, 139.7, 127.7, 125.4, 123.9 (*i*-, *o*-, *m*-, *p*-Ar), 98.7 ( $\gamma$ -CH), 29.2, 28.1 (CH(CH<sub>3</sub>)<sub>2</sub>), 26.9, 24.9, 24.5, 23.8 (CH(CH<sub>3</sub>)<sub>2</sub>), 23.2 ( $\beta$ -CH<sub>3</sub>), 8.5 (AlCH<sub>2</sub>CH<sub>3</sub>), –1.0 (br, AlCH<sub>2</sub>CH<sub>3</sub>) ppm. IR (Nujol mull, cm<sup>–1</sup>):  $\tilde{\nu}$  = 3062 (s), 1587 (m), 1558 (s), 1534 (s), 1517 (s), 1442 (s), 1344 (s), 1319 (s), 1259 (s), 1177 (m), 1101 (m), 1021 (s), 938 (m), 878 (w), 834 (w), 801 (m), 777 (w), 759 (w), 718 (w), 648 (w), 618 (m), 533 (m). EI-MS: *m/z* (%): 479 (100) [M<sup>+</sup>–Et]. Anal. Calc. for C<sub>31</sub>H<sub>46</sub>AlClN<sub>2</sub> (509.1): C, 73.13; H, 9.11; N, 5.50. Found: C, 72.45; H, 8.86; N, 5.43%.

#### 4.3. Synthesis of LAIEt(OH) (**2**) [13]

To a mixture of **1** (2.04 g, 4 mmol) and [CN(*i*Pr)<sub>2</sub>Me<sub>2</sub>N(*i*Pr)] (:C, 0.72 g, 4 mmol) in toluene (60 mL) at 0 °C, distilled H<sub>2</sub>O (18  $\mu\text{L}$ , 4 mmol) was added. The suspension was allowed to warm to room temperature and stirred for 12 h. The insoluble solid was removed by filtration and from the filtrate all volatiles were removed in vacuo and the resulting residue was washed with *n*-pentane (5 mL) to afford a white solid. X-ray quality crystals of **2** were grown from THF at 4 °C. Yield 1.43 g (73%).

M.p. 163 °C. <sup>1</sup>H NMR (500.13 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  –0.23 (q,  $J$  = 8.2 Hz, 2H, AlCH<sub>2</sub>CH<sub>3</sub>), 0.63 (s, 1H, OH), 0.71 (t,  $J$  = 8.2 Hz, 3H, AlCH<sub>2</sub>CH<sub>3</sub>), 1.06 (d,  $J$  = 6.8 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.21 (d,  $J$  = 7.0 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.32 (d,  $J$  = 7.0 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.34 (d,  $J$  = 6.6 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.58 (s, 6H, CMe), 3.22 (sept,  $J$  = 6.8 Hz, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 3.68 (sept,  $J$  = 6.8 Hz, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 4.93 (s, 1H,  $\gamma$ -CH), 7.07–7.15 (m, Ar) ppm. <sup>13</sup>C NMR (125.8 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  169.3 (CN), 145.4, 143.4, 140.8, 127.3, 124.9, 123.9 (*i*-, *o*-, *m*-, *p*-Ar), 97.3 ( $\gamma$ -CH), 28.9, 27.8 (CH(CH<sub>3</sub>)<sub>2</sub>), 26.1, 24.9, 24.4, 24.0 (CH(CH<sub>3</sub>)<sub>2</sub>), 23.1 ( $\beta$ -CH<sub>3</sub>), 9.2 (AlCH<sub>2</sub>CH<sub>3</sub>), –2.4 (br, AlCH<sub>2</sub>CH<sub>3</sub>) ppm. IR (Nujol mull, cm<sup>–1</sup>):  $\tilde{\nu}$  = 3729 (m, OH), 1654 (w), 1552 (w), 1529 (w), 1319 (m), 1261 (w), 1179 (w), 1101 (w), 1059 (w), 1021 (w), 938 (w), 875 (w), 834 (w), 802 (w), 761 (w), 723 (w), 657 (w). EI-MS: *m/z* (%): 473.3 (24) [M<sup>+</sup>–OH], 461.3 (100) [M<sup>+</sup>–Et]. Anal. Calc. for C<sub>31</sub>H<sub>47</sub>AlN<sub>2</sub>O (490.7): C, 75.88; H, 9.65; N, 5.71. Found: C, 75.24; H, 9.44; N, 5.62%.

#### 4.4. Synthesis of $LAlEt(\mu-O)ZrMeCp_2$ (**3**)

Toluene (40 mL) was added to the mixture of **2** (0.49 g, 1 mmol) and  $Cp_2ZrMe_2$  (0.26 g, 1 mmol). The resulting solution was stirred for 2 h at room temperature, and then continuously for 24 h at 100 °C. After concentration and keeping the solution at room temperature for 1 day, colorless crystals of **3** (0.51 g) were isolated. Yield 0.48 g (66 %).

M.p. 368–369 °C.  $^1H$  NMR (500.13 MHz,  $CDCl_3$ ):  $\delta$  –0.32 (s, 3H,  $ZrMe$ ), –0.14 (q,  $J = 7.9$  Hz, 2H,  $AlCH_2CH_3$ ), 1.04 (d,  $J = 6.8$  Hz, 6H,  $CH(CH_3)_2$ ), 1.14 (t,  $J = 7.9$  Hz, 3H,  $AlCH_2CH_3$ ), 1.25 (d,  $J = 6.8$  Hz, 6H,  $CH(CH_3)_2$ ), 1.37 (d,  $J = 6.8$  Hz, 6H,  $CH(CH_3)_2$ ), 1.41 (d,  $J = 6.8$  Hz, 6H,  $CH(CH_3)_2$ ), 1.77 (s, 6H,  $CMe$ ), 3.15 (sept,  $J = 6.8$  Hz, 2H,  $CH(CH_3)_2$ ), 3.29 (sept,  $J = 6.8$  Hz, 2H,  $CH(CH_3)_2$ ), 5.02 (s, 1H,  $\gamma-CH$ ), 5.30 (s, 10H,  $C_5H_5$ ), 7.24–7.27 (m, *Ar*) ppm.  $^{13}C$  NMR (125.8 MHz,  $CDCl_3$ ):  $\delta$  170.5 (CN), 144.7, 143.9, 141.2, 127.0, 124.7, 124.2 (*i*-, *o*-, *m*-, *p*-*Ar*), 109.9 ( $C_5H_5$ ), 97.3 ( $\gamma-CH$ ), 28.7, 27.1 ( $CH(CH_3)_2$ ), 25.3, 25.2, 24.6, 24.6 ( $CH(CH_3)_2$ ), 23.8 ( $\beta-CH_3$ ), 17.6 ( $ZrMe$ ), 9.4 ( $AlCH_2CH_3$ ), 3.4 (br,  $AlCH_2CH_3$ ) ppm. IR (Nujol mull,  $cm^{-1}$ ):  $\tilde{\nu} = 1734$  (m), 1653 (w), 1624 (w), 1591 (w), 1530 (m), 1396 (s), 1317 (m), 1259 (m), 1177 (m), 1099 (m), 1059 (w), 1019 (m), 940 (w), 872 (w), 839 (m), 795 (s), 759 (w), 724 (w), 643 (w), 599 (w), 587 (w), 568 (w), 530 (w), 442 (w). EI-MS:  $m/z$  (%): 709.3 (88) [ $M^+ - Me$ ], 695.3 (100) [ $M^+ - 2Me + 1$ ]. Anal. Calc. for  $C_{42}H_{59}AlN_2OZr$  (726.1): C, 69.47; H, 8.19; N, 3.86. Found: C, 69.40; H, 8.32; N, 3.52%.

#### 4.5. Synthesis of $LAlEt(\mu-O)Yb(THF)Cp_2$ (**4**)

THF (40 mL) was added to the mixture of **2** (0.84 g, 1.71 mmol) and  $Cp_3Yb$  (0.63 g, 1.71 mmol) at room temperature. The resulting solution was stirred for 12 h until the color of the solution turned from dark green to brown. Finally all volatiles were removed in vacuo, and then the residual was extracted with THF (30 mL). The resulting solution was kept at room temperature for 1 day to afford yellow crystals. Yield 0.62 g (42%).

M.p. 208–210 °C. IR (Nujol mull,  $cm^{-1}$ ):  $\tilde{\nu} = 3063$  (m), 1624 (w), 1586 (w), 1525 (m), 1504 (m), 1314 (m), 1259 (m), 1195 (w), 1176 (w), 1100 (m), 1057 (m), 1017 (m), 949 (w), 936 (w), 907 (m), 799 (m), 776 (m), 762 (m), 722 (w), 663 (w), 643 (w), 624 (w), 597 (w), 571 (w), 447 (w). EI-MS:  $m/z$  (%): 764.4 (100) [ $M^+ - THF - Et$ ], 698.3 (12) [ $M^+ - THF - Et - Cp$ ]. Anal. Calc. for  $C_{45}H_{64}AlN_2O_2Yb$  (865.0): C, 62.48; H, 7.46; N, 3.24. Found: C, 61.91; H, 7.30; N, 3.24%.

#### 4.6. Synthesis of $LAlEt(\mu-O)Er(THF)Cp_2$ (**5**)

The procedure is the same as that described for **4** with  $Cp_3Er$  (0.36 g, 1 mmol) instead of  $Cp_3Yb$ . Yield 0.18 g (21%).

M.p. 235 °C. IR (Nujol mull,  $cm^{-1}$ ):  $\tilde{\nu} = 3063$  (w), 1585 (w), 1525 (w), 1313 (w), 1254 (w), 1195 (w), 1175

(w), 1100 (w), 1057 (w), 1015 (w), 936 (w), 903 (m), 799 (w), 772 (m), 762 (m), 722 (w). EI-MS:  $m/z$  (%): 758.3 (100) [ $M^+ - THF - Et$ ], 693.3 (6) [ $M^+ - THF - Et - Cp$ ]. Anal. Calc. for  $C_{45}H_{64}AlErN_2O_2$  (859.2): C, 62.90; H, 7.51; N, 3.26. Found: C, 61.40; H, 7.36; N, 3.08%.

#### 4.7. Synthesis of $LAlEt(\mu-O)Dy(THF)Cp_2$ (**6**)

The procedure is the same as that described for **4** with  $Cp_3Dy$  (0.35 g, 1 mmol) instead of  $Cp_3Yb$ . Yield 0.24 g (28%).

M.p. 208–210 °C. IR (Nujol mull,  $cm^{-1}$ ):  $\tilde{\nu} = 1623$  (w), 1585 (w), 1528 (w), 1314 (w), 1260 (w), 1175 (w), 1099 (w), 1058 (w), 1018 (w), 936 (w), 898 (w), 799 (w), 772 (w), 761 (w), 722 (w), 664 (w). EI-MS:  $m/z$  (%): 754.3 (100) [ $M^+ - THF - Et$ ], 688.3 (20) [ $M^+ - THF - Et - Cp$ ]. Anal. Calc. for  $C_{45}H_{64}AlDyN_2O_2$  (854.5): C, 63.25; H, 7.55; N, 3.28. Found: C, 62.71; H, 7.61; N, 3.26%.

#### 4.8. Synthesis of $LAlEt(\mu-O)Y(THF)Cp_2$ (**7**)

The procedure is the same as that described for **4** with  $Cp_3Y$  (0.36 g, 1 mmol) instead of  $Cp_3Yb$ . Yield 0.34 g (44%).

M.p. 208–210 °C.  $^1H$  NMR (500.13 MHz,  $C_6D_6$ ):  $\delta$  0.40 (q,  $J = 8.0$  Hz, 2H,  $AlCH_2CH_3$ ), 1.15 (d,  $J = 6.8$  Hz, 6H,  $CH(CH_3)_2$ ), 1.31 (d,  $J = 6.8$  Hz, 6H,  $CH(CH_3)_2$ ), 1.34 (br, 4H,  $O-(CH_2CH_2)_2$ ), 1.50 (d,  $J = 6.8$  Hz, 6H,  $CH(CH_3)_2$ ), 1.51 (d,  $J = 6.8$  Hz, 6H,  $CH(CH_3)_2$ ), 1.52 (s, 6H,  $CMe$ ), 1.60 (t,  $J = 8.0$  Hz, 3H,  $AlCH_2CH_3$ ), 3.08 (br, 4H,  $O-(CH_2CH_2)_2$ ), 3.45 (sept,  $J = 6.8$  Hz, 2H,  $CH(CH_3)_2$ ), 3.64 (sept,  $J = 6.8$  Hz, 2H,  $CH(CH_3)_2$ ), 4.84 (s, 1H,  $\gamma-CH$ ), 5.85 (s, 10H,  $C_5H_5$ ), 7.14–7.19 (m, *Ar*) ppm.  $^{13}C$  NMR (125.8 MHz,  $C_6D_6$ ):  $\delta$  170.6 (CN), 145.2, 144.0, 143.0, 126.9, 124.6, 124.5 (*i*-, *o*-, *m*-, *p*-*Ar*), 110.0 ( $C_5H_5$ ), 99.2 ( $\gamma-CH$ ), 71.0 (br,  $O-(CH_2CH_2)_2$ ), 28.8, 27.6 ( $CH(CH_3)_2$ ), 26.6, 25.6 ( $O-(CH_2CH_2)_2$ ), 25.4, 24.9, 24.8 ( $CH(CH_3)_2$ ), 23.9 ( $\beta-CH_3$ ), 12.2 ( $AlCH_2CH_3$ ), 6.6 (br,  $AlCH_2CH_3$ ) ppm. IR (Nujol mull,  $cm^{-1}$ ):  $\tilde{\nu} = 3060$  (s), 2414 (w), 2069 (w), 1954 (w), 1930 (w), 1754 (w), 1626 (w), 1584 (w), 1524 (s), 1503 (m), 1313 (s), 1255 (s), 1194 (w), 1175 (m), 1100 (m), 1057 (m), 1015 (s), 948 (w), 936 (m), 901 (s), 799 (s), 772 (s), 761 (s), 722 (m), 642 (w), 622 (m), 597 (m), 569 (s). EI-MS:  $m/z$  (%): 461.3 [ $M^+ - Et - Y(THF)Cp_2$ ] (100). Anal. Calc. for  $C_{45}H_{64}AlN_2O_2Y$  (780.9): C, 69.21; H, 8.26; N, 3.59. Found: C, 68.76; H, 7.48; N, 3.55%.

#### 4.9. X-ray crystal structure determinations for **2** and **3**

The structures were solved by direct methods (SHELXS-97) [14] and refined with all data by full-matrix least-squares on  $F^2$  (SHELXL-97). The hydrogen atoms of C–H bonds were placed in idealized positions. The Flack parameter for **2** is –0.10(18). Other structural details are listed in Table 1.

#### 4.10. Polymerization of ethylene

On a vacuum line ( $10^{-5}$  Torr), polymerizations were carried out in a 200 mL autoclave (Büchi). In a typical experiment, 100 mL of dry toluene (from Na/K) was vacuum-transferred into the polymerization flask, pre-saturated with 1.0 atm of rigorously purified ethylene. The catalyst (0.009 g in toluene; 10 mL, 12.4  $\mu$ mol) was placed into the Schlenk flask and appropriate MAO (1.6 M in toluene) was added. The mixture was stirred for 20 min to activate the catalyst. The catalyst solution was then quickly injected into the rapidly stirred flask using a gas-tight syringe. After a measured time interval, the polymerization was quenched by the addition of methanol (5 mL) and the reaction mixture was then poured into methanol (800 mL). The polymer was allowed to fully precipitate overnight and then collected by filtration, washed with fresh methanol, and dried.

#### 4.11. Polymer characterization

$^{13}\text{C}$  NMR assay of polymer microstructure was conducted in 1,1,2,2-tetrachloroethane- $\text{d}_2$  at 120 °C. Resonances were assigned according to the literature [15] for polyethylene. Differential Scanning Calorimetric measurements of the polymer melting curves were performed on a TA instrument 2920 (Modulated Differential Scanning Calorimeter), which was calibrated against indium metal. Typically ca. 4 mg samples were used (10 °C/min).

#### Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the Göttinger Akademie der Wissenschaften. Ying Yang thanks the Chinese Scholarship Council for a fellowship.

#### Appendix A. Supplementary material

CCDC 651788 and 651789 contain the supplementary crystallographic data for **2** and **3**. These data can be obtained free of charge via <http://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 e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk).

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