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# Bidentate N, O-aluminum complexes: Synthesis, characterization and catalytic study for MPV reduction reactions



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## ABSTRACT

Treatment of AlMe<sub>3</sub> with bidentate N, O-ligands, HOC(Me)(Ph)C<sub>6</sub>H<sub>4</sub>-NMe<sub>2</sub>-2 ( $L^{1}$ H) or HOC(CH<sub>2</sub>)<sub>5</sub>C<sub>6</sub>H<sub>4</sub>  $(L^2H)$ different molar ratios, four novel aluminum -NMe<sub>2</sub>-2 in complexes  $[Me_{2}AIOC(Me)(C_{6}H_{5})C_{6}H_{4}-NMe_{2}-2] (1), [Me_{2}AIOC(CH_{2})_{5}C_{6}H_{4}-NMe_{2}-2] (2), [MeAI_{1}OC(Me)(C_{6}H_{5})C_{6}H_{4}-NMe_{2}-2]_{2}] (3)$ and [MeAI{OC(CH<sub>2</sub>)<sub>5</sub>C<sub>6</sub>H<sub>4</sub>-NMe<sub>2</sub>-2}<sub>2</sub>] (4) were obtained in good yield. Complexes 1–4 were characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, elemental analyses and single crystal X-ray diffraction techniques. Each of the complexes 1, 2, 3 and 4 was tested for the capable of catalyzed Meerwein–Ponndorf–Verley (MPV) reduction of ketones or aldehydes with low catalyst loadings under mild conditions and showed good to excellent catalytic activities.

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# 1. Introduction

Selective synthesis of primary and secondary alcohols is an important process for the pharmaceutical, fragrance and food aroma industries [1]. They can be produced by alkylation of aldehydes [2] or by oxidation of olefins [3], but a general route is the selective reduction of carbonyls to alcohols. Meerwein–Ponndorf–Verley (MPV) reduction appears to be one of the potential answers because of its characteristic features, i.e., high chemoselectivity, mild reaction conditions, simple and safe operations, and the low cost and toxicity of reagents [4].

The MPV reaction was first reported in the mid 1920s [5], it is performed with aluminum isopropoxide as a catalyst and 2propanol as a hydride source. Subsequently, a number of catalyst systems of metal alkoxide/hydride source combinations have been investigated. For example, aluminum alkoxides [6], alkali metal alkoxides [7], rare earth metal alkoxides [8], metal oxides [9], transition metal complexes of zirconium, hafnium, iridium, ruthenium [10], MCM-41-grafted metal isopropoxides [11] and various other catalysts [12] have been reported. But, the reaction is usually conducted under the influence of excessive amounts of 2-propanol, high loading of catalyst, high temperature, long reaction time or removal of produced acetone. Attempts to design and development of new catalysts to improve the MPV reaction in a milder and less expensive environment has been attracted much more attentions. Very recently, McNerney and co-workers reported that siloxidesupported aluminum isopropoxide was used to promote the MPV reaction in good yield under mild conditions and with low catalyst loadings [6j]. We now report the synthesis of heteroleptic bidentate N, O-aluminum complexes **1–4** (Scheme 1) and their use as precatalysts for the reduction of carbonyl moieties to produce their analogous alcohols.

### 2. Results and discussions

# 2.1. Synthesis and characterization

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Scheme 1. Preparation of complexes 1-4.

respectively. Accordingly, treatment of  $L^1$ H or  $L^2$ H with 0.5 equivalent of AlMe<sub>3</sub> in hexane generated the five-coordinated aluminum-monoalkyl complexes  $[MeA_1^{1}{OC(Me)(C_6H_5)C_6H_4-N}Me_2-2_{2}]$  (3) and  $[MeA_1^{1}{OC(CH_2)_5C_6H_4-N}Me_2-2_{2}]$  (4) in good yields, respectively (Scheme 1). Further more, 1 and 2 were transferred readily to 3 and 4 via treatment of 1 or 2 with equivalent amount of  $L^1$ H or  $L^2$ H in diethyl ether at 0 °C, respectively.

The structures of complexes **1**–**4** were characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR spectroscopy and elemental analyses, as shown in Experimental Section. Fortunately, the colorless crystals of **1**–**4** suitable for X-ray diffraction analysis were also isolated. The ORTEP drawing of the molecular structure and selected bond lengths and angles of complexes **1**–**4** are given in Figs. 1–4, respectively.

#### 2.2. X-ray single crystal structures of 1-4

The Al atom is four-coordinated in a distorted tetrahedral

geometry in the title complex **1** (Fig. 1). The four-coordination around the Al atom involves the N atom and the O atom from the ligand and two methyl-C atoms. The six-membered chelate ring, O1Al1N1C1C2C9, has a boat conformation with the C9 and N1 atoms occupying the apex positions. In comparison with the idealized tetrahedral angle, the intra-ring angle O(1)–Al–N(1) (93.42 (6) °) is remarkably narrow. The Al(1)–O(1) (1.7277 (14) Å) is slightly longer than the classic normal Al–O bonds (1.69 Å) [13], while the Al(1)–N(1) (2.0156 (15) Å) is slightly shorter than the average bond length of Al–N (2.08 Å) [13,14]. The molecular structure of complex **2** is very similar to that of **1**, and its selected bond lengths and angles are given in Fig. 2.

The Al atom in **3** adopts five-coordination mode (Fig. 3), where two mono-anionic ligands coordinated to the central aluminum atom by their O atom and N atom, forming two distorted sixmembered rings. The structural features of the both of the sixmember ring are similar to that of **1**. The bond length of Al(1)-O(1) (1.7212 (15) Å) is very closely to that of **1**, while the bond



**Fig. 1.** Molecular structure of the complex **1**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Al(1)-O(1) 1.7277(14), Al(1)-N(1) 2.0156(15), Al(1)-C(17) 1.952(2), Al(1)-C(18) 1.951(2); O(1)-Al-N(1) 93.42(6), O(1)-Al-C(17) 114.79(9), O(1)-Al-C(18) 113.25(9).



**Fig. 2.** Molecular structure of the complex **2**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Al(1)-O(1) 1.7317(14), Al(1)-N(1) 2.0089(18), Al(1)-C(15) 1.959(2), Al(1)-C(16) 1.966(2); O(1)-Al-N(1) 93.25(7), O(1)-Al-C(15) 117.66(9), O(1)-Al-C(16) 112.22(9).

length of Al(1)–N(1) (2.2056 (19) Å) is longer than that of **1**. The molecular structure of complex **4** is similar to that of complex **3**, and the corresponding bond lengths and angles of **4** are given in Fig. 4. The dihedral angle (56.60°) between the N(1)O(1)Al(1) and N(2)O(2)Al(1) planes is slightly narrower than that in complex **3** (58.14°).

# 2.3. The MPV reduction reaction catalyzed by 1-4

The MPV reduction reactions were systematically studied with complexes **1**–**4** as precatalysts. Firstly, benzaldehyde was selected as a model substrate and dry 2-propanol was employed as the reducing agent. As shown in Table 1, the reduction reaction of benzaldehyde was carried out in toluene with 10% mole of **1**–**4** under reflux condition. All of complexes **1**–**4** showed good catalytic activity ( $\geq$ 90%, Table 1, entries 1–4) and the corresponding benzyl alcohol was obtained in almost quantitative yield when **2** was



**Fig. 3.** Molecular structure of the complex **3.** Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Al(1)-O(1) 1.7212(15), Al(1)-O(1)' 1.7212(15), Al(1)-O(1)' 1.7212(15), Al(1)-O(1)' 1.7212(15), Al(1)-O(1)' 1.970(4), Al(1)-N(1) 2.2056(19), Al(1)-N(1)' 2.2056(19); O(1)'-Al(1)-O(1) 122.48(12), O(1)'-Al(1)-C(17) 118.76(6), O(1)'-Al(1)-N(1) 87.88(7), O(1)-Al(1)-N(1) 87.03(7), C(17)-Al(1)-N(1)' 95.29(6), O(1)'-Al(1)-N(1)' 87.03(7), O(1)-Al(1)-N(1)' 87.88(7), O(1)-Al(1)-N(1)' 95.29(6), N(1)-Al(1)-N(1)' 169.41(12).



**Fig. 4.** Molecular structure of the complex **4**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Al(1)-O(1) 1.7385(18), Al(1)-O(2) 1.7332(17), Al(1)-C(29) 1.983(3), Al(1)-N(1) 2.213(2), Al(1)-N(2) 2.190(2); O(2)-Al(1)-O(1) 123.38(9), O(2)-Al(1)-C(29) 117.74(11), O(1)-Al(1)-C(29) 118.79(10), O(2)-Al(1)-N(1) 89.67(8), O(1)-Al(1)-N(1) 85.60(9), C(29)-Al(1)-N(1) 91.80(11), O(2)-Al(1)-N(2) 87.17(8), O(1)-Al(1)-N(2) 92.64(8), C(29)-Al(1)-N(2) 93.38(11), N(1)-Al(1)-N(2) 174.74(9).

employed as the catalyst within 15 min (Table 1, entry 2). As we hoped, the similar yield was obtained by increasing the reaction time to 60 min, 135 min or 90 min when **1**, **3** or **4** was used as catalyst, respectively (Table 1, entries 1–7). The further tests showed that the reduction of benzaldehyde by **2** under solvent-free condition also gave the quantitative yield (Table 1, entry 9) while **1**, **3** and **4** gave a 95%, 91%, or 94% yield of benzyl alcohol, respectively (Table 1, entries 8, 10 and 11). With the decrease of 2-propanol and catalyst, the yield was decreased (Table 1, entries 12–27). Hope-fully, complex **2** at 5 mol % loading and 1.2 equivalents of 2-propanol under solvent-free in 15 min promoted the almost

#### Table 1

# Complex 1–4 catalyzed MPV reduction of benzaldehyde.<sup>a</sup>



Entry	Catalyst	Catalyst [mol%]	2-propanol [Equiv]	Solvent	Yield (%) <sup>b</sup>
1	1	10	2	Toluene	93
2	2	10	2	Toluene	>99
3	3	10	2	Toluene	90
4	4	10	2	Toluene	92
5	1	10	2	Toluene	>99 <sup>c</sup>
6	3	10	2	Toluene	99 <sup>d</sup>
7	4	10	2	Toluene	99 <sup>e</sup>
8	1	10	2	None	95
9	2	10	2	None	>99
10	3	10	2	None	91
11	4	10	2	None	94
12	1	10	1.5	None	94
13	2	10	1.5	None	>99
14	3	10	1.5	None	88
15	4	10	1.5	None	92
16	1	5	1.5	None	90
17	2	5	1.5	None	99
18	3	5	1.5	None	85
19	4	5	1.5	None	88
20	1	5	1	None	74
21	2	5	1	None	83
22	3	5	1	None	71
23	4	5	1	None	73
24	1	5	1.2	None	89
25	2	5	1.2	None	99
26	3	5	1.2	None	83
27	4	5	1.2	None	87
28	Al(O <sup>i</sup> Pr) <sub>3</sub>	5	1.2	None	92

<sup>a</sup> Conditions: reflux 15 min

<sup>b</sup> Determined by <sup>1</sup>H NMR spectroscopy.

<sup>c</sup> 60 min.

<sup>d</sup> 135 min.

<sup>e</sup> 90 min.

quantitative reduction of benzaldehyde to benzyl alcohol (Table 1, entry 25). For comparison, the traditional  $Al(O^{i}Pr)_{3}$  as catalyst for MPV reduction reaction also been carried out with 92% yield (Table 1, entries 28). In any case, the catalytic activity was in the sequence of  $2 > Al(O^{i}Pr)_{3} > 1 > 4 > 3$  under the tested conditions. It would attribute to the benzyloxy for 1 and the steric hindrance for 3 and 4, which reduced the Lewis acidity and the electrophilicity of aluminum center, decreased the attack probability to benzaldehyde. The results are consistent with the literature reports [6].

With the above results in hand, a variety of aldehyde and ketone substrates were examined for the MPV reaction, using 2 as catalyst (Table 2). As expected, the aromatic aldehydes with an electronwithdrawing group on the phenyl ring gave higher yields than the aldehyde with an electron-donating group (Table 2, entries 2–4). Citronellal, a raw material for the spice, could achieve 93% vield under the optimized conditions (Table 2, entry 5), and some challenging  $\alpha$ ,  $\beta$ -unsaturated aldehydes selectively reduced to alcohols were also achieved in good yields with lower 2-propanol loadings, such as cinnamaldehyde and citral (Table 2, entries 6, 7). It should be noted that the side reaction of Tishchenko or aldol, which is usually found in MPV reactions, is not observed in our system. Generally, low active cyclohexanone and acetophenone were also reduced to corresponding alcohols under our catalytic system in 67% and 87% yields (GC-MS yield), respectively (Table 2, entries 8, 9).

#### Table 2

Complex 2 catalyzed MPV reduction of selected carbonyl compounds.<sup>a</sup>





а	Conditions: reflux, 5% mol catalyst, 1.2 equiv 2-propanol, solvent-free, 15 min.
b	Determined by <sup>1</sup> H NMR spectroscopy.

<sup>c</sup> Determined by GC–MS.

# 3. Conclusions

In conclusion, four novel bidentate N, O-aluminum complexes **1–4** have been synthesized, characterized and used for catalytic study of MPV reduction reactions. Reductions were conducted with low catalyst loadings (5% mol) and low equivalents of 2-propanol (1.2 equiv) under mild conditions. The complex **2** showed the best catalytic activities toward the MPV reaction and a range of aldehydes and ketones are rapidly, selectively transferred to the corresponding primary or secondary alcohols in good or excellent yields.

# 4. Experimental section

#### 4.1. General remarks

All experiments were carried out under purified dry nitrogen atmosphere by using standard Schlenk techniques. Solvents were dried and freshly distilled under nitrogen. Elemental analyses were performed on a Vario ELIII instrument. Melting points were determined on a STUART SMP10 melting point apparatus and uncorrected. The NMR spectra were recorded in CDCl<sub>3</sub> and C<sub>6</sub>D<sub>6</sub> with an AVANCE DRX 300 spectrometer (Bruker), using TMS as an internal standard.

#### 4.2. Preparation

# 4.2.1. $HOC(Me)(Ph)C_6H_4-NMe_2-2$ ( $L^1H$ )

A dry 250 mL two-necked flask was filled with N, N-dimethylaniline (9.65 g, 0.0797 mol), 100 mL of anhydrous diethyl ether and 11.87 mL of TMEDA and the solution was stirred under nitrogen atmosphere. 33 mL of a 2.87 M of n-butyllithium in hexane was added at -78 °C. The solution was allowed to warm to room temperature and stirred for 2 h. Acetophenone (11.2 mL, 0.096 mol) was added dropwise to the reaction mixture at 0 °C and stirred for 2 h. The solution was hydrolyzed by 50 mL of distilled water, and then washed with aqueous 5% hydrochloric acid (5  $\times$  50 mL). The aqueous phase was combined and made alkaline with 10% sodium hydroxide aqueous solution. The aqueous phase was then extracted with diethyl ether  $(3 \times 20 \text{ mL})$  and the organic phase was dried over anhydrous magnesium sulfate. The crude product by vacuum distillation at 134 °C to give the product as pale yellow oil in 73% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ/ppm): 1.84 (s, 3H, CCH<sub>3</sub>), 2.93 (s, 6H, NC<sub>2</sub>H<sub>6</sub>), 7.11–7.51 (m, 4H, C<sub>6</sub>H<sub>4</sub>). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, δ/ppm): 32.12 (CCH<sub>3</sub>), 45.15-46.36(br, NC<sub>2</sub>H<sub>6</sub>), 77.30 (CCH<sub>3</sub>), 123.81 (C<sub>6</sub>H<sub>4</sub>), 125.61 (C<sub>6</sub>H<sub>5</sub>), 126.15 (C<sub>6</sub>H<sub>4</sub>), 126.49 (C<sub>6</sub>H<sub>5</sub>), 127.73 (C<sub>6</sub>H<sub>5</sub>), 128.22 (C<sub>6</sub>H<sub>4</sub>), 128.65 (C<sub>6</sub>H<sub>4</sub>), 143.44 (C<sub>6</sub>H<sub>4</sub>), 150.94 (C<sub>6</sub>H<sub>5</sub>), 151.98 (C<sub>6</sub>H<sub>4</sub>).

#### 4.2.2. $HOC(CH_2)_5C_6H_4-NMe_2-2$ ( $L^2H$ )

The reaction was carried out by a similar procedure as described for **L**<sup>1</sup>H, except that 16.0 g (0.08 mol) of cyclohexanone was used instead of acetophenone, and the product as colorless oil was obtained by vacuum distillation at 118 °C in 78% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ /ppm): 0.99–2.56 (br., 10H, C<sub>5</sub>H<sub>10</sub>), 2.60 (s, 6H, NC<sub>2</sub>H<sub>6</sub>), 7.30–8.01 (m, 4H, C<sub>6</sub>H<sub>4</sub>). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>,  $\delta$ /ppm): 22.41(C<sub>6</sub>H<sub>10</sub>), 26.27 (C<sub>6</sub>H<sub>10</sub>), 40.38 (NC<sub>2</sub>H<sub>6</sub>), 47.03 (C<sub>6</sub>H<sub>10</sub>), 75.24 (C<sub>5</sub>H<sub>10</sub>CO–), 123.90 (C<sub>6</sub>H<sub>4</sub>), 126.67 (C<sub>6</sub>H<sub>5</sub>), 127.03 (C<sub>6</sub>H<sub>4</sub>), 127.91 (C<sub>6</sub>H<sub>4</sub>), 144.72 (C<sub>6</sub>H<sub>4</sub>), 151.82 (C<sub>6</sub>H<sub>4</sub>).

$$[Me_{2}A]OC(Me)(C_{6}H_{3})C_{6}H_{4}-NMe_{2}-2]$$

$$\tag{1}$$

0.93 mL AlMe<sub>3</sub> (hexane, 2 M solution) was added dropwise at -78 °C to a solution of L<sup>1</sup>H (0.45 g, 1.85 mmol) in diethyl ether (10 mL). The reaction mixture was then warmed to room temperature and stirred for 2 h. The reaction mixture was cooled to -30 °C, and a colorless solid was obtained that was recrystallized from hexane to give the product as colorless crystals. Yield: 0.53 g (96%). Mp 206–210 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ/ppm): -1.25 (s, 3H, AlCH<sub>3</sub>), -0.94 (s, 3H, AlCH<sub>3</sub>), 1.69 (s, 3H, CCH<sub>3</sub>), 2.34 (br. s, 3H, NCH<sub>3</sub>), 2.67 (br. s, 3H, NCH<sub>3</sub>), 6.92–6.94(m, H, C<sub>6</sub>H<sub>4</sub>), 7.00–7.02 (m, 2H, C<sub>6</sub>H<sub>4</sub>), 7.11 (m, 2H, C<sub>6</sub>H<sub>5</sub>), 7.27–7.30 (m, 2H, C<sub>6</sub>H<sub>5</sub>), 7.34 (s, H,  $C_6H_4$ ). <sup>13</sup>C NMR (CDCl<sub>3</sub>,  $\delta$ /ppm): -11.19 (AlCH<sub>3</sub>), -10.03 (AlCH<sub>3</sub>), 37.80 (CCH<sub>3</sub>), 45.78 (NCH<sub>3</sub>), 49.58 (NCH<sub>3</sub>), 78.26 (CCH<sub>3</sub>), 120.28 (C<sub>6</sub>H<sub>4</sub>), 126.43 (C<sub>6</sub>H<sub>5</sub>),126.82 (C<sub>6</sub>H<sub>4</sub>), 127.40 (C<sub>6</sub>H<sub>5</sub>), 128.58 (C<sub>6</sub>H<sub>5</sub>), 131.94 (C<sub>6</sub>H<sub>4</sub>), 143.64 (C<sub>6</sub>H<sub>4</sub>), 146.07 (C<sub>6</sub>H<sub>4</sub>), 152.35 (C<sub>6</sub>H<sub>5</sub>). Anal. Calcd for C<sub>18</sub>H<sub>24</sub>AlNO: C, 72.70; H, 8.13; N, 4.71. Found: C, 72.43; H, 8.27; N, 5.02.

$$[Me_2AIOC(CH_2)_5C_6H_4NMe_2-2]$$
(2)

The reaction was carried out as described for complex **1** except that 0.54 g (2.44 mmol) of **L**<sup>2</sup>H was used instead of **L**<sup>1</sup>H. Colorless crystals were obtained from hexane at -20 °C. Yield: 0.63 g (93%). Mp 112–114 °C. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>,  $\delta$ /ppm): -0.46 (s, AlC<sub>2</sub>H<sub>6</sub>), 1.35–1.39 (m, H, C<sub>6</sub>H<sub>10</sub>), 1.69–2.02 (m, 7H, C<sub>6</sub>H<sub>10</sub>), 2.33 (s, 6H, NC<sub>2</sub>H<sub>6</sub>), 2.37–2.45 (m, 2H, C<sub>6</sub>H<sub>10</sub>), 6.72–6.75 (d, 2H, JH–H = 9 Hz, C<sub>6</sub>H<sub>4</sub>), 6.92–6.97 (t, 2H, C<sub>6</sub>H<sub>4</sub>), 7.02–7.04 (s, 2H, C<sub>6</sub>H<sub>4</sub>), 7.24–7.27 (d, 2H, JH–H = 9 Hz, C<sub>6</sub>H<sub>4</sub>). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>,  $\delta$ /ppm): -11.05 (AlC<sub>2</sub>H<sub>6</sub>), 22.08(C<sub>6</sub>H<sub>10</sub>), 26.27 (C<sub>6</sub>H<sub>10</sub>), 42.50 (C<sub>6</sub>H<sub>10</sub>), 46.95 (NC<sub>2</sub>H<sub>6</sub>), 75.13 (C<sub>5</sub>H<sub>10</sub>CO–), 119.08 (C<sub>6</sub>H<sub>4</sub>), 126.74 (C<sub>6</sub>H<sub>5</sub>), 129.84 (C<sub>6</sub>H<sub>4</sub>), 145.75 (C<sub>6</sub>H<sub>4</sub>), 146.21 (C<sub>6</sub>H<sub>4</sub>). Anal. Calcd for C<sub>16</sub>H<sub>26</sub>AlNO: C, 69.79; H, 9.52;

#### N, 5.09. Found: C, 69.37; H, 9.97; N, 5.42.

$$[MeAl(OC(Me)(C_{6}H_{5})C_{6}H_{4}-NMe_{2}-2)_{2}]$$
(3)

1.2 mL AlMe<sub>3</sub> (hexane, 2 M solution) was added dropwise at  $-78 \degree$ C to a solution of L<sup>1</sup>H (1.13 g, 4.8 mmol) in hexane (10 mL). The reaction mixture was then warmed to room temperature and stirred for 2 h. The reaction mixture was cooled to  $-20 \degree$ C, and a colorless solid was obtained that was recrystallized from diethyl ether to give the product as colorless crystals. Yield: 1.13 g (92%). Mp 231–235 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ /ppm): -1.62 (s, 2H, AlCH<sub>3</sub>), -0.70 (s, H, AlCH<sub>3</sub>), 0.71 (s, 2H, CH<sub>3</sub>), 1.85 (s, 5H, CH<sub>3</sub>), 2.11–3.15 (br, 12H, 2(NC<sub>2</sub>H<sub>6</sub>)), 7.03 (m, 4H, C<sub>6</sub>H<sub>4</sub>), 7.40–7.42 (m, 9H, C<sub>6</sub>H<sub>5</sub> and C<sub>6</sub>H<sub>4</sub>), 7.37–7.39 (m, 2H, C<sub>6</sub>H<sub>5</sub>), 7.56–7.59 (m, 2H, C<sub>6</sub>H<sub>4</sub>), 7.65(m, H, C<sub>6</sub>H<sub>5</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>,  $\delta$ /ppm): -12.10 (AlCH<sub>3</sub>), 31.47 (CCH<sub>3</sub>), 37.26 (CCH<sub>3</sub>), 39.12(CCH<sub>3</sub>), 47.5(CCH<sub>3</sub>), 42.87–51.97(br, 2N (C<sub>2</sub>H<sub>6</sub>)), 119.42, 123.17, 125.84, 126.83, 127.99, 129.64, 129.89, 146.87, 148.68(C<sub>6</sub>H<sub>5</sub> and C<sub>6</sub>H<sub>4</sub>), 151.38 (C<sub>6</sub>H<sub>5</sub>). Anal. Calcd for C<sub>33</sub>H<sub>39</sub>AlN<sub>2</sub>O<sub>2</sub>: C, 75.83; H, 7.52; N, 5.36. Found: C, 75.48; H, 7.83; N, 5.75.

 $[MeAl(OC(CH_2)_5C_6H_4-NMe_2-2)_2]$ (4)

1.1 mL AlMe<sub>3</sub> (hexane, 2 M solution) was added dropwise at -78 °C to a solution of  $L^2$ H (0.96 g, 4.4 mmol) in diethyl ether (10 mL). The reaction mixture was then warmed to room temperature and stirred for 2 h. Colorless crystals were obtained from diethyl ether at -20 °C. Yield: 1.98 g (94%). Mp 142–145 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ /ppm): -1.03 (s, 3H, AlCH<sub>3</sub>), 7.15–7.33 (m, 20H, C<sub>6</sub>H<sub>4</sub>), 3.04 (s, 12H, 2(NC<sub>2</sub>H<sub>6</sub>)), 7.23 (m, 4H, C<sub>6</sub>H<sub>4</sub>), 7.40–7.42 (d, 2H, C<sub>6</sub>H<sub>4</sub>), 23.75(C<sub>6</sub>H<sub>10</sub>), 24.05(C<sub>6</sub>H<sub>10</sub>), 27.45 (C<sub>6</sub>H<sub>10</sub>), 42.51 (C<sub>6</sub>H<sub>10</sub>), 43.54 (C<sub>6</sub>H<sub>10</sub>), 76.40 (C<sub>5</sub>H<sub>10</sub>CO–), 121.13 (C<sub>6</sub>H<sub>4</sub>), 126.16 (C<sub>6</sub>H<sub>4</sub>), 127.63 (C<sub>6</sub>H<sub>4</sub>), 129.88 (C<sub>6</sub>H<sub>4</sub>), 146.87 (C<sub>6</sub>H<sub>4</sub>), 150.82 (C<sub>6</sub>H<sub>4</sub>). Anal. Calcd for C<sub>29</sub>H<sub>43</sub>AlN<sub>2</sub>O<sub>2</sub>: C, 72.77; H, 9.06; N, 5.85. Found: C, 72.36; H, 10.27; N, 6.34.

# 4.3. Typical procedure employed for MPV reactions

A 25 mL Schlenk flask was charged with aluminum complex (0.2 mmol) and the carbonyl compound (4.0 mmol) was added, followed by the addition of 2-propanol (0.37 mL, 4.8 mmol). The reaction mixture was then refluxed for 15 min, and the yield was determined by <sup>1</sup>H NMR spectroscopic studies based on the integration in the methylene and the CHO region of the benzyl group.

# 4.4. X-ray crystallography

All crystals were coated in oil and then directly mounted on the diffractometer under a stream of cold nitrogen gas. Single X-ray diffraction data of the compounds were collected on a Bruker Smart Apex CCD diffractometer using monochromated Mo K $\alpha$  radiation,  $\lambda = 0.71073$  Å. A total of N reflections were collected by using  $\omega$  scan mode. Corrections were applied for Lorentz and polarization effects as well as absorption using multi-scans (SADABS) [15]. Each structure was solved by direct method and refined on  $F^2$  by full matrix least squares (SHELX97) using all unique data [16]. Then the remaining non-hydrogen atoms were obtained from the successive difference fourier map. All non-hydrogen atoms were refined with anisotropic displacement parameters, whereas the hydrogen atoms were constrained to parent sites, using a riding mode (SHELXTL) [17]. Details of the modeling of disorder in the crystals can be found in their CIF files.

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# Supplementary material

CCDC 1047506–1047509 contains the supplementary crystallographic data for **1**, **2**, **3** and **4**, respectively. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, 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. Supplementary data associated with this article can be found in the online version or by direct contacting the authors.

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