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Reduction of Aldehydes and Ketones Catalyzed by a Novel Aluminum Alkoxide: Mechanistic Studies of Meerwein−Ponndorf−Verley Reaction

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Treatment of 2,2′-methylenebis(4,6-di(1-methyl-1-phenylethyl)phenol (MMPEP-H_2) with 1 molar equiv of Me_3Al in toluene gives $[(\mu\text{-MMPEP})AlMe]_2$, which further reacts with 2 molar equiv of 2-propanol or benzyl alcohol, affording a four-coordinated aluminum complex, $[(MMPEP)Al(\mu\text{-}OR)]_2$ (**1**, R = ^{i}Pr; **2**, R = Bn) in high yield, whereas $[(MMPEP)Al(\mu\text{-}OBn)(O{=}CHPh)]_2$ (**3**) can be obtained either by the reaction of **2** with 2 molar equiv of benzaldehyde or by the reaction of **1** with 4 molar equiv of benzaldehyde. Compound **1** has shown great catalytic activities toward Meerwein−Ponndorf−Verley (MPV) hydrogen transfer reactions of aldehydes and ketones. A melting point depressing experiment indicates that in the catalytic reaction a four-coordinated aluminum complex $[(MMPEP)Al(O^iPr)(OCRR')]$ formed as an intermediate.

Introduction

Because of high selectivity and mild reaction conditions, Meerwein−Ponndorf−Verley (MPV) reductions of aldehydes and ketones by employing an aluminum alkoxide[1] or a transition metal complex as a catalyst[2] with 2-propanol as a hydride source are still of great interest, though a variety of reagents are available in the literature[3] for the same. The generally accepted mechanism for MPV reactions proceeds via an intermediate in which both the carbonyl compound and reducing alcohol are bound to the metal ion. The carbonyl is then activated upon coordination to Al(III), followed by a hydride transfer from the alcoholate to the carbonyl group via a six-membered transition state, as shown in Scheme 1.[4] However, the truly active aluminum species for this reaction is still not well-known because aluminum alkoxides tend to form aggregates and exist as a mixture of several species in most of the cases.[5] For example, $Al(O^iPr)_3$ forms a tetranuclear aggregate in the crystalline state in which one six-coordinated aluminum center is surrounded by three bridging $Al(O^iPr)_4$ fragments, but in solution several other species including a trimer are present, and the interconversion between these species complicates the reaction mechanism.[6] Therefore, preparation of an aluminum complex with single-site activity for the MPV reduction of organic carbonyls is highly desirable.

Recently, we have synthesized an excellent catalyst, $[(EDBP)Al(\mu\text{-}O^iPr)]_2$ (**A**), for MPV reductions of aldehyde.[7] Based on reactions of **A** with substituted aldehydes and single-crystal structure studies of $[(EDBP)Al(\mu\text{-}OBn)(O{=}CHC_6H_5)]_2$,[7] it is evident that, during the catalytic MPV reductions of aldehydes, a pentacoordinated intermediate is forming between the carbonyl group of the aldehyde molecule and the aluminum center upon coordination. Unfortunately, **A** is inactive toward MPV reduction of ketones.

To increase the activity of the aluminum center, a little fine-tuning can be achieved either by increasing the electron-withdrawing group in the ligand to enhance the Lewis acidity of the aluminum center or by introducing a sterically more bulky ligand to make a four-coordinated intermediate possible. To fulfill this requirement, we synthesized a novel aluminum alkoxide, $[(MMPEP)Al(\mu\text{-}O^iPr)]_2$(**1**). Experimental results show this complex efficiently catalyzes the reduction of aldehydes and ketones in the presence of 2-propanol.

Results and Discussions

Synthesis and Spectroscopic Studies. The reaction of 2,2′-methylenebis(4,6-di(1-methyl-1-phenylethyl)-

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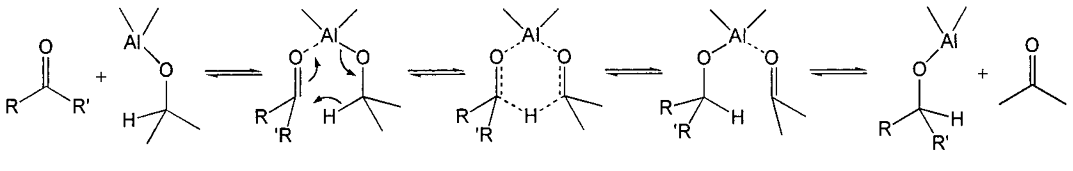
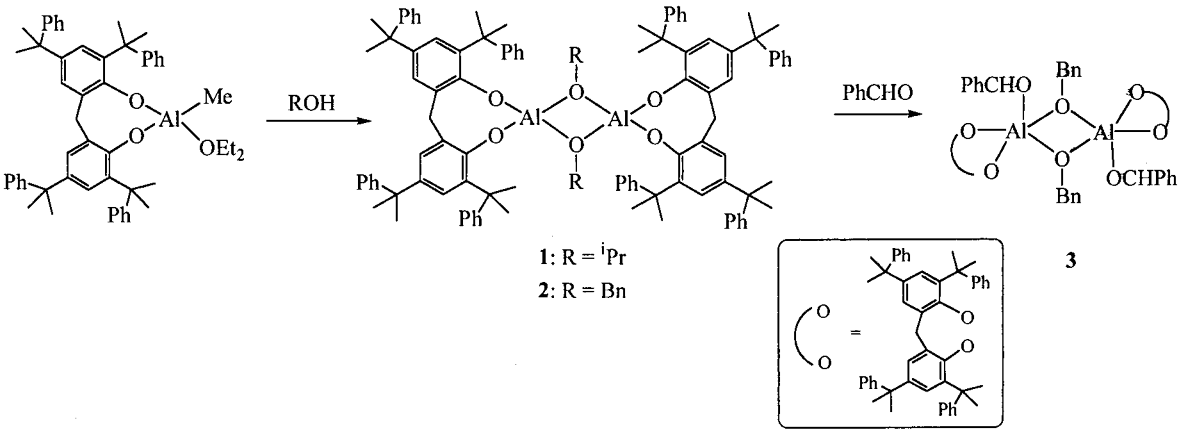
Scheme 1



Scheme 2



phenol (MMPEP-H_2) with 1 molar equiv of Me_3Al in toluene gives $[(\mu\text{-MMPEP})AlMe]_2$,[8] which further reacts with 2 molar equiv of 2-propanol or benzyl alcohol at ambient temperature, followed by the crystallization from toluene, affording a four-coordinated aluminum complex, $[(MMPEP)Al(\mu\text{-OR})]_2$ (**1**, R = ^{i}Pr; **2**, R = Bn[8]) in high yield, whereas the reaction of **2** with 2 molar equiv of benzaldehyde yields the pentacoordinated complex $[(MMPEP)Al(\mu\text{-OBn})(O{=}CHPh)]_2$ (**3**), as shown in Scheme 2. Compound **3** can also be prepared from the reaction of **1** with 4 molar equiv of benzaldehyde. ^{1}H NMR spectra and microanalyses of complexes **1** and **3** are consistent with our expectation. The observation of two singlet peaks for both $-C(CH_3)_2Ph$ groups in the NMR spectra of these complexes suggests that these two aryl moieties are chemically equivalent and that requires a σ plane of symmetry passing through the methine carbon bridging the two phenyl rings and the aluminum atom, similar to other aluminum biphenoxide systems.[7,9] This is further verified by the crystal structures of **1** and **3**.

Crystal Structures of 1 and 3. The molecular structures of **1** and **3** are shown in Figures 1 and 2, respectively. Selected bond lengths and bond angles of **1** and **3** are listed in Tables 1 and 2, respectively. The structure of **1** shows a dimeric feature containing an Al_2O_2 core bridging through the oxygen atom of the isopropoxy group, and the immediate geometry around Al is distorted tetrahedral. The bridging oxygen atom bond distances are roughly equivalent to the two Al centers, with the Al−O(3) distance of 1.806(2) Å and Al−O(3a) distance of 1.814(2) Å. The terminal Al−O bond distances from the aryloxide ligand are Al−O(1) 1.696(2) Å and Al−O(2) 1.697(2) Å, well within the normal range previously reported for a four-coordinated aluminum compound, [(EDBP)AlX(S)].[7] The crystal structure of **3** shows a dimeric form, and the geometry around Al is a distorted trigonal bipyramidal, with the carbonyl oxygen, O(4), and one bridging benzyloxy oxygen, O(3a),

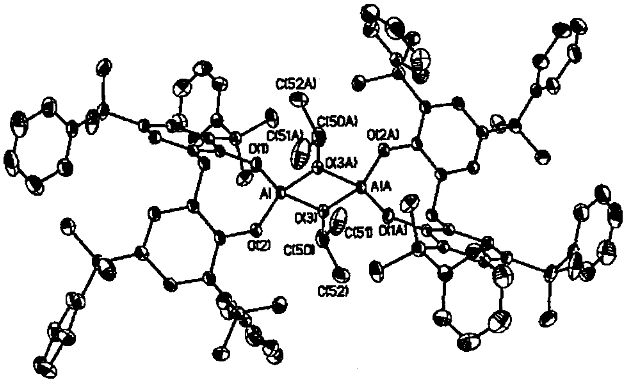


Figure 1. Molecular structure of **1** as 20% ellipsoids. Hydrogen atoms are omitted for clarity.

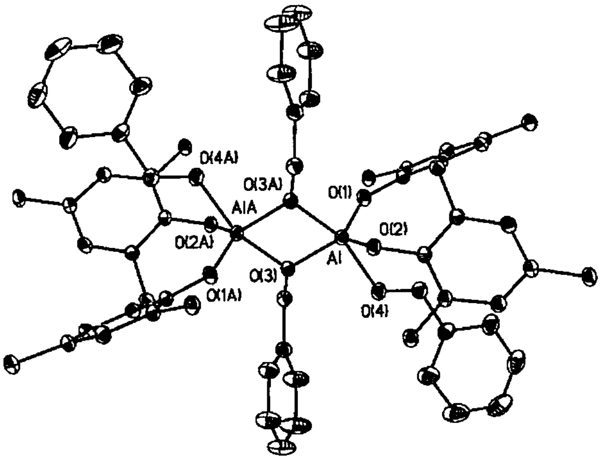


Figure 2. Molecular structure of **3** as 20% ellipsoids. Carbon atoms and phenyl rings of the MMPEP^{2-} groups and hydrogen atoms are omitted for clarity.

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Table 1. Bond Lengths (Å) and Angles (deg) for 1

Al−O(1)	1.6955(16)	Al−O(2)	1.6970(16)
Al−O(3)	1.8062(16)	Al−O(3a)	1.8136(16)
Al−Al#1	2.7460(12)	O(3)−Al(a)	1.8136(16)
O(1)−Al−O(2)	118.43(8)	O(1)−Al−O(3)	109.75(8)
O(2)−Al−O(3)	108.43(8)	O(1)−Al−O(3a)	116.07(8)
O(2)−Al−O(3a)	115.97(8)	O(3)−Al−O(3a)	81.31(8)
C(50)−O(3)−Al	124.46(14)	C(50)−O(3)−Al(a)	136.68(15)
Al−O(3)−Al(a)	98.69(8)		

Table 2. Bond Lengths (Å) and Angles (deg) for 3

Al−O(1)	1.740(2)	Al−O(2)	1.760(2)
Al−O(3)	1.824(2)	Al−O(3a)	1.886(2)
Al−O(4)	2.006(2)	Al−Al(a)	2.9036(17)
O(3)−Al(a)	1.886(2)		
O(1)−Al−O(2)	119.65(11)	O(1)−Al−O(3)	114.74(10)
O(2)−Al−O(3)	125.56(10)	O(1)−Al−O(3a)	101.73(10)
O(2)−Al−O(3a)	93.98(9)	O(3)−Al−O(3a)	77.01(10)
O(1)−Al−O(4)	92.79(10)	O(2)−Al−O(4)	87.92(9)
O(3)−Al−O(4)	87.31(9)	O(3a)−Al−O(4)	161.99(10)
Al−O(3)−Al(a)	102.99(10)		

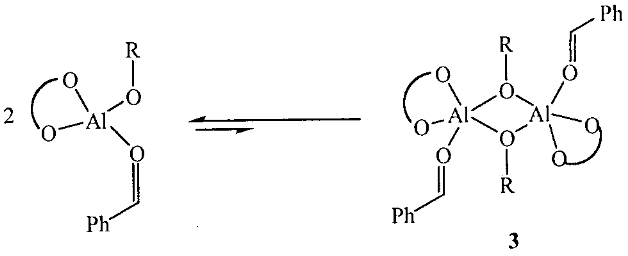
Table 3. MPV Reductions of Aldehydes and Ketones with 2−Propanol in Refluxed Toluene Catalyzed by 1

entry	substrate	[Al]:[Sub]:[IPA]	t (h)	conv (%)
1	benzaldehyde	1:10:20	0.25	99
2	2-methoxybenzaldehyde	1:10:20	0.25	100
3	4-nitrobenzaldehyde	1:10:20	0.25	99
4	4-chlorobenzaldehyde	1:10:20	0.25	100
5	4-methoxybenzaldehyde	1:10:20	0.25	75
6	cinnamaldehyde	1:10:20	0.25	53
7	2-bromoacetophenone	1:10:20	0.25	92
8	acetophenone	1:10:20	0.25	86
9	acetophenone	1:10:50	0.25	94
10	acetophenone	1:10:50	1	99
11	acetophenone	1:20:100	1	98
12	acetophenone	1:40:100	1	93

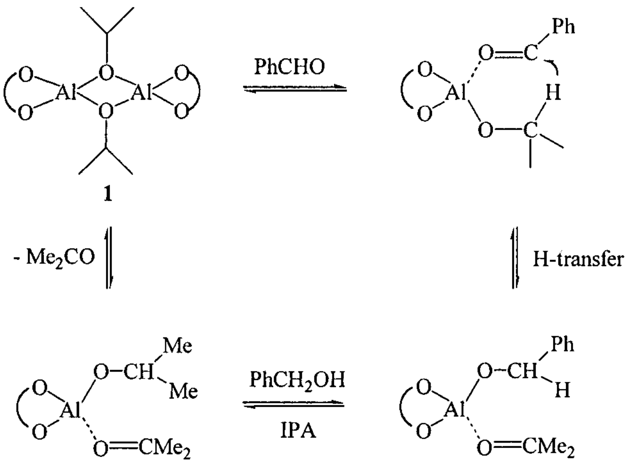
on axial positions. Two phenoxy oxygens, O(1) and O(2), and a bridging benzyloxy oxygen, O(3), are located in equatorial positions. The Al−O distances are shorter for the four-coordinated compounds **1** and **2** than the pentacoordinated compound **3**, as expected.

Catalytic MPV Reactions. The catalytic activities of **1** toward MPV hydrogen transfer reactions have been studied. In general, reduction of aldehydes in the presence of 2-propanol was carried out at 50 °C in toluene (10 mL) using 10% mole of **1** (0.05 mmol) as the initiator. Reduction of different aldehydes and ketones has been systematically conducted as shown in Table 3. Preliminary results reveal that $[(MMPEP)Al(\mu\text{-}O^iPr)]_2$ shows great catalytic activities toward aromatic aldehydes and acetophenones. Benzaldehydes and substituted benzaldehydes were reduced to give their corresponding alcohols in quantitative yield within 15 min by employing **1** as catalyst (entries 1−4). The reduction of acetophenone to 1-phenylethanol can be achieved within 1 h in the presence of a very low concentration (2.5% mole) of **1** as catalyst (entry 12). Compound **1** also catalyzes the reduction of aliphatic aldehyde (entry 6) with reduced reaction rate compare to that of aromatic aldehydes. However, the catalytic activity of **1** is much faster than other aluminum alkoxide systems.[10] It is also worthwhile to note that the drawback of aldol condensation, which is usually found in MPV reactions, is not observed in our system.[11]

Scheme 3



Scheme 4



The observation of the pentacoordinated compound **3** suggests that during the catalytic MPV reductions of aldehydes by **1** a five-coordinated intermediate may be formed, as found in the catalysis of **A**.[7] However, **A** is not active at all toward ketones, and the catalytic rate of **1** is much faster than that of **A**. Therefore, we speculate that in the catalytic MPV reduction by compound **1** a four-coordinated intermediate may be formed due to **1** that is much more sterically hindered than **A**. Unfortunately compounds **1** and **3** have low solubility in common organic solvents, which prevented us from obtaining good ^{27}Al NMR spectra suitable for this kind of study. To overcome this, a melting point depressing experiment was carried out. Compound **3** dissociated into two species in naphthalene used as solvent in this experiment. In addition to that, ^{1}H NMR spectra of **3** show only one set of peaks in the temperature range −90 to 60 °C and no uncoordinated benzaldehyde was observed. On the basis of these observations, we conclude that in solution compound **3** exists as an equilibrium between monomer and dimer (Scheme 3). Thereby, the catalytic MPV reduction of aldehydes and ketones by **1** is through a four-coordinated intermediate as shown in Scheme 4.

In conclusion, we have prepared a novel aluminum complex, $[(MMPEP)Al(\mu\text{-}O^iPr)]_2$, which has shown great catalytic activities toward MPV reduction of aldehydes and ketones. The catalytic activity of **1** is better than other aluminum alkoxides and can be used in a catalytic amount as low as 2.5% mole of substrate. Further study of MPV reduction using a chiral alcohol as hydride source is being undertaken.

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Experimental Section

General Procedures. All manipulations were carried out under a dry nitrogen atmosphere. Solvents, benzaldehyde, 2-propanol, and deuterated solvents were purified before use. Me_3Al (2.0 M in toluene), formaldehyde, 2,4-bis(α,α-dimethylbenzyl)phenol, and benzenesulfonic acid were purchased and used without further purification. [(MMPEP)Al(CH_3)(Et_2O)] and [(MMPEP)Al(μ-OBn)]$_2$ were prepared according to the literature method.[8] ^1H and ^{13}C NMR spectra were recorded on a Varian Mercury-400 (400 MHz) or a Varian Gemini-200 (200 MHz) spectrometer with chemical shifts given in ppm from the internal TMS. Microanalyses were performed using a Heraeus CHN-O-RAPID instrument. Infrared spectra were obtained from a Bruker Equinox 55 spectrometer. The GPC measurements were performed on a Hitachi L-7100 system equipped with a differential Bischoff 8120 RI detector using THF (HPLC grade) as an eluent. Molecular weights and molecular weight distributions were calculated using polystyrene as standard. Melting point depression was measured by using naphthalene as standard with a Beckman apparatus.

[(MMPEP)Al(μ-O^{i}Pr)]$_2$ (1). To a rapidly stirring solution of [(MMPEP)Al(CH_3)(Et_2O)] (1.57 g, 2 mmol) in toluene (30 mL) was added 2-propanol (0.153 mL, 2.0 mmol), and the reaction mixture was stirred at 25 °C for 2 h. The volatile materials were removed under vacuum, and the residue was redissolved in hot toluene (30 mL). The extract was then concentrated to ca. 10 mL and was allowed to cool to −20 °C, affording colorless crystalline solids after 2 days. Yield: 1.35 g (86%). Anal. Calcd for $C_{108}H_{124}Al_2O_6$: C, 82.51; H, 7.95. Found: C, 82.61; H, 7.52. ^1H NMR ($CDCl_3$, ppm): δ 7.32−6.96 (m, 24H, Ph); 3.54 (d, 1H, CH_2, J_{H-H} = 14.4 Hz); 3.48 (d, 1H, CH_2, J_{H-H} = 14.4 Hz); 3.18 (m, 1H, $CH(CH_3)_2$, J_{H-H} = 6.4 Hz); 1.80 (s, 6H, CH_3), 1.57 (s, 12H, CH_3), 1.52 (s, 6H, CH_3); 0.65 (d, 6H, $CH(CH_3)_2$, J_{H-H} = 6.4 Hz). ^{13}C NMR ($CDCl_3$, ppm): δ 151.37, 151.22, 151.06, 140.24, 135.93, 128.79, 127.81, 126.69, 126.30, 125.80 (Ph); 71.30 ($CH(CH_3)_2$); 43.24, 42.22 ($PhC(CH_3)_2$); 33.38 (CH_2); 30.98 ($CH(CH_3)_2$); 28.26, 24.26 ($PhC(CH_3)_2$). IR (KBr, cm^{-1}): 1443 (s), 1415 (s), 1382 (s), 1263 (m), 1231 (m), 1202 (m), 1097 (m), 1075 (m), 1029 (m), 928 (m), 766 (m), 700 (s). Mp = 215−217 °C.

[(MMPEP)Al(μ-OBn)(O═CHPh)]$_2$ (3). To a rapidly stirring solution of [(MMPEP)Al(μ-OBn)]$_2$ (1.60 g, 1.0 mmol) in toluene (20 mL) was added benzaldehyde (0.20 mL, 2.0 mmol), and the reaction mixture was stirred at 25 °C for 2 h. The volatile materials were removed under vacuum, and the residue was redissolved in hot toluene (30 mL). The extraction was then concentrated to ca. 10 mL and was allowed to cool to −20 °C, affording colorless crystalline solids after 2 days. Yield: 1.26 g (69%). Anal. Calcd for $C_{63}H_{63}AlO_4$: C, 83.05; H, 6.97. Found: C, 83.24; H, 6.70. ^1H NMR ($CDCl_3$, ppm): δ 9.91 (s, 1H, PhCHO), 7.86−6.66 (m, 34H, Ph); 3.56 (s, 2H, OCH_2); 2.45 (d, 1H, CH_2, J_{H-H} = 15.2 Hz); 2.24 (d, 1H, CH_2, J_{H-H} = 15.2 Hz); 1.81 (s, 6H, CH_3), 1.55 (s, 12H, CH_3), 1.46 (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$, ppm): δ 193.47 (C═O); 151.72, 151.64, 151.30, 139.79, 137.63, 136.08, 135.31, 130.56, 129.84, 129.01, 128.94, 128.21, 127.93, 127.75, 127.70, 127.04, 126.69, 126.57, 125.93, 125.56, 125.21, 124.81 (Ph); 66.32 (OCH_2); 43.22, 42.10 ($PhC(CH_3)_2$). 32.90, 32.77, 30.87, 30.70 ($PhC(CH_3)_2$); 28.13 (CH_2). IR (KBr, cm^{-1}): 3509 (m), 3082 (m), 3056 (m), 2966 (s), 2870 (m), 1599 (m), 1487 (s), 1443 (s), 1416 (m), 1382 (m), 1361 (m), 1325 (m), 1286 (m), 1263 (m), 1230 (m), 1202 (m), 1145 (m), 1098 (s), 1075 (m), 924 (m), 878 (m), 797 (m), 766 (s), 733 (m), 700 (s), 671 (m), 617 (m), 574 (m). Mp = 142−144 °C.

Typical Experimental Procedure for MPV Reduction of Aldehydes. To a solution of **1** (0.157 mg, 0.1 mmol) in toluene (10 mL) was added benzaldehyde (0.2 mL, 2.0 mmol), followed by the addition of 2-propanol (0.306 mL, 4.0 mmol). The reaction mixture was then refluxed for 15 min, and the conversion yield was determined by ^1H NMR spectroscopic studies based on the integration in the methylene and the CHO region of the benzyl group.

Table 4. Crystallographic Data for 1 and 3

	1	**3**
chemical formula	$C_{63}H_{65}AlO_3.0.5C_7H_8$	$C_{63}H_{63}AlO_4$
M	936.69	911.11
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2(1)/n$
a/Å	14.1975(12)	10.9730(17)
b/Å	14.4624(12)	18.010(3)
c/Å	16.8416(14)	25.878(4)
α/deg	101.694(2)	90
β/deg	103.034(2)	98.512(3)
γ/deg	117.633(2)	90
V/Å^3	2789.1(4)	5057.9(14)
Z	2	4
μ(Mo Kα)/mm^{-1}	0.081	0.089
N_{ref}(obs) ($F > 4\sigma(F)$)	5986	4510
no. of params	649	613
R1[a]	0.0577	0.0617
wR2[b]	0.1854	0.1485
GoF[c]	0.996	0.899
min., max. residual density/e Å^{-3}	−0.303, 0.210	−0.326, 0.298

[a] $R1 = |\sum(|F_o| - |F_c|)/|\sum|F_o||$. [b] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2/\sum[w(F_o^2)^2]]^{1/2}$; $w = 0.10$. [c] $GoF = [\sum w(F_o^2 - F_c^2)^2/(N_{rflns} - N_{params})]^{1/2}$.

Melting Point Depression Measurement. [(MMPEP)Al(μ-OBn)(PhCHO)]$_2$ (5.68 g) was dissolved in a hot naphthalene (32.59 g). The freezing point of the mixture was measured by slowly cooling the mixture, and the temperature was recorded once every 30 s. This procedure was repeated three times.

X-ray Crystallographic Studies. Suitable crystals of **1** and **3** were sealed in thin-walled glass capillaries under a nitrogen atmosphere and mounted on a Bruker AXS SMART 1000 diffractometer. Intensity data were collected in 1350 frams with increasing ω (width of 0.3° per frame). Unit cell dimensions were determined by a least-squares fit of 4219 reflections for **1** and 3770 reflections for **3**. The absorption correction was based on the symmetry equivalent reflections using the SADABS program. The space group determination was based on a check of the Laue symmetry and systematic absences and was confirmed using the structure solution. The structure was solved by direct methods using a Siemens SHELXTL PLUS package. All non-H atoms were located from successive Fourier maps, and hydrogen atoms were refined using a riding model. Anisotropic thermal parameters were used for all non-H atoms, and fixed isotropic parameters were used for H atoms. Crystallographic data for **1** and **3** are shown in Table 4.

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Supporting Information Available: For **1** and **3**, tables providing full details of the crystal data are available. These materials are available free of charge via the Internet at http://pubs.acs.org.

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