1864 *Organometallics* **2000,** *19,* 1864−1869

Preparation, Characterization, and Reactions of $[(EDBP)Al(\mu\text{-}O^iPr)]_2$, a Novel Catalyst for MPV Hydrogen Transfer Reactions

Bao-Tsan Ko, Chen-Chang Wu, and Chu-Chieh Lin*

Department of Chemistry, National Chung-Hsing University, Taichung 402, Taiwan, Republic of China

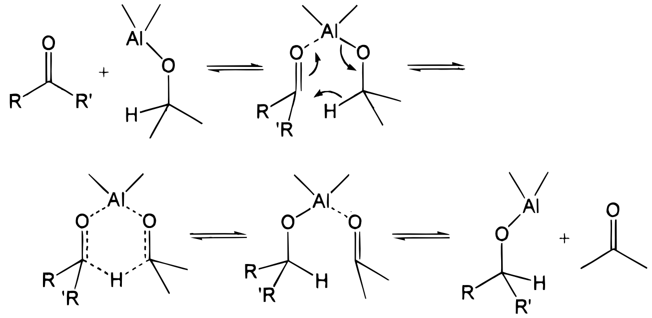
Received December 7, 1999

The reaction of $[(\mu\text{-}EDBP)AlMe]_2$ ($EDBP\text{-}H_2$ = 2,2′-ethylidenebis(4,6-di-*tert*-butylphenol) with 2 mol equiv of 2-propanol at ambient temperature yields $[(EDBP)Al(\mu\text{-}O^iPr)]_2$ (**1**), which has shown excellent catalytic activities toward hydrogen transfer reactions between aldehydes and 2-propanol (Meerwein−Ponndorf−Verley (MPV) reactions). The addition of 4 mol equiv of benzaldehyde, 4-methoxybenzaldehyde, or 4-chlorobenzaldehyde to $[(EDBP)Al(\mu\text{-}O^iPr)]_2$ yields $[(EDBP)Al(\mu\text{-}OBz\text{-}p\text{-}X)(O{=}CHC_6H_4\text{-}p\text{-}X)]_2$ (**2**, X = H; **3,** X = OMe; **4**, X = Cl). However, in the reaction of **1** with excess 4-nitrobenzaldehyde, only the four-coordinated complex $[(EDBP)Al(\mu\text{-}OBz\text{-}p\text{-}NO_2)]_2$ (**5**) was obtained. Complex **1** further reacts with 2 mol equiv of $OPPh_3$ or hexamethylphosphoramide (HMPA), yielding the four-coordinated monomeric complex $[(EDBP)Al(O^iPr)(S)]$ (**6**, S = $OPPh_3$; **7**, S = HMPA). Compounds **1**, **3**, **6,** and **7** have been characterized by X-ray crystal structure determinations, enabling us to describe the intermediate of the MPV reactions.

Introduction

Although aldehydes and ketones can be reduced to alcohols by a variety of reagents,[1] Meerwein−Ponndorf−Verley (MPV) reductions of aldehydes and ketones are still interesting, as they are highly selective and can be performed under mild conditions. In general, the reductants in MPV reactions are simple organic molecules, such as 2-propanol, and these reductions employ an aluminum alkoxide[2] or a transition-metal complex as a catalyst.[3] Since the discovery of MPV reactions, many aluminum alkoxides have been used,[2] and their reaction mechanisms have been studied. The generally accepted mechanism for MPV reactions proceeds via a complex in which both the carbonyl compound and the reducing alcohol are bound to the metal ion as shown in Scheme 1. 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.[4] But interestingly, none of the intermediates for MPV reactions have ever been isolated and thoroughly characterized. Therefore, the crystal structure determination of an MPV reaction intermediate as well as the catalyst will be of immense help in understanding the MPV reactions and thereby modifying the catalytic activity. Our recent interest has been the preparation and use of some novel aluminum derivatives as Lewis acids for the catalysis of various reactions such as Diels−Alder reactions,[5] ring-opening polymerizations (ROP) of lactones,[6] and MPV reactions. We report herein the synthesis, characterization, and catalytic studies of a novel aluminum alkoxide. Preliminary results show that this complex efficiently catalyzes the reduction of different aldehydes in the presence of 2-propanol.

Scheme 1



Results and Discussion

Synthesis. The reaction of $[(\mu\text{-}EDBP)AlMe]_2$[7] ($EDBP\text{-}H_2$ = 2,2′-ethylidenebis(4,6-di-*tert*-butylphenol)) with 2

---

(1) (a) Brown, W. G. *Organic Reactions*; Roger, A., Ed.; Wiley: New York, 1951; Vol. 6, p 469. (b) Hajos, A. *Complex Hydrides & Related Reducing Agents in Organic Synthesis*; Elsevier: New York, 1979. (c) Subha Rao, Y. V.; Choudary, B. M. *Synth. Commun.* **1992**, *22*, 2711. (d) Hudlicky, M. *Reductions in Organic Synthesis*; Ellis Horwood: Chichester, U.K., 1984. (e) Hutchins, R. O.; Kandasamy, D. *J. Am. Chem. Soc.* **1973**, *95*, 6131.

(2) (a) Ooi, T.; Takahashi, M.; Maruoka, K. *J. Am. Chem. Soc.* **1996**, *118*, 11307. (b) Akamanchi, K. G.; Noorani, V. R. *Tetrahedron Lett.* **1995**, *36*, 5085. (c) Konishi, K.; Makita, K.; Aida, T.; Inoue, S. *J. Chem. Soc., Chem. Commun.* **1988**, 643. (d) Namy, J. L.; Scouppe, J.; Collin, J.; Kagon, H. B. *J. Org. Chem.* **1984**, *49*, 2045.

(3) (a) Evans, D. A.; Nelson, S. G.; Gagñe, M. R.; Muci, A. R. *J. Am. Chem. Soc.* **1993**, *115*, 9800. (b) Noyori, R.; Hashiguchi, S. *Acc. Chem. Res.* **1997**, *30*, 97. (c) Chowdhury, R. L.; Backvall, J.-E. *J. Chem. Soc., Chem Commun.* **1991**, 1063. (d) Krasik, P.; Alper, H. *Tetrahedron* **1994**, *50*, 4347.

(4) (a) Moulton, W. N.; van Atta, R. E.; Ruch, R. R. *J. Org. Chem.* **1960**, *26*, 290. (b) Ashby, E. C. *Acc. Chem. Res.* **1988**, *21*, 414.

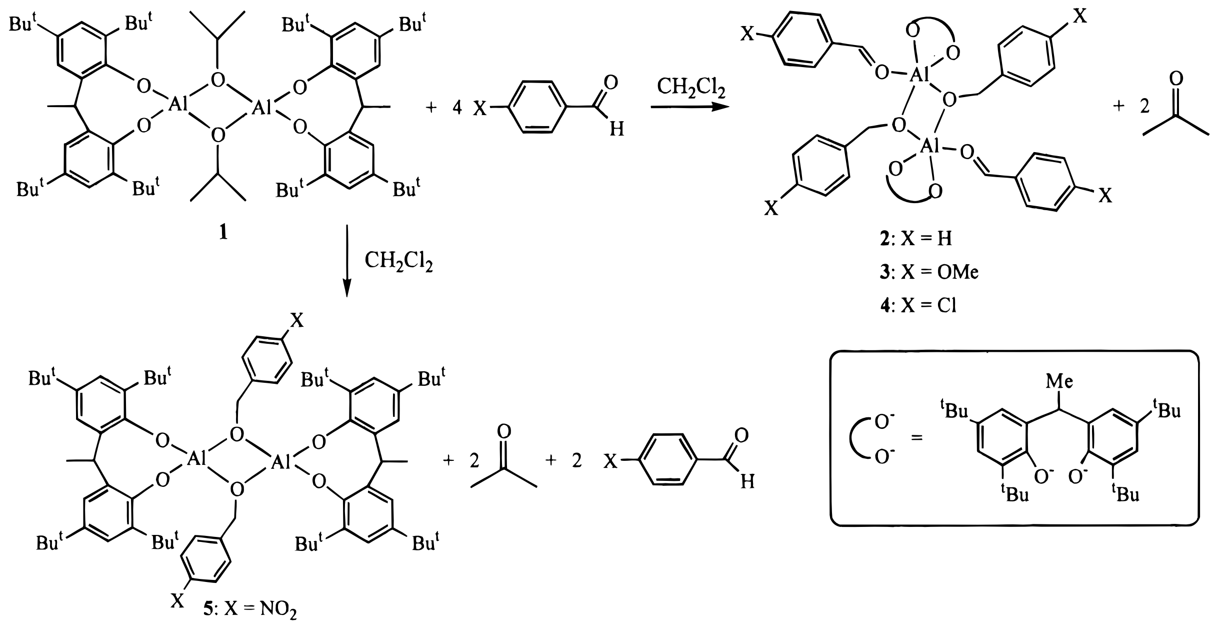
(5) (a) Lin, C. H.; Yan, L. F.; Wang, F. C.; Sun, Y. L.; Lin, C. C. *J. Organomet. Chem.* **1999**, 587, 151. (b) Ko, B. T.; Lee, M. D.; Lin, C. C. *J. Chin. Chem. Soc.* **1997**, *44*, 163.

(6) Ko, B. T.; Lin, C. C. *Macromolecules* **1999**, *32*, 8296.

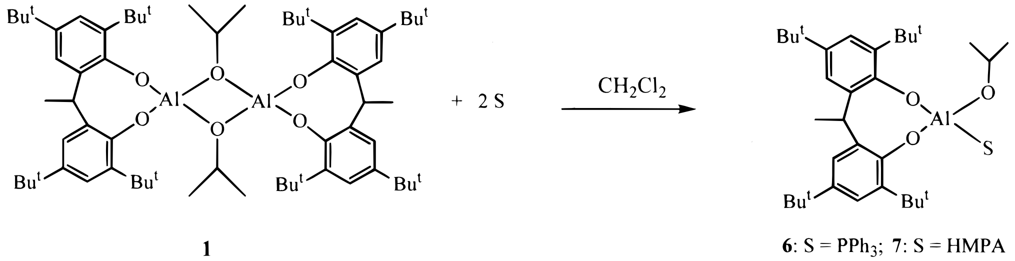
(7) Ko, B. T.; Chao, Y. C.; Lin, C. C. *Inorg. Chem.*, in press.

10.1021/om9909690 CCC: $19.00

Scheme 2



Scheme 3



mol equiv of 2-propanol at ambient temperature, followed by crystallization from toluene, affords the catalyst $[(EDBP)Al(\mu\text{-}O^iPr)]_2$ (**1**) in high yield. The reaction of 4 mol equiv of benzaldehyde, 4-methoxybenzaldehyde, or 4-chlorobenzaldehyde with $[(EDBP)Al(\mu\text{-}O^iPr)]_2$ yields the pentacoordinated complex $[(EDBP)Al(\mu\text{-}OBz\text{-}p\text{-}X)(O{=}CHC_6H_4\text{-}p\text{-}X)]_2$ (**2**, X = H; **3**, X = OMe; **4**, X = Cl), as shown in Scheme 2. The compound **2** can also be prepared in high yield from the reaction of $[(\mu\text{-}EDBP)AlMe]_2$ with 2 mol equiv of benzyl alcohol in the presence of 2 mol equiv of benzaldehyde or from the reaction of $[(EDBP)Al(\mu\text{-}OBz)]_2$ with 2 mol equiv of benzaldehyde.[6] However, unlike other benzaldehydes, in the reaction of **2** with 4 equiv of 4-nitrobenzaldehyde, only the four-coordinated complex $[(EDBP)Al(\mu\text{-}OBz\text{-}p\text{-}NO_2)]_2$ (**5**) was isolated. The isolation of the four-coordinated complex **5** instead of a pentacoordinated complex indicates that the strongly electron withdrawing $-NO_2$ group decreases its basicity of 4-nitrobenzaldehyde, thereby retarding further coordination.

In contrast to complexes **2**−**5**, the reaction of **1** with 2 mol equiv of triphenylphosphine oxide or HMPA yields the four-coordinated monomeric compound $[Al(EDBP)(O^iPr)(OPPh_3)]$ (**6**) or $[Al(EDBP)(O^iPr)(HMPA)]$ (**7**) (Scheme 3). The Al−O (bridging alkoxide) bond of the Al_2O_2 core is broken by the presence of $OPPh_3$ or HMPA. ^1H NMR spectra and microanalyses of complexes **1**−**7** are consistent with our expectations. The observation of two singlet peaks for both *tert*-butyl groups in the NMR spectra of these complexes suggests that these two aryl moieties are chemically equivalent, which requires a σ plane of symmetry passing through the methine carbon bridging of two phenyl rings and the aluminum atom. Similar results have been found in [(MMBP)Al(R)(S)] and [(MDBP)Al(R)(S)] systems.[5,6] This is further verified by the crystal structure studies of **1**, **3**, **6**, and **7**.

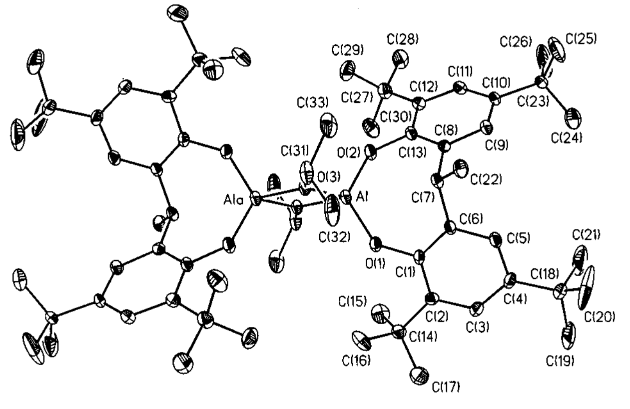


Figure 1. Molecular structure of **1** as 20% ellipsoids. All hydrogen atoms are omitted for clarity.

Molecular Structure Studies of 1, 3, 6, and 7. The molecular structures of **1** and **3** are shown in Figure 1 and Figure 2, respectively. Selected bond lengths and bond angles of **1**−**3** and **a** are given in Table 1. The structure of **1** shows a dimeric feature containing an Al_2O_2 core bridging through the oxygen atom of the

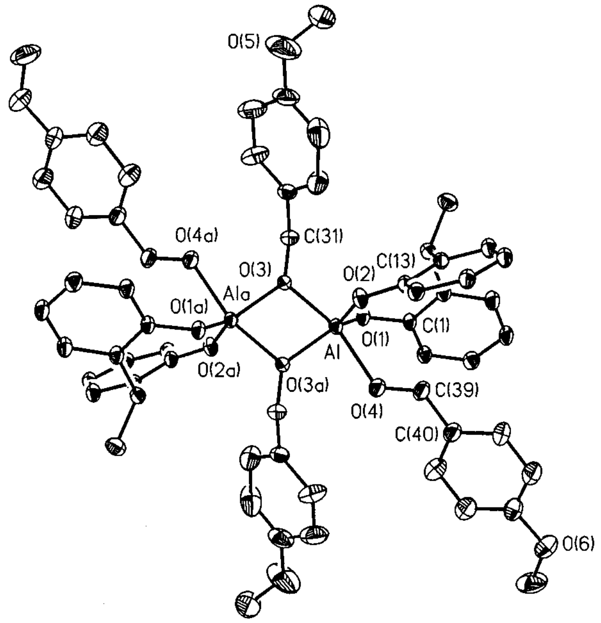


Figure 2. Molecular structure of **3** as 30% ellipsoids. All hydrogen atoms and carbon atoms of the *tert*-butyl groups are omitted for clarity.

Table 1. Comparison of Selected Bond Distances and Bond Angles for [(EDBP)Al(μ-O^{i}Pr)$_2$] (1), [(EDBP)Al(μ-OBz)$_2$] (a),[6] [(EDBP)Al(μ-OBz)(OCHPh)]$_2$ (2),[6] and [(EDBP)Al(μ-OBz)(O=CHC$_6$H$_4$-*p*-OMe)]$_2$ (3)

	1	a	2	3
Al−O(1)	1.693(3)	1.689(2)	1.753(4)	1.765(2)
Al−O(2)	1.694(3)	1.683(2)	1.745(6)	1.742(2)
Al−O(3)	1.813(3)	1.812(2)	1.809(3)	1.816(2)
Al−O(3a)	1.816 (3)	1.816(2)	1.900(3)	1.906(2)
Al−O(4)			2.030(3)	2.017(2)
O(1)−C(1)	1.378(5)	1.379(4)	1.352(5)	1.367(3)
O(2)−C(13)	1.380(4)	1.368(3)	1.358(8)	1.358(3)
O(3)−C(31)	1.462(5)	1.452(4)	1.442(5)	1.444(3)
O(4)−C(39)			1.241(8)	1.239(3)
O(4)−C(39)−C(40)			125.0(5)	125.3(3)

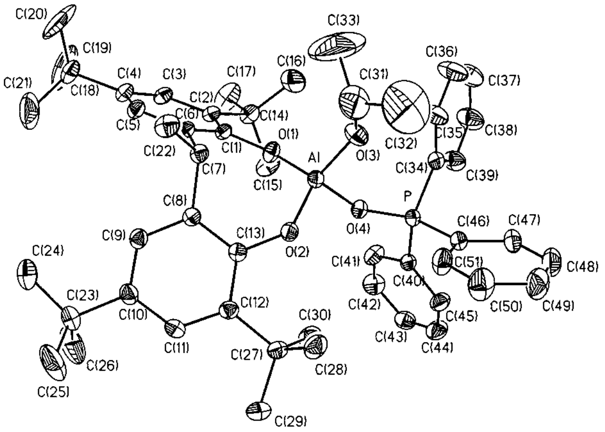


Figure 3. Molecular structure of **6** as 20% ellipsoids. All hydrogen atoms are omitted for clarity.

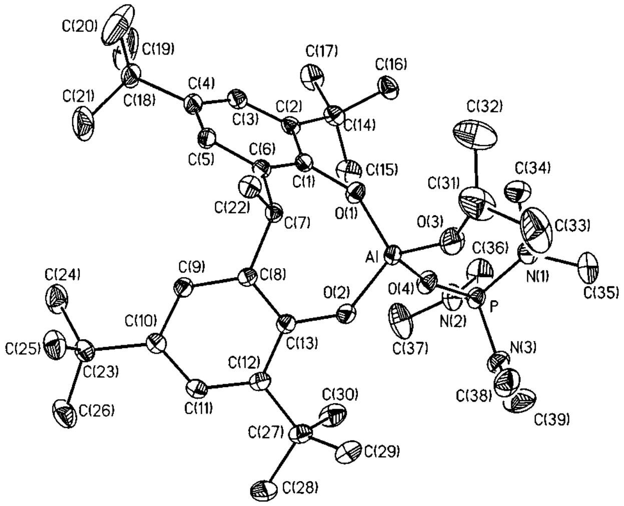


Figure 4. Molecular structure of **7** as 20% ellipsoids. All hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Distances and Bond Angles for [(EDBP)Al(O^{i}Pr)(OPPh$_3$)] (6) and [(EDBP)Al(O^{i}Pr)(HMPA)] (7)

	6	7
Al−O(1)	1.709(2)	1.726(2)
Al−O(2)	1.739(2)	1.733(2)
Al−O(3)	1.701(2)	1.684(2)
Al−O(4)	1.794(2)	1.790(2)
P−O(4)	1.512(2)	1.502(2)
O(1)−C(1)	1.354(3)	1.342(3)
O(2)−C(13)	1.359(3)	1.343(3)
O(3)−C(31)	1.388(5)	1.305(5)
Al−O(4)−P	150.6(1)	155.2(1)
Al−O(3)−C(31)	136.4(3)	146.4(3)

isopropoxide group, and the geometry around Al is distorted from tetrahedral. The bridging oxygen atom bond distances are roughly equivalent to the two Al centers with an Al−O(3) distance of 1.813(3) Å and Al−O(3a) distance of 1.816(3) Å. The terminal Al−O bond distances from the aryloxide ligand are Al−O(1) = 1.693(3) Å and Al−O(2) = 1.694(3) Å, well within the normal range previously reported for a four-coordinated aluminum compound, [(EDBP)AlX(S)].[7] The X-ray structure analysis of **3** reveals a dimeric form, and the geometry around Al is a distorted trigonal bipyramid, with the carbonyl oxygen O(4) and one bridging benzyloxy oxygen O(3) on axial positions and the two phenoxy oxygens O(1) and O(2) and the bridging benzyloxy oxygen O(3a) on the equatorial positions. As may be seen from the comparison in Table 1, the Al−O distances are shorter for the four-coordinated compounds **1** and **a** than for the pentacoordinated compounds **2** and **3**, as expected. However, there is little effect in the Al−O distance of the methoxy group on the phenyl ring. The electronegativity of the oxygen of the methoxy substituent on the para position to the carbonyl group in the phenyl ring has no effect on the aluminum−oxygen bond, as indicated by the almost identical bond lengths in the isostructural complexes **2** and **3**.

The molecular structures of **6** and **7** are shown in Figure 3 and Figure 4, respectively. Selected bond lengths and bond angles of **6** and **7** are given in Table 2. Compound **6** crystallizes in the space group $P2_1/n$, and the geometry around Al is a distorted tetrahedron with the bond distances of Al−O(1) (phenoxy) at 1.709(2) Å, Al−O(2) (phenoxy) at 1.739(2) Å, Al−O(3) (isopropoxy) at 1.701(2) Å, and Al−O(4) (OPPh$_3$) at 1.794(2) Å, which are all compatible with the bond lengths observed for four-coordinated aluminum derivatives of steric bulky phenoxides. Compound **7,** which differs

Table 3. Catalytic MPV Reduction of Aldehydes with 2-Propanol in the Presence of 1 (10 mol %)

entry	substrate	hydride source (amt, equiv)	time (h)	conversn yield (%)
1	PhCHO	^{i}PrOH (2)	1	64
2	PhCHO	^{i}PrOH (2)	9	85
3	PhCHO	^{i}PrOH (2)	24	93
4	PhCHO	^{i}PrOH (1)	24	85
5	4-MeO-C_6H_4CHO	^{i}PrOH (2)	1	25
6	4-MeO-C_6H_4CHO	^{i}PrOH (2)	9	53
7	4-MeO-C_6H_4CHO	^{i}PrOH (2)	24	60
8	4-Cl-C_6H_4CHO	^{i}PrOH (2)	1	99
9	4-NO_2-C_6H_4CHO	^{i}PrOH (2)	0.5	99

from compound **6** by replacing the $OPPh_3$ with HMPA, crystallizes in the space group $P2_12_12_1$. The geometry around Al is nearly identical with that for **6**, with the bond distances of Al−O(1) (phenoxy) at 1.726(2) Å, Al−O(2) (phenoxy) at 1.733(2) Å, Al−O(3) (isopropoxy) at 1.684(2) Å, and Al−O(4) (HMPA) at 1.790(2) Å, similar to the values for compound **6**.

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 25 °C in $CDCl_3$ (1.2 mL) using 10 mol % of **1** (0.05 mmol) as the initiator. Reduction of different aldehydes has been systematically conducted as shown in Table 3. Preliminary results reveal that [(EDBP)Al(μ-O^{i}Pr)]$_2$ shows great catalytic activities toward 4-nitrobenzaldehyde and 4-chlorobenzaldehyde. These two aldehydes were reduced to give their corresponding alcohols in quantitative yield at room temperature within 1 h by employing **1** as catalyst (entries 8 and 9). Compound **1** can also catalyze the reduction of benzaldehyde (entries 1−4) and 4-methoxybenzaldehyde (entries 5−7), with reduced reaction rates compared to those of 4-nitrobenzaldehyde and 4-chlorobenzaldehyde. The enhanced reaction rate is probably due to the increasing positive charge of the carbonyl carbon atom caused by the electron-withdrawing group on the para position.[8] The catalytic activity of **2** is compatible with the trifluoroacetic acid/aluminum isopropoxide system reported by Akamanchi[9] but is better than other aluminum alkoxide systems. In addition, the drawback of aldol condensation, which is usually found in MPV reactions, is not observed in our system.[10]

The structural determination of the pentacoordinated compound **3** suggests that, during the catalytic MPV reductions of aldehydes, an aldehyde molecule coordinates to the aluminum center to form the pentacoordinated intermediate **A**, followed by a hydride transfer from the alcoholate to the carbonyl group via a six-membered transition state to give the bridging ketone **B**, as depicted in Scheme 4. Double coordination of carbonyl groups with two metals has been observed on several occasions.[11] Because acetone is a much weaker base than a bridging alkoxide, **B** isomerizes rapidly, forming the alkoxy-bridged intermediate **C,** which then loses acetone to give the four-coordinated intermediate **D**, as observed in **5**. In the presence of excess aldehyde, **D** readily reacts with aldehyde, yielding the pentacoordinated complexes **2**−**4**. **D** can also exchange slowly with 2-propanol to regenerate the catalyst **1**, thereby restarting the reaction cycle. We believe that during the catalysis the bridging alkoxide skeleton remains unchanged, because the Al−O (bridging alkoxide) bond of the Al_2O_2 core can only be broken by a very strong Lewis base such as HMPA or triphenylphosphine oxide.

In conclusion, a new catalyst, [(EDBP)Al(μ-O^{i}Pr)]$_2$, for the reduction of aldehydes has been synthesized and this catalyst has demonstrated excellent activities toward the reduction of aldehydes. Its catalytic activity is better than those of other aluminum alkoxides and can be used in catalytic amounts. The crystal structure studies of [(EDBP)Al(μ-OBz-*p*-X)(O=CHC$_6$H$_4$-*p*-X)]$_2$ (X = H, OMe) have enabled us to describe the intermediate of the MPV reactions. The isolation of [(EDBP)Al(μ-OBz-*p*-NO$_2$)]$_2$ also offers useful information toward an understanding of these reactions. Further studies of this catalyst in the reduction of ketones are currently underway.

Experimental Section

General Considerations. All experiments were carried out under a dry nitrogen atmosphere. Solvents were dried by refluxing at least for 24 h over sodium/benzophenone (toluene, hexane), phosphorus pentaoxide (CH_2Cl_2), or magnesium (2-propanol) and freshly distilled prior to use. Deuterated solvents were dried over molecular sieves. 2,2′-Ethylidenebis(4,6-di-*tert*-butylphenol), 4-nitrobenzaldehyde, 4-chlorobenzaldehyde, 4-methoxybenzaldehyde, and benzaldehyde were dried prior to use. $AlMe_3$ (2.0 M in toluene) was purchased and used without further treatment. Melting points were determined with a Buchi 535 digital melting point apparatus. ^{1}H and ^{13}C NMR spectra were recorded on a Varian VXR-300 (300 MHz) or a Mercury-400 (400 MHz) spectrometer with chemical shifts given in ppm and TMS as internal standard. Microanalyses were performed using a Heraeus CHN-O-RAPID instrument. Infrared spectra were obtained from a Bruker Equinox 55 spectrometer.

[Al(EDBP)(μ-O^{i}Pr)]$_2$ (1). To a rapidly stirred solution of [Al(μ-EDBP)Me]$_2$ (0.96 g, 1.0 mmol) in toluene (30 mL) was added 2-propanol (0.15 mL, 2.0 mmol) at 25 °C. Stirring was continued for 16 h, during which time a white precipitate was formed. The volatile materials were removed under vacuum, and the residue was redissolved in hot toluene (30 mL) and this solution cooled to room temperature, affording a colorless crystalline solid after 12 h. Yield: 0.98 g (86%). Anal. Calcd for $C_{66}H_{102}Al_2O_6$: C, 75.82; H, 9.83. Found: C, 75.20; H, 9.75. ^{1}H NMR ($CDCl_3$, ppm): δ 7.40 (d, 2H, Ph, J = 2.4 Hz); 7.16 (d, 2H, Ph, J = 2.4 Hz); 4.63 (m, 1H, OC*H*(CH$_3$)$_2$, J = 6.4 Hz); 4.26 (q, 1H, C*H*(CH$_3$), J = 6.8 Hz); 1.82 (d, 3H, CH(C*H*$_3$), J = 6.8 Hz); 1.59 (d, 6H, OCH(C*H*$_3$)$_2$, J = 6.4 Hz); 1.40 (s, 18H, C(CH$_3$)$_3$); 1.32 (s, 18H, C(CH$_3$)$_3$). ^{13}C NMR ($CDCl_3$, ppm): δ 150.58, 140.79, 136.98, 132.39, 121.72, 120.92 (Ph); 71.64 (O*C*H(CH$_3$)$_2$); 35.45, 34.47, 31.78, 30.40 (t-Bu); 33.21 (*C*H(CH$_3$)); 24.99 (OCH(*C*H$_3$)$_2$), 22.61 (CH(*C*H$_3$)). IR (KBr, cm^{-1}): 2959 (s), 2908 (s), 1476 (s), 1445 (s), 1270 (s), 1239 (m), 938 (s), 878(s). Mp: 196−198 °C dec.

[Al(EDBP)(μ-OBz)(O=CHPh)]$_2$ (2). To a rapidly stirred solution of [Al(EDBP)(μ-O^{i}Pr)]$_2$ (0.52 g, 0.50 mmol) in CH_2Cl_2 (30 mL) was added benzaldehyde (0.20 mL, 2.0 mmol) at room temperature; the mixture was stirred for a further 4 h, and

---

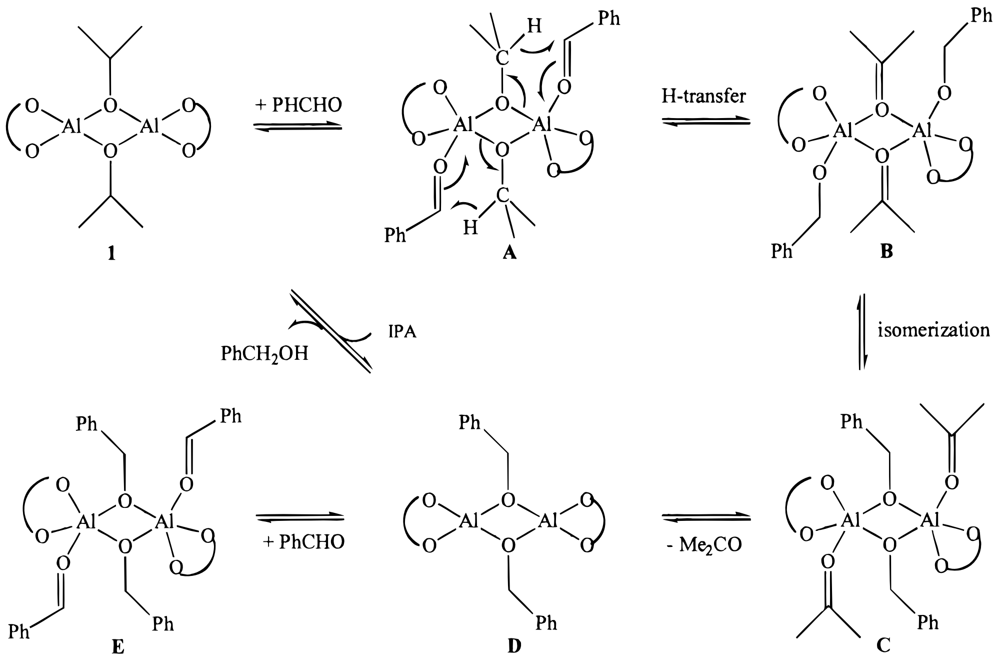
[8] Pickkart, D. E.; Hancock, C. K. *J. Am. Chem. Soc.* **1955**, *77*, 4642.

[9] Akamanchi, K. G.; Varalakshmy, N. R.; Chaudhari, B. A. *Synlett* **1997**, 371.

[10] de Graauw, C. F.; Peters, J. A.; van Bekkum, H.; Huskens, J. *Synthesis* **1994**, 1007.

[11] (a) Adams, H.; Bailey, N. A.; Gauntlett, J. T.; Winter, M. J. *J. Chem. Soc., Chem. Commun.* **1984**, 1360. (b) Rao, C. P.; Rao, A. M.; Rao, C. N. R. *Inorg. Chem.* **1984**, *23*, 2080. (c) Bachand, B. Wuest, J. D. *Organometallics* **1991**, *10*, 2015. (d) Palm, J. H.; Macgillavry, C. H. *Acta Crystallogr.* **1963**, *16*, 963.

Scheme 4



the volatile materials were removed in vacuo, giving an orange solid. The residue was washed with hexane twice and dried under vacuum. Yield: 0.54 g (79%). Anal. Calcd for $C_{88}H_{114}Al_2O_8$: C, 78.07; H, 8.49. Found: C, 77.81; H, 8.55. ^{1}H NMR ($CDCl_3$, ppm): δ 8.74 (s, 1H, PhC*H*O); 6.99−7.59 (m, 14H, Ph); 5.60 (s, 2H, OCH_2); 4.21 (q, 1H, C*H*(CH_3), *J* = 6.8 Hz); 1.36 (s, 18H, $C(CH_3)_3$); 1.24 (s, 18H, $C(CH_3)_3$); 1.04 (d, 3H, CH(C*H*$_3$), *J* = 6.8 Hz). ^{13}C NMR ($CDCl_3$, ppm): δ 195.1(C=O); 151.9, 140.2, 137.8, 137.1, 135.9, 134.6, 134.1, 130.8, 128.8, 120.3, 127.1, 125.9, 121.0, 120.9 (Ph); 67.4 (OCH_2); 35.4, 34.3, 31.8, 30.8 (t-Bu); 31.1 (*C*H(CH_3)); 22.0 (CH(*C*H$_3$)). IR (KBr, cm^{-1}): 2954 (s), 2904 (s), 1639 (s), 1476 (s), 1456 (m), 1441 (s), 1268 (m), 1238 (m), 855 m). Mp: 224−226 °C dec.

[Al(EDBP)(*μ*-OC$_6$H$_4$-*p*-OMe)(O=CHC$_6$H$_4$-*p*-OMe)]$_2$ (3). This compound was prepared according to the method described for **2** using 4-methoxybenzaldehyde (0.24 mL, 2.0 mmol). Yield: 0.59 g (80%). Anal. Calcd for $C_{92}H_{122}Al_2O_{12}$: C, 74.97; H, 8.34. Found: C, 74.46; H, 8.10. ^{1}H NMR ($CDCl_3$, ppm): δ 8.46 (s, 1H, PhC*H*O), 6.73−7.47 (m, 14H, Ph); 5.52 (s, 2H, OCH_2); 4.32 (q, 1H, C*H*(CH_3), *J* = 6.8 Hz); 3.84 (s, 3H, OCH_3); 3.73 (s, 3H, OCH_3); 1.36 (s, 18H, $C(CH_3)_3$); 1.25 (s, 18H, $C(CH_3)_3$); 1.11 (d, 3H, CH(C*H*$_3$), *J* = 6.8 Hz). ^{13}C NMR ($CDCl_3$, ppm): δ 192.87 (C=O); 165.9, 158.6, 152.3, 139.8, 137.0, 134.3, 133.5, 130.6, 127.9, 127.4, 120.9, 114.3, 113.7 (Ph); 66.9 (OCH_2); 55.7, 55.3 (OCH_3); 35.4, 34.3, 31.9, 30.8 (t-Bu); 30.5 (*C*H(CH_3)); 22.3 (CH(*C*H$_3$)). IR (KBr, cm^{-1}): 2958 (s), 2905 (s), 1640 (s), 1600 (s), 1568 (s), 1514 (s), 1474 (s), 1442 (s), 1303 (s), 1270 (s), 1246 (m), 1163 (s), 1026 (m), 880 (m). Mp: 124−126 °C dec.

[Al(EDBP)(*μ*-OC$_6$H$_4$-*p*-Cl)(O=CHC$_6$H$_4$-*p*-Cl)]$_2$ (4). This compound was prepared according to the method described for **2** using 4-chlorobenzaldehyde (0.28 g, 2.0 mmol). Yield: 0.61 g (81%). Anal. Calcd for $C_{88}H_{110}Al_2Cl_2O_8$: C, 70.86; H, 7.43. Found: C, 70.88; H, 7.38. ^{1}H NMR ($CDCl_3$, ppm): δ 8.73 (s, 1H, PhC*H*O); 7.01−7.51 (m, 14H, Ph); 5.55 (s, 2H, OCH_2); 4.11 (q, 1H, C*H*(CH_3), *J* = 7.2 Hz); 1.35 (s, 18H, $C(CH_3)_3$); 1.25 (s, 18H, $C(CH_3)_3$); 1.06 (d, 3H, CH(C*H*$_3$), *J* = 7.2 Hz). ^{13}C NMR ($CDCl_3$, ppm): δ 194.6 (C=O); 151.7, 143.5, 140.5, 137.0, 136.6, 134.1, 132.9, 132.3, 132.1, 129.4, 128.4, 127.2, 121.1, 121.0 (Ph); 66.7 (OCH_2); 35.4, 34.4, 31.9, 30.8 (t-Bu); 30.1 (*C*H(CH_3)); 22.1 (CH(*C*H$_3$)). IR (KBr, cm^{-1}): 2959 (s), 2905 (s), 1643 (s), 1593 (s), 1473 (s), 1443 (s), 1299 (s), 1269 (s), 1236 (s), 1092 (m), 1033 (m), 875 (s), 851 (s). Mp: 154−156 °C dec.

[Al(EDBP)(*μ*-OCH$_2$C$_6$H$_4$-*p*-NO$_2$)]$_2$ (5). 4-Nitrobenzaldehyde (0.15 g, 1.0 mmol) in CH_2Cl_2 (10 mL) was added to a rapidly stirred solution of [Al(EDBP)(*μ*-O^{i}Pr)]$_2$ (0.52 g, 0.5 mmol) in CH_2Cl_2 (30 mL). The reaction mixture was stirred at room temperature for 12 h. The volatile materials were removed under vacuum. The residue was washed twice with hexane (10 mL), followed by crystallization induced by a slow diffusion of hexane into a CH_2Cl_2 solution, resulting in yellow solids. Yield: 0.48 g (77%). Anal. Calcd for $C_{37}H_{50}AlNO_5$: C, 72.17; H, 8.18; N, 2.27. Found: C, 71.59; H, 7.62; N, 2.88. ^{1}H NMR ($CDCl_3$, ppm): δ 7.07−8.13 (m, 8H, Ph); 5.68 (s, 2H, OCH_2); 4.00 (q, 1H, C*H*(CH_3), *J* = 6.8 Hz); 0.89 (d, 3H, CH(C*H*$_3$), *J* = 6.8 Hz); 1.39, 1.23 (s, 36H, $C(CH_3)_3$). ^{13}C NMR ($CDCl_3$, ppm): δ 151.2, 147.1, 145.1, 140.9, 136.8, 133.3, 126.1, 123.7, 121.3, 121.1 (Ph); 66.3 (OCH_2); 35.5, 34.4, 31.7, 30.7 (t-Bu); 30.5 (*C*H(CH_3)); 21.9 (CH(*C*H$_3$)). IR (KBr, cm^{-1}): 2957 (s), 2906 (s), 2869 (s), 1689 (m), 1526 (s), 1475 (s), 1445 (s), 1416 (m), 1347 (s), 1301 (s), 1268 (s), 1240 (s), 1046 (m), 878 (s), 674 (m). Mp: 172−174 °C dec.

[Al(EDBP)(O^{i}Pr)(OPPh$_3$)] (6). To a rapidly stirred solution of [Al(EDBP)(*μ*-O^{i}Pr)]$_2$ (1.04 g, 1.0 mmol) in toluene (30 mL) was added triphenylphosphine oxide (0.56 mL, 2.0 mmol). The reaction mixture was stirred at room temperature for 2 h, and the volatile materials were removed under vacuum. The residue was extracted with hot toluene (15 mL), and the extractor was then cooled to room temperature, affording colorless crystals after standing overnight. Yield: 1.28 g (80%). Anal. Calcd for $C_{51}H_{66}AlO_4P$: C, 76.47; H, 8.30. Found: C, 76.87; H, 8.67. ^{1}H NMR ($CDCl_3$, ppm): δ 6.99−7.87 (m, 19H, Ph); 4.68 (q, 1H, $CH(CH_3)$, *J* = 7.0 Hz); 4.04 (m, 1H, $OCH(CH_3)_2$, *J* = 6.0 Hz); 1.66 (d, 3H, $CH(CH_3)$, *J* = 7.0 Hz); 1.28, 1.20 (s, 36H, $C(CH_3)_3$); 0.87 (d, 6H, $OCH(CH_3)_2$, *J* = 6.0 Hz). Mp: >260 °C.

[Al(EDBP)(O^{i}Pr)(HMPA)] (7). The procedure is the same as for [Al(EDBP)(O^{i}Pr)(OPPh$_3$)], except hexamethylphosphoramide (0.35 mL, 2.0 mmol) was used. Yield: 1.19 g (85%). Anal. Calcd for $C_{39}H_{69}AlN_3O_5P$: C, 66.73; H, 9.91; N, 5.99. Found: C, 66.75; H, 9.41; N, 5.79. ^{1}H NMR ($CDCl_3$, ppm): δ 7.35, 7.03 (d, 4H, Ph, *J* = 2.8 Hz); 4.65 (q, 1H, $CH(CH_3)$, *J* = 6.8 Hz); 4.28 (m, 1H, $OCH(CH_3)_2$, *J* = 6.0 Hz); 2.74 (d, 18H, $O{=}P[N(CH_3)_2]$, J_{H-P} = 9.6 Hz); 1.68 (d, 3H, $CH(CH_3)$, *J* = 6.8 Hz); 1.39, 1.29 (s, 36H, $C(CH_3)_3$); 1.12 (d, 6H, $OCH(CH_3)_2$, *J* = 6.0 Hz). ^{13}C NMR ($CDCl_3$, ppm): δ 153.35, 137.84, 135.51,

Table 4. Crystallographic Data for 1, 3, 6, and 7

	1·C_7H_8	**3**	**6**	**7**
formula	$C_{40}H_{59}AlO_3$	$C_{46}H_{61}AlO_6$	$C_{51}H_{66}AlO_4P$	$C_{39}H_{69}AlN_3O_4P$
fw	614.9	763.9	801.0	701.9
space group	$P2_1/c$	$P\bar{1}$	$P2_1/n$	$P2_12_12_1$
a (Å)	19.121(2)	11.9923(7)	14.044(3)	12.955(1)
b (Å)	10.935(1)	12.1666(7)	21.008(4)	14.170(1)
c (Å)	19.650(2)	15.3901(9)	17.004(3)	23.612(2)
α (deg)		77.511(1)		
β (deg)	109.41(1)	87.329(1)	97.19(4)	
γ (deg)		73.994(1)		
V (Å^3)	3875.1(7)	2107.2(2)	4977.2(2)	4334.7(6)
Z	4	2	4	4
D_{calcd} (Mg m^{-3})	1.054	1.161	1.069	1.076
λ(Mo Kα) (Å)	0.7107	0.7107	0.7107	0.7107
abs coeff (mm^{-1})	0.085	0.094	0.112	0.122
2θ range, deg	4.0−45.0	3.54−50.04	3.50−52.24	3.44−52.00
no. of obsd rflns	5002 ($F > 4\sigma(F)$)	7319 ($F > 4\sigma(F)$)	9736 ($F > 4\sigma(F)$)	8462 ($F > 4\sigma(F)$)
no. of refined params	397	478	514	433
R1[a]	0.0737	0.0640	0.0567	0.0449
wR2[b]	0.1094	0.1997	0.1625	0.1323
GOF[c]	1.45	1.55	1.12	1.05

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

134.07, 120.82, 120.47 (Ph); 63.26 ($OCH(CH_3)_2$); 36.86 (d, $O{=}P[N(CH_3)_2]$, $J_{C-P} = 21.2$ Hz), 35.30, 34.31, 31.94, 30.04 (t-Bu); 30.69 ($CH(CH_3)$); 28.08 ($OCH(CH_3)_2$); 21.99 ($CH(CH_3)$). Mp: 200−202 °C dec.

Typical Experimental Procedure for MPV Reduction of Aldehydes. To a solution of **1** (26 mg, 0.05 mmol) in $CDCl_3$ (1.2 mL) was added benzaldehyde (50 μL, 0.5 mmol), followed by the addition of 2-propanol (77 μL, 1.0 mmol). The reaction mixture was stirred for 1 h at 25 °C. The conversion yield was determined by ^{1}H NMR spectroscopic studies, on the basis of the integration in the methylene and the CHO region of the benzyl group.

X-ray Crystallographic Studies. Suitable crystals of **1** were sealed in thin-walled glass capillaries under a nitrogen atmosphere and mounted on a a Siemens P4 diffractometer. The crystallographic data were collected using a $\omega-2\theta$ scan mode with Mo Kα radiation. Cell constants were obtained by least-squares analysis on positions of 35 randomly selected reflections. Suitable crystals of **3**, **6**, and **7** 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 frames with increasing ω (width of 0.3° per frame). Unit cell dimensions were determined by a least-squares fit of 5316 reflections for **3**, 7740 reflections for **6**, and 5507 reflections for **7**. The absorption correction was based on 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**, **3**, **6**, and **7** are listed in Table 4.

Acknowledgment. Financial support from the National Science Council of the Republic of China is gratefully acknowledged.

Supporting Information Available: Tables giving further data from the crystal structure determinations of **1**, **3**, **6**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM9909690