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Electronic and steric factors affecting the formation of four or five-coordinated aluminum complexes: syntheses and crystal structures of some aluminum alkoxides

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Abstract

The reaction of 2-phenoxyethanol with AlX_3 affords a five-coordinated dimeric product $[(\mu\text{-}OCH_2CH_2OPh)AlX_2]_2$ (**1**, X = Cl; **2**, X = Br) in high yields. However, the reaction of 2-phenoxyethanol with $Al(Bu^i)_3$ yields a four-coordinated dimeric product $[(\mu\text{-}O(CH_2)_2OPh)Al(Bu^i)_2]_2$ (**3**). A mixture, $[(\mu\text{-}O(CH_2)_2OPh)Al(Et)_{0.75}(Cl)_{1.25}]_2$ (**4**) is obtained from the reaction of 2-phenoxyethanol with one equivalent of Et_2AlCl. The reaction of 2-methoxybenzyl alcohol with AlR_3 gives a semi-pentacoordinated dimeric product $[(\mu\text{-}OCH_2C_6H_4OMe)AlR_2]_2$ (**5**, R = Me; **6**, X = Bu^i) in high yields. Crystal structure studies of these compounds reveal that the distance between Al and the phenoxy oxygen or the methoxy oxygen is $\mathbf{3} > \mathbf{6} > \mathbf{5} \gg \mathbf{4} > \mathbf{1} \sim \mathbf{2}$. Although both the electronic and steric effect influence the nature of the *O*,*O*′-bifunctional ligand chelating on the aluminum center to generate a five- or four-coordinated aluminum, the electronic effect is considered to play a major role. The interaction of aluminum and ethereal oxygen can be monitored by ^{13}C-NMR spectroscopic studies. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Aluminum; Ether alcohol; Bifunctional; 2-Phenoxyethanol; 2-Methoxybenzyl alcohol

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1. Introduction

Aluminum alkoxides are interesting because of their regioselective and stereoselective catalytic activities in organic synthesis [1] and their practical uses as precursors for ceramic materials [2]. Organoaluminum complexes coordinated with *O*,*O*′-bifunctional ligands are potentially important due to the fluxionalities of the oxygen–aluminum dative bond. Typically, when organoaluminum derivatives react with *O*,*O*′-bifunctional ligands, five-coordinated dimeric aluminum complexes are obtained. The first structurally characterized example is $[(\mu\text{-}OC(CH_3)N(Ph)CO(Ph))AlMe_2]_2$ in which the carbonyl group coordinated to the Al center through an oxygen atom [3]. Recently, many more pentacoordinated or tetracoordinated aluminum complexes with *O*,*O*′-chelate ligands have been reported by the Benn [4], Oliver [5], Schumann [6], Lewinski [7] and Barron [8] groups, respectively. However, structurally characterized dimeric four-coordinated aluminum complexes with *O*,*O*′-bifunctional ligands are rare. Although $[Et_2Al\{O(CH_2)_2O(CH)_2OCH_2CH_3\}]_2$ has been characterized as a four-coordinated complex using ^{27}Al-NMR spectroscopic studies, however, no crystal structure has been reported [9]. Most recently, we found that the reaction of 2-phenoxyethanol with $AlMe_3$ affords a four-coordinated dimeric compound [10]. In the meantime, Lewinski pointed out that the rearrangement of aluminum complexes in solution is determined by the electronic effect of the ligand [7]. Due to the potential utility of aluminum chelate complexes, the formation of four-coordinate complex led us to further study this system in order to determine the factors influencing the coordination numbers on the Al center. In this paper,

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we report the preparation and crystal structures of several four- and five-coordinated aluminum complexes. Factors that influence the coordination sphere of aluminum complexes will also be discussed.

2. Experimental section

2.1. Reagents and general techniques

All manipulations were carried out under dry nitrogen atmosphere. Solvents were dried by refluxing at least 24 h over sodium/benzophenone (toluene, hexane, ether) or over P_2O_5 (CH_2Cl_2) and freshly distilled before use. Deuterated solvents (Aldrich) were dried over molecular sieves. The compounds $AlMe_3$ (2.0 M in hexane), $AlBr_3$ and $AlCl_3$ were purchased from Aldrich and used without further purification. The compounds Et_2AlCl (15% in hexane) and $Al(Bu^i)_3$ (0.58 M in hexane) were purchased from TCI and used as obtained. 2-Phenoxyethanol and 2-methoxybenzyl alcohol (Aldrich) were purchased and stored over molecular sieves prior to use. 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 or Varian 400 spectrometer with chemical shifts given in ppm from the internal TMS. Microanalyses were performed using a Heraeus CHN-O-RAPID instrument. IR spectra were obtained from a Bruker Equnox 55 spectrometer.

2.2. Preparation of $[(\mu\text{-}OCH_2CH_2OPh)AlCl_2]_2$ (**1**)

To a solution of 2-phenoxyethanol (0.50 ml, 5.0 mmol) in toluene (20 ml), $AlCl_3$ (0.533 g, 4.0 mmol) in toluene (50 ml) was added slowly at 25°C. The mixture was stirred for 4 h and was then dried in vacuo to give a white powder. The white residue was extracted with CH_2Cl_2 (50 ml) and filtered. Volatile materials were removed under vacuum to give a white powder. Yield: 0.79 g (84%). Found: C, 40.55, H, 3.91%. Anal. Calc. for $C_{16}H_{18}O_4Al_2Cl_4$: C, 40.88; H, 3.86%. ^{1}H-NMR ($CDCl_3$): δ 7.26–7.44 (m, 5H, Ph), 4.53 (t, 2H, $J_{H-H} = 5.6$ Hz, CH_2), 4.26 (t, 2H, $J_{H-H} = 5.6$ Hz, CH_2). ^{13}C-NMR ($CDCl_3$): δ 154.30, 129.94, 126.89, 120.92 (Ph), 74.22 ($-CH_2OPh$), 58.66 ($-CH_2OAl$). IR (KBr, cm^{-1}): 2965.2 (s, br), 2904.6 (s), 1598.8 (s), 1489.1 (s), 1455.0 (s), 1359.7 (s), 1238.0 (s), 1184.2 (s), 1084.9 (s, br). M.p.: 141.0–142.0°C (dec.).

2.3. Preparation of $[(\mu\text{-}OCH_2CH_2OPh)AlBr_2]_2$ (**2**)

To a solution of 2-phenoxyethanol (0.50 ml, 5.0 mmol) in toluene (20 ml), $AlBr_3$ (1.28 g, 4 mmol) in toluene (30.0 ml) was added slowly at 25°C. The mixture was stirred for 4 h and was then dried in vacuo to yield a white powder. The white residue was extracted with CH_2Cl_2 (40 ml). The extract was dried under vacuum to give a white powder. Yield: 1.24 g (96%). Found: C, 29.48, H, 2.65%. Anal. Calc. for $C_{16}H_{18}O_4Al_2Br_4$: C, 29.66; H, 2.80%. ^{1}H-NMR ($CDCl_3$): δ 7.32–7.53 (m, 5H, Ph), 4.56 (t, 2H, $J_{H-H} =$ 6.0 Hz, CH_2), 4.28 (t, 2H, $J_{H-H} = 6.0$ Hz, CH_2). ^{13}C-NMR ($CDCl_3$): δ 154.39, 129.89, 126.73, 121.02 (Ph), 74.12 (CH_2OPh), 59.03 ($-CH_2OAl$). M.p.: 130–132°C (dec.).

2.4. Preparation of $[(\mu\text{-}OCH_2CH_2OPh)Al(Bu^i)_2]_2$ (**3**)

To an ice cold (0°C) solution of 2-phenoxyethanol (0.46 ml, 4.0 mmol) in ether (20 ml), (i-Bu)$_3$Al (0.58 M in hexane, 8.0 ml, 4.0 mmol) was added slowly. After addition of all the (i-Bu)$_3$Al, the mixture was stirred for 2 h and then was dried under vacuum to give a white powder. The white residue was extracted with 30 ml of toluene. The extract was concentrated to ca. 5 ml at 30°C. Colorless crystals were obtained after 24 h after cooling to 4°C. Yield: 0.99 g (89%). Found: C, 67.83; H, 9.39%. Anal. Calc. for $C_{32}H_{54}Al_2O_4$: C, 69.04; H, 9.78%. ^{1}H-NMR ($CDCl_3$, ppm): δ 6.9–7.3 (m, 5H, Ph), 4.05–4.11 (m, 4H, CH_2), 1.77–1.81 (m, 2H, CH), 0.85–0.90 (m, 12H, $(CH_3)_2CH$), -0.07 (d, 2H, CH_2Al, $J_{H-H} = 6.0$ Hz). ^{13}C-NMR ($CDCl_3$, ppm): δ 157.6, 129.3, 121.3, 114.3 (Ph), 67.7 ($-CH_2OPh$), 61.6 ($-CH_2OAl$), 28.4, 25.7, 21.8 (Bu^i). IR (KBr, cm^{-1}): 2937.9 (s, br), 2872.1 (s, br), 1600.5 (s), 1498.5 (s), 1458.5 (s), 1239.6 (s), 1083.7 (s), 928.9 (s), 754.1 (s), 669.6 (s, br). M.p.: 95–100°C (dec.).

2.5. The reaction of 2-phenoxyethanol with Et_2AlCl

To an ice cold (0°C) solution of 2-phenoxyethanol (0.50 ml, 5.0 mmol) in hexane (20 ml), Et_2AlCl (5.8 ml, 15% in hexane, 5.0 mmol) was added slowly. The mixture was stirred for 3 h and was then dried in vacuo to give a white solid. The white residue was extracted with toluene (20 ml) and then was concentrated to ca. 10 ml. Colorless crystals, **4**, were obtained after 2 days at 27°C. Yield: 0.80 g (70%). Anal. Calc. for $C_{9.5}H_{12.75}AlCl_{1.25}O_2$: C, 49.56; H, 5.58%. Found: C, 49.45, H, 5.62%. ^{1}H-NMR ($CDCl_3$): 7.12–7.42 (m, 5H, Ph), 4.16–4.40 (m, 4H, CH_2), 1.02 (t, 3H, $J_{H-H} = 8.4$ Hz, CH_3(AlEt)), 0.99 (t, 3H, $J_{H-H} = 8.4$, CH_3(AlEt)), -0.131 (q, 2H, $J_{H-H} = 8.0$ Hz, CH_2(AlEt)), -0.134 (q, 2H, $J_{H-H} = 8.0$ Hz, CH_2(AlEt)). ^{13}C-NMR ($CDCl_3$): δ 156.20, 155.11, 129.78, 129.64, 125.68, 124.01, 123.92, 119.50, 117.37, 117.20 (Ph), 72.15, 69.58, 69.36 ($-CH_2OPh$), 60.39, 60.32, 59.36 ($-CH_2OAl$), 8.68, 8.52 ($-CH_3CH_2Al$), -0.69, -0.78 ($-CH_2Al$). IR (KBr, cm^{-1}): 2956.9 (m, br), 2938.7 (m, br), 2898.1 (s), 2866.0 (s), 1592.4 (s), 1497.4 (s), 1463.8 (s), 1212.6 (s), 1082.6 (s), 923.3 (s).

2.6. Preparation of [μ-$OCH_2C_6H_4OMe)AlMe_2]_2$ (**5**)

To an ice cold (0°C) solution of 2-methoxybenzyl alcohol (0.41 ml, 3.0 mmol) in ether (20 ml), $AlMe_3$ (1.8 ml, 2.0 M in toluene, 3.6 mmol) was added slowly. The mixture was stirred for 2 h and was then dried in vacuo to yield a white powder. The white residue was extracted with ether (15 ml) and filtered. The filtrate was concentrated to about 10 ml at 27°C and cooled to -20°C. White crystals were obtained after 12 h. Yield: 0.55 g (95%). Found: C: 61.90, H: 7.70; Anal. Calc. for $C_{10}H_{15}AlO_2$: C, 61.85; H, 7.79%. ^{1}H-NMR ($CDCl_3$, ppm) δ 6.86–7.33 (m, 4H, Ph), 4.65 (s, 2H, $PhCH_2O$), 3.84 (s, 3H, OCH_3), -0.96 (s, 6H, $AlCH_3$). M.p.: 105–106°C.

2.7. Preparation of [(μ-$OCH_2C_6H_4OMe)Al(Bu^i)_2]_2$ (**6**)

To an ice cold (0°C) solution of 2-methoxybenzyl alcohol (0.27 ml, 2.0 mmol) in ether (30 ml), $Al(Bu^i)_3$ (4.1 ml, 0.58 M in toluene, 2.4 mmol) was added slowly. The mixture was stirred for 2 h and was then dried in vacuo to yield a white powder. The white residue was extracted with ether (15 ml) and filtered. The filtrate was concentrated to about 5 ml at 27°C and cooled to -20°C to give white crystals after 24 h. Yield: 0.45 g (80%). ^{1}H-NMR ($CDCl_3$): δ 6.86–7.33 (m, 4H. Ph), 4.65 (s, 2H, $PhCH_2O$), 3.84 (s, 3H, OCH_3), -0.96 (s, 6H, Al–CH_3). ^{13}C-NMR ($CDCl_3$): δ 157.46, 130.73, 129.93, 126.08, 120.28, 110.16 (Ph), 61.05 ($PhCH_2O$), 55.00 (OCH_3), 28.37, 25.47, 21.70 (Bu^i). IR (KBr, cm^{-1}): 2947.6 (s, br), 2886.1 (s, br), 1606.5 (s), 1494.4 (s), 1466.6 (s), 1322.3 (m), 1241.3 (s), 1204.1 (m), 1178.9 (m), 1123.7 (s), 1069.7 (s, br), 1030.8 (s, br), 1002.8 (s, br), 818.5 (m). M.p.:71–74°C

2.8. X-ray crystallographic studies

Suitable crystals of **1**–**6** were sealed in thin-walled glass capillaries under nitrogen atmosphere and mounted on a Siemens P4 diffractometer. The crystallographic data were collected using a θ-2θ scan mode with Mo–K_α radiation. Cell constants were obtained by least-squares analysis on positions of 42 randomly selected reflections for **1**, 33 reflections for **2**, 26 reflections for **3**, 42 reflections for **4**, 38 reflections for **5** and 42 reflections for **6** in the 2θ range of 9–30°. The space group determination was based on a check of the Laue symmetry and systematic absences, and was confirmed by the structure solution. The structure was solved by direct methods using Siemens SHELXTL PLUS package [11]. All non-H atoms were located from successive Fourier maps. Anisotropic thermal parameters were used for all non-H atoms, and fixed isotropic parameters were used for H atoms that were refined using a riding model [11,12]. Crystallographic data of **1**–**6** are given in Table 1.

3. Results and discussion

3.1. Syntheses and spectroscopic studies

The reaction of 2-phenoxyethanol with AlX_3 in toluene at 25°C affords the pentacoordinated complexes **1** and **2** (**1**: X = Cl; **2**: X = Br) in a moderate to high yield as shown in Scheme 1. However, when 2-phenoxyethanol reacts with $Al(Bu^i)_3$ in diethyl ether, a four-coordinated compound **3** is obtained as shown in Scheme 2. The reaction of 2-methoxybenzyl alcohol with AlR_3 in diethylether furnishes semi four-coordinated compounds **5** and **6** (**5**: R = Me; **6**: R = Bu^i) as illustrated in Scheme 3. Compounds **1** and **2** are insoluble in hydrocarbon solvents but are only scarcely soluble in methylene chloride. The others are readily soluble in hydrocarbon solvents. ^{1}H-NMR spectra of complexes **1**–**3**, **5**, and **6** are essentially identical as expected. There is no OH resonance indicating loss of hydroxyl proton. These compounds are stable as solids or in solution under an inert atmosphere. However, compounds **3**, **5** and **6** are rather less stable than **1** and **2** toward moisture. In order to distinguish two different methylene groups on [(μ-$PhOCH_2CH_2O)AlR_2$, nuclear overhauser effect was observed for complex **1**. It demonstrated a H-1 ($-OCH_2Al$, 4.12 ppm) and H-3 (Ph, 7.21 ppm) hydrogen signal enhancement upon irradiation of H-2 ($PhOC\mathbf{H}_2-$, 4.26 ppm). A 2D-Hetcor NMR spectrum study of **1** indicates that $PhOC\mathbf{H}_2-$ resonance at lower field and $-CH_2C\mathbf{H}_2OAl$ resonance at higher field for both ^{1}H- and ^{13}C-NMR spectra. Et_2AlCl reacts with 2-phenoxyethanol in hexane to give a mixture of **4**. ^{1}H-NMR spectroscopic studies of **4** illustrates three sets of triplets peaks for each methylene protons indicating that **4** is a mixture of [(μ-$O(CH_2)_2OPh)AlCl_2]_2$, and [(μ-$O(CH_2)_2OPh)Al(Et)(Cl)]_2$ with a ratio of 1:3. The result has been verified by the elemental analysis and X-ray crystal structure determination. Attempts to separate these two compounds have been unsuccessful. The observation of [(μ-$O(CH_2)_2OPh)AlCl_2]_2$ indicates that a small degree of disproportionation of Et_2AlCl into Et_3Al and $EtAlCl_2$ may occur in solution. $EtAlCl_2$ then reacts with 2-phenoxyethanol independently to give the product [(μ-$O(CH_2)_2OPh)AlCl_2]_2$.

Both *cis* and *trans* isomers (shown in Scheme 4) of [(μ-$O(CH_2)_2OPh)Al(Et)(Cl)]_2$ are detected in the ^{1}H-NMR spectrum. However only *trans*-form is observed in the X-ray crystal structure determination.

3.2. Molecular structures of 1–6

Single crystals of **1**, **2** and **4** suitable for X-ray structure determination were recrystallized from CH_2Cl_2. Selected bond lengths and bond angles are listed in Tables 2–4, respectively. ORTEP [13] diagrams

Table 1
Crystallographic data of complex **1**–**6**

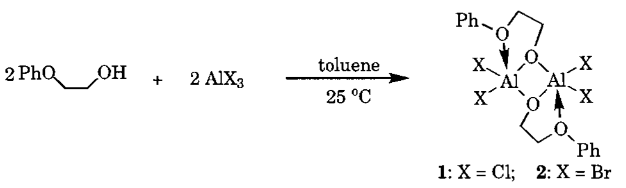
	1	**2**	**3**	**4**	**5**	**6**
Empirical formula	$C_8H_9AlCl_2O_2$	$C_8H_9AlBr_2O_2$	$C_{16}H_{27}AlO_2$	$C_{9.5}H_{12.75}AlCl_{1.25}O_2$	$C_{10}H_{15}AlO_2$	$C_{16}H_{27}AlO_2$
Formula weight	235.0	324.0	278.4	228.6	194.2	278.4
Crystal system	Orthorhombic	Orthorhombic	Triclinic	Monoclinic	Monoclinic	Triclinic
Space group	*Pbca*	*Pbca*	$P\bar{1}$	$P2_1/c$	$P2_1/n$	$P\bar{1}$
Unit cell dimensions						
a (Å)	11.120(1)	8.082(1)	9.675(2)	12.061(3)	9.609(2)	8.666(2)
b (Å)	7.882(1)	11.224(2)	10.050(2)	12.839(3)	7.790(2)	10.423(2)
c (Å)	23.946(3)	24.306(3)	10.242(2)	7.641(2)	15.388(2)	11.406(2)
α (°)			91.76(2)			101.46(2)
β (°)			116.59(2)	106.08(2)	100.23(2)	102.59(2)
γ (°)			98.91(2)			114.42(2)
V (Å^3)	2098.7(4)	2204.7(7)	874.1(3)	1136.8(6)	1133.5(4)	865.8 (3)
Z	8	8	2	4	4	2
$D_{calc.}$ (Mg m^{-3})	1.488	1.952	1.058	1.345	1.138	1.068
λ(Mo–K$_\alpha$) (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Absorption coefficient (mm^{-1})	0.666	7.399	0.113	0.443	0.148	0.114
2θ range (°)	3.5–46.0	3.5–46.	03.5–46.0	4.0–45.0	4.0–48.0	4.0–45.0
Scan type	θ-2θ	θ-2θ	θ-2θ	θ-2θ	θ-2θ	θ-2θ
Reflections collected	1445	1519	2549	1593	1842	2339
Observed reflections	1092 ($F>4.0\sigma(F)$)	1026 ($F>4.0\sigma(F)$)	1784 ($F>4.0\sigma(F)$)	1200 ($F>4.0\sigma(F)$)	1409 ($F>4.0\sigma(F)$)	1854 ($F>4.0\sigma(F)$)
No. of refined parameter	118	118	190	136	118	172
R^a for significant reflections (%)	3.29	5.98	6.21	4.77	5.70	6.71
$R_w{}^b$ (%)	3.67	6.00	6.94	5.32	6.55	7.96
GOF^c	1.02	1.65	1.98	1.41	1.77	2.56

[a] $R=|\Sigma(|F_o-F_c|)/\Sigma|F_o||$.

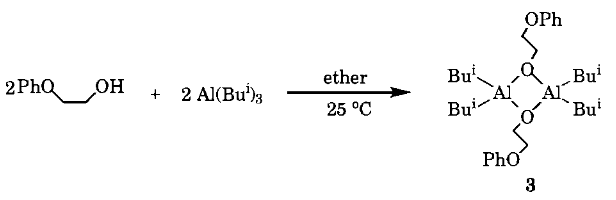
[b] $|\Sigma\sqrt{w}(|F_o-F_c|)/\Sigma\sqrt{w}|F_o||$; $w=1/[\sigma^2(F)+0.001)F^2$ for **1**–**4** and **6** and $w=1/[\sigma^2(F)+0.0015)F^2$ for **5**.

[c] GOF, $[\Sigma w(|F_o|-|F_c|)^2/(N_{rf\ \ln\ s}-N_{params})]^{1/2}$.

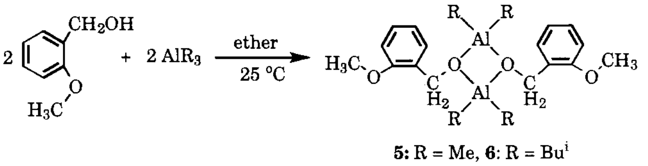
of **1**, **2** and **4** with atomic numbering are shown in Fig. 1. Complex **1** and **2** crystallize in the centrosymmetric orthorhombic space group *Pbca* (no. 61). The structure of **1** shows dimeric feature which contains 5.4.5-fused rings with an Al_2O_2 core and the phenoxy group bonded to Al through the oxygen atom. The Al_2O_2 core is undoubtedly coplanar due to its symmetry. Although similar fused rings have been found in many cases [5,10,14], however, the interesting feature is that the mean plane of the five-membered ring is almost coplanar with the Al_2O_2 core in which the dihedral angle between the five and four-membered ring is only 3.7°. The constraints of the fused 5.4.5 ring system result in the rather small O(1)–Al–O(2) angle of 79.1(1)°. The coordination geometry around Al is ca. a trigonal bipyramidal, with two chlorides and an oxygen atom, O(1), on equatorial positions. O(1) sits over a center of inversion and occupies an apical site of the second Al(a) atom with a longer Al(a)–O(1) distance (0.052(2) Å longer). The four atoms Al, Cl(1), Cl(2), and O(1) are almost coplanar with the mean deviation of 0.0098 Å. The phenoxy oxygen atom and another bridged oxygen atom are in axial positions with the O(2)–Al–O(1a) angle of 154.1(1)°. The distances between bridging alkoxides and aluminum, Al–O(1) and Al–O(1a) are 1.811(2) and 1.863(2) Å, respectively within the normal range for an Al_2O_2 core [15]. The distance between phenoxy oxygen and aluminum, Al(1)–O(2), with 2.028(2) Å is much longer than the distance between bridging alkoxide and aluminum indicating that O(2) is apparently much more weakly bonded to aluminum than O(1). The distance between Al and Cl with 2.131(1) and 2.137(1) Å, respectively is also within a normal range for an Al–Cl bond [16]. The structure of



Scheme 1.



Scheme 2.

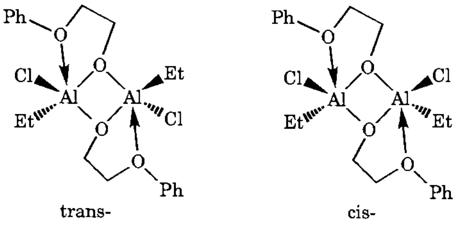


Scheme 3.

2 is essentially the same as that of **1** with the difference only in the Br instead of Cl. The distance between the phenoxy oxygen and aluminum, Al(1)–O(2), with 2.001(7) Å is within the same range as the chloride analogs. The Al–O distances in the Al_2O_2 core are asymmetric with 1.798(7) and 1.860(7) Å, respectively, which are also compatible with the chloride congener. Al is almost coplanar with O(1)Br(1)Br(2) and it is only 0.0190 Å above the O(1)Br(1)Br(2) plane.

The structure of **4** is determined in the $P2_1/c$ space group. The geometry of Al also shows a distorted trigonal bipyramidal. The ethyl group positions are disordered with respect to chloride/ethyl occupancy, and therefore the least-square refinement method is carried out so that for each chloride and ethyl atom site a single set of coordinates and temperature factors were used, but the site occupancy is refined as a fraction of a chlorine atom and a fraction of a ethyl atom such that two fractions summed to unity. The value corresponds to ca. 0.25 Cl and 0.75 C for Cl′/C(1). The Al–O(2) distance of 2.253(3) is somewhat longer than that of **1** and **2**. The average bond distance of Al–O in the Al_2O_2 core of 1.845(2) Å is within a normal range for an Al_2O_2 ring. Due to disorder of the chloro and ethyl groups, the average bond distances of the Al–C, Al–Cl and the bond angle of C–Al–Cl are not reliable.

Single crystals of **3** suitable for X-ray structure determination were recrystallized from toluene at −20°C. Complex **3** crystallizes in the triclinic space group $P\bar{1}$ (no. 2). The atomic geometries of **3** are listed in Table 5. The ORTEP diagram of **3** with atomic numbering is shown in Fig. 2. The coordination geometry around Al is a distorted tetrahedral in which Al is 0.3184 Å above the O(1)C(1)C(5) basal plane. The result is totally different to that observed for five-coordinated aluminum complexes in which Al is coplanar with the basal plane. It is interesting to note that the distance between Al and the phenoxy oxygen atom, O(2), is 2.999(3) Å which is about 0.7–1.0 Å longer than a normal Al–O coordinated covalent bond in a pentacoordinated *O*,*O*′-chelate aluminum complex [17]. It is the longest distance between an aluminum and alkoxy oxygen ever found for an organoaluminum complex with a *O*,*O*′-bifunctional ligand. Because it is only somewhat shorter than the combined van der Waals radius (3.45 Å) of Al and O, it is considered that no or very weak interaction exists between Al and O(2) [18]. The Al_2O_2 core of **3** is asymmetric in which the Al–O(1) distance of 1.828(3) Å is 0.036 Å shorter than the Al–O(1A) distance of 1.864(3) Å. One of the *iso*-butyl groups are disordered with two positions for C(2) and C(4), respectively. The site occupancies were refined as a fraction of ca. 0.70/0.30 for C(2)/C(2′) and C(4)/C(4′).



Scheme 4.

Table 2
Selected bond lengths (Å) and bond angles (°) of **1**

Bond distance (Å)			
Al–Cl(1)	2.131(1)	Al–Cl(2)	2.137(1)
Al–O(1)	1.811(2)	Al–O(2)	2.028(2)
Al–AlA	2.901(2)	Al–O(1A)	1.863(2)
O(1)–C(1)	1.425(4)	O(1)–AlA	1.862(2)
O(2)–C(2)	1.456(4)	O(2)–C(3)	1.424(3)
Bond angle (°)			
Cl(1)–Al–Cl(2)	114.5(1)	Cl(1)–Al–O(1)	118.9(1)
Cl(2)–Al–O(1)	126.5(1)	Cl(1)–Al–O(2)	96.4(1)
Cl(2)–Al–O(2)	93.2(1)	O(1)–Al–O(2)	79.1(1)
Cl(1)–Al–AlA	114.9(1)	Cl(2)–Al–AlA	116.8(1)
O(2)–Al–AlA	117.3(1)	Cl(1)–Al–O(1A)	100.7(1)
Cl(2)–Al–O(1A)	97.1(1)	O(1)–Al–O(1A)	75.7(1)
O(2)–Al–O(1A)	154.1(1)	Al–O(1)–C(1)	122.3(2)
Al–O(1)–AlA	104.3(1)	C(1)–O(1)–AlA	133.1(2)
Al–O(2)–C(2)	110.3(2)	Al–O(2)–C(3)	129.2(2)

Single crystals of **5** and **6** suitable for X-ray structure determination is recrystallized from ether at −20°C. The atomic geometries of **5** and **6** are listed in Table 6 and Table 7, respectively. The ORTEP diagram of **5** and

Table 3
Selected bond lengths (Å) and bond angles (°) of **2**

Bond lengths (Å)			
Al–Br(1)	2.284(4)	Al–Br(2)	2.298(3)
Al–O(1)	1.801(8)	Al–O(2)	1.999(8)
Al–AlA	2.890(6)	Al–O(1A)	1.860(7)
O(1)–C(1)	1.421(14)	O(1)–AlA	1.855(8)
O(2)–C(2)	1.482(14)	O(2)–C(3)	1.446(12)
Bond angles (°)			
Br(1)–Al–Br(2)	113.9(1)	Br(1)–Al–O(1)	119.3(3)
Br(2)–Al–O(1)	126.7(3)	Br(1)–Al–O(2)	96.9(2)
Br(2)–Al–O(2)	93.6(2)	O(1)–Al–O(2)	79.0(3)
Br(1)–Al–AlA	115.0(2)	Br(2)–Al–AlA	116.7(2)
O(2)–Al–AlA	117.2(3)	Br(1)–Al–O(1A)	100.5(3)
Br(2)–Al–O(1A)	96.9(3)	O(1)–Al–O(1A)	75.5(4)
O(2)–Al–O(1A)	153.9(3)	Al–O(1)–C(1)	123.0(6)
Al–O(1)–AlA	104.5(4)	C(1)–O(1)–AlA	132.5(7)
Al–O(2)–C(2)	110.9(6)	Al–O(2)–C(3)	130.8(6)

Table 4
Selected bond lengths (Å) and bond angles (°) of **4**

Bond lengths (Å)			
Al–Cl	2.152(2)	Al–O(1)	1.804(2)
Al–C(1)	1.966(20)	Al–O(1A)	1.871(3)
O(1)–C(3)	1.423(5)	Al–O(2)	2.253(3)
O(2)–C(4)	1.424(5)	O(2)–C(5)	1.400(4)
Bond angles (°)			
Cl–Al–O(1)	122.1(1)	Cl–Al–C(1)	121.3(7)
O(1)–Al–C(1)	115.2(8)	Cl–Al–O(1A)	98.9(1)
O(1)–Al–O(1A)	76.4(1)	C(1)–Al–O(1A)	106.1(6)
Al–O(1)–C(3)	122.9(2)	Al–O(1)–AlA	103.6(1)
C(3)–O(1)–AlA	133.0(2)	Al–C(1)–C(2)	116.9(11)

Table 5
Selected bond lengths (Å) and bond angles (°) of **3**

Bond lengths (Å)			
Al–O(1)	1.828(2)	Al–C(1)	1.957(6)
Al–C(5)	1.951(4)	Al–AlA	2.836(2)
Al–O(1A)	1.864(2)	O(1)–C(9)	1.442(4)
O(1)–AlA	1.864(2)	O(2)–C(10)	1.425(4)
O(2)–C(11)	1.368(5)		
Bond angles (°)			
O(1)–Al–C(1)	109.2(2)	O(1)–Al–C(5)	120.9(2)
C(1)–Al–C(6)	121.7(2)	C(1)–Al–AlA	116.0(1)
C(6)–Al–AlA	121.1(1)	O(1)–Al–O(1A)	79.6(1)
C(1)–Al–O(1A)	110.2(2)	C(6)–Al–O(1A)	106.4(1)
Al–O(1)–C(9)	126.7(2)	Al–O(1)–AlA	100.4(1)
C(9)–O(1)–AlA	127.5(2)	Al–C(1)–C(2)	129.1(6)
Al–C(6)–C(6)	122.6(2)		

6 with atomic numbering is shown in Fig. 3. While this work was in progress, the preparation and crystal structure of [$Me_2Al(\mu\text{-}OCH_2C_6H_4CH_2OMe)$] was reported [6], which is almost the same as the structure of **5**. Therefore, a detailed discussion of this structure will not be presented here. However, because their preparation and crystallization conditions are quite different, the bond distance between Al and the methoxy oxygen is somewhat different with 2.625(3) in **5** compared to 2.572(2) Å as reported. Compound **6** was determined in the triclinic $P\bar{1}$ space group. The coordination geometry around Al is a distorted tetrahedral in which Al is 0.2700 Å above the O(1)C(1)C(5) basal plane. The distance between Al and the methoxy oxygen atom, O(2) is 2.800(3) Å which is much longer than a normal Al–O bond in a pentacoordinated *O,O′*-chelate aluminum complexes. Therefore, it is also considered that no or very weak interaction exists between Al and O(2). The Al_2O_2 core of **6** is also asymmetric in which the Al–O(1) distance of 1.832(2) is 0.045 Å shorter than the Al–O(1A) distance of 1.877(3) Å. The Al–O(2) distance in **5** or **6** is ca. 0.5–0.7 Å longer than that of compounds **1** and **2**, however it is ca. 0.7–0.9 Å shorter than the sum of the van der Waals radii for an Al–O bond. It is considered the methoxy oxygen is semi-coordinated to Al.

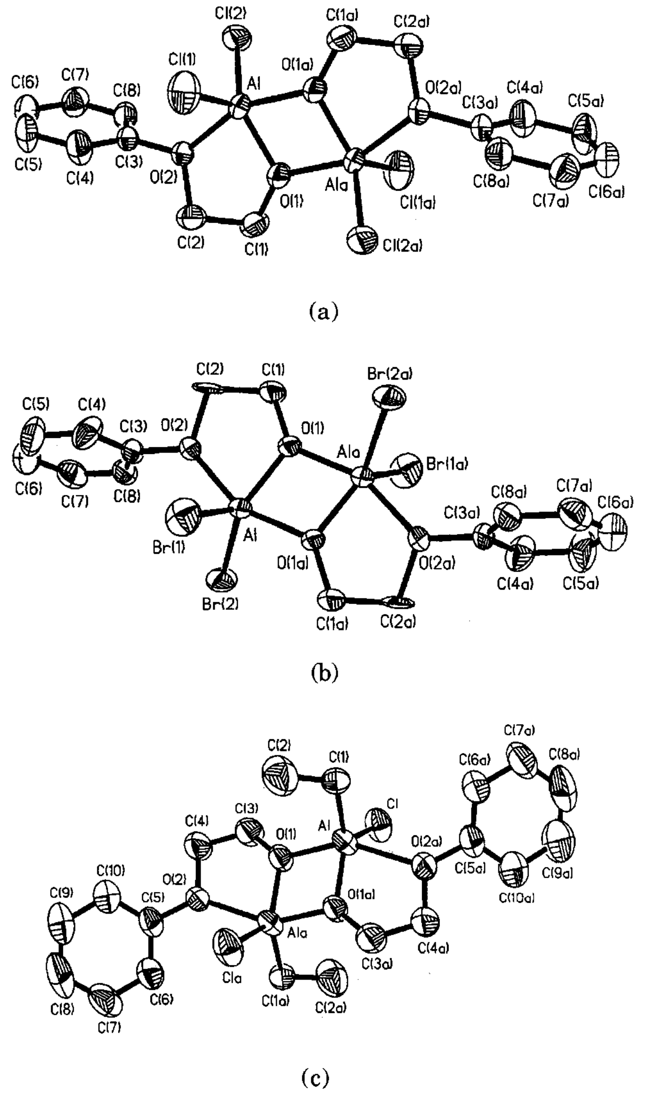


Fig. 1. Molecular structures of (a) [$(\mu\text{-}OCH_2CH_2OPh)AlCl_2]_2$ (**1**) (b) [$(\mu\text{-}OCH_2CH_2OPH)AlBr_2]_2$ (**2**) and (c) [$(\mu\text{-}O(CH_2)_2OPh)Al(Et)_{0.75}(Cl)_{1.25}]_2$ (**4**).

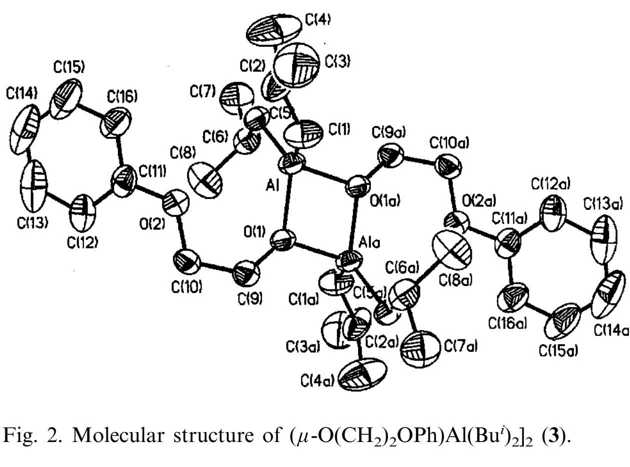


Fig. 2. Molecular structure of $(\mu\text{-}O(CH_2)_2OPh)Al(Bu^i)_2]_2$ (**3**).

Table 6
Selected bond lengths (Å) and bond angles (°) of **5**

Bond lengths (Å)			
Al–O(1)	1.821(2)	Al–C(1)	1.960(3)
Al–C(2)	1.936(3)	Al–AlA	2.868(2)
Al–O(1A)	1.878(2)	O(1)–C(3)	1.421(4)
O(1)–AlA	1.878(2)	O(2)–C(9)	1.372(4)
O(2)–C(10)	1.422(6)		
Bond angles (°)			
O(1)–Al–C(1)	117.2(1)	O(1)–Al–C(2)	116.6(1)
C(1)–Al–C(2)	122.9(2)	C(1)–Al–AlA	117.2(1)
C(2)–Al–AlA	116.6(1)	O(1)–Al–O(1A)	78.8(1)
C(1)–Al–O(1A)	104.7(1)	C(2)–Al–O(1A)	106.3(1)
Al–O(1)–C(3)	133.3(2)	Al–O(1)–AlA	101.2(1)
C(3)–O(1)–AlA	126.3(2)		

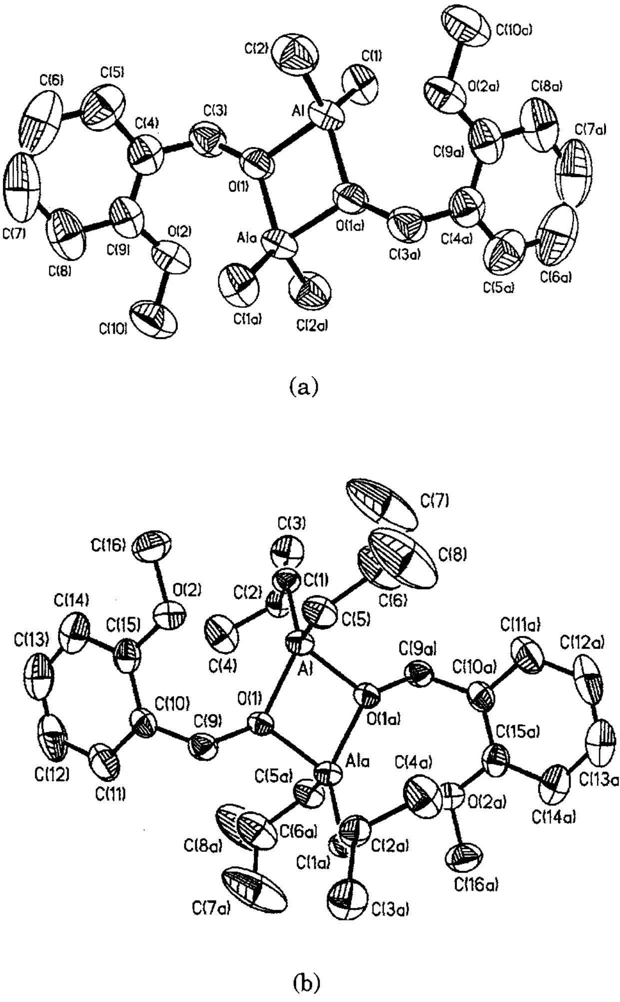


Fig. 3. Molecular structures of (a) $[(\mu\text{-}OC_6H_4OMe)AlMe_2]_2$ (**5**) and (b) $[(\mu\text{-}OC_6H_4OMe)Al(Bu^i)_2]_2$ (**6**).

When organoaluminum derivatives react with *O*,*O*′-bifunctional ligands, five-coordinated aluminum complexes are usually obtained. Five-coordinated Al possessing a trigonal bipyramidal geometry has been found in many cases in which the distance between Al and alkoxy oxygen atom ranges from 1.93 to 2.27 Å [3–7,17]. For example in $[(\mu\text{-}O(CH_2)_2OMe)AlMe_2]_2$, the methoxy group coordinates on Al with the Al–O distance of 2.269 Å [5]. However, the distance between aluminum and the phenoxy oxygen is 2.999(3) in **3**, and 2.761(3) Å in **a**. The distance between the phenoxy oxygen and aluminum (Al–O(2)) in $[(\mu\text{-}O(CH_2)_2OPh)AlR_2]_2$ is significantly longer than that in $[(\mu\text{-}O(CH_2)_2OMe)AlMe_2]_2$ (shown in Table 8) due to the reduced Lewis basicity of the phenoxy oxygen compared to the methoxy oxygen resulting from the conjugation of the oxygen lone pair with the π system of the phenyl ring. It is interesting to note that a five-coordinated complex is obtained when the Me or Bu^i groups attaching on Al are substituted by Cl or Br. The Al–O(2) distance decreases from 2.999(3) for **3** to 2.028(2) for **1** and 2.010(2) Å for **2**, respectively. The shortening of the Al–O(2) distance is believed to be due to the electronic effect because chloride and bromide derivatives are better electron withdrawing groups than Me and Bu^i groups with the result that $AlCl_2(OR)$ is a stronger Lewis acid than $AlMe_2(OR)$. The average distance between Al and the bridging oxygen of the five-coordinated complexes is also slightly shorter than that of four-coordinated complexes. This is also consistent with the fact that compounds **3**, **5** and **6** are rather more unstable than **1** and **2** toward moisture due to the coodinatively unsaturation of these compound.

Table 7
Selected bond lengths (Å) and bond angles (°) of **6**

Bond lengths (Å)			
Al–O(1)	1.832(2)	Al–C(1)	1.968(4)
Al–C(6)	1.962(6)	Al–AlA	2.860(2)
Al–O(1A)	1.877(3)	O(1)–C(9)	1.447(4)
O(1)–AlA	1.877(3)	O(2)–C(16)	1.363(4)
O(2)–C(16)	1.412(7)		
Bond angles (°)			
O(1)–Al–C(1)	120.6(1)	O(1)–Al–C(6)	111.8(1)
C(1)–Al–C(6)	121.6(2)	C(1)–Al–AlA	119.6(1)
C(6)–Al–AlA	116.6(2)	O(1)–Al–O(1A)	79.6(1)
C(1)–Al–O(1A)	104.7(2)	C(6)–Al–O(1A)	108.4(2)
Al–O(1)–C(9)	128.4(2)	Al–O(1)–AlA	100.4(1)
C(9)–O(1)–AlA	126.7(2)	Al–C(1)–C(2)	121.6(3)
Al–C(5)–C(6)	119.9(4)		

The distance between Al and methoxy oxygen in the pentacoordinated complex $[Me_2Al(\mu\text{-}OC_6H_4\text{-}2\text{-}OCH_3)]_2$ is 2.198(2) Å [7]. However, when 2-methoxy benzyl alcohol reacts with AlR_3 ($R = Me$ or Bu^i), only a four-coordinated aluminum complex is obtained with the distance between aluminum and the methoxy oxygen being 2.625(3) for **5** and 2.800(3) Å for **6**. The longer Al–O distance in $[Me_2Al(\mu\text{-}OCH_2C_6H_4\text{-}2\text{-}OCH_3)]_2$ than that of $[Me_2Al(\mu\text{-}OC_6H_4\text{-}2\text{-}OCH_3)]_2$ indicates that the methoxy group of $[-OC_6H_4\text{-}2\text{-}OCH_3]$ is more basic than that of $[-OCH_2C_6H_4\text{-}2\text{-}OCH_3]$ resulting from the conjugation of the alkoxide lone pair with

Table 8
Comparison of selected bond distances (Å) and bond angles (°) of **1**–**6** and compounds reported in literature

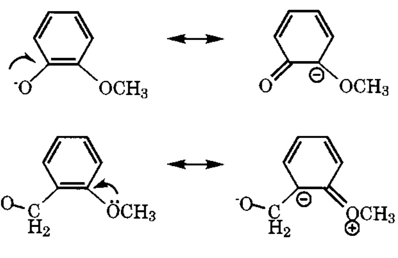
Compound	**1**	**2**	**3**	**4**	**a**[a,d]	**5**	**6**	**b**[b,e]	**c**[c,f]
Al–O(1) (bridged)	1.811(2) 1.863(2)	1.798(7) 1.860(7)	1.828(2) 1.864(2)	1.804(2) 1.871(3)	1.817(3) 1.865(3)	1.821(2) 1.878(2)	1.832(2) 1.877(3)	1.827(3) 1.892(3)	1.859(3) 1.952(3)
Al–O(2) (alkoxy group)	2.028(2)	2.001(7)	2.999(3)	2.253(3)	2.761(3)	2.625(3)	2.800(3)	2.269(3)	2.249(3)
Al–C (ave.)	–	–	1.954(6)	1.97(2)	1.945(5)	1.943(3)	1.965(5)	1.951(5)	1.955(5)
Al–Cl (ave.)	2.134(1)	–	–	2.152(2)	–	–	–	–	–
Al–Br (ave.)	–	2.292(3)	–	–	–	–	–	–	–
Al–Al(a)	2.901(2)	2.890(6)	2.836(2)	2.955(3)	2.855(2)	2.858(2)	2.850(2)	2.924(2)	3.018(2)
Al–O(1)–Al(a) (Al_2O_2)	104.3 (3)	104.4(3)	100.4(1)	103.6(1)	101.7(1)	101.2(1)	100.4(1)	103.1	104.7(1)
O(1)–Al–O(1a) (Al_2O_2)	75.7(1)	75.6(3)	79.6(1)	76.4(1)	78.3(1)	78.8(1)	79.6(1)	76.3	73.3(1)
O(1)–Al–O(2) (ring)	79.1(2)	79.1(6)	–	76.5	–	–	–	75.9	75.2(1)
Coordination number	5	5	4	5	4	4	4	5	5

[a] **a**, $[(\mu\text{-}O(CH_2)_2OPh)AlMe_2]_2$.
[b] **b**, $[(\mu\text{-}O(CH_2)_2OMe)AlMe_2]_2$.
[c] **c**, $[(\mu\text{-}OC_6H_4\text{-}2\text{-}OMe)AlEt_2]_2$.
[d] Reference [10].
[e] Reference [4].
[f] Reference [5].

the phenyl ring, avoiding the conjugation of the methoxy oxygen with the phenyl ring as shown in Scheme 5. However, a resonance occurs between the methoxy oxygen with the π system in $[-OCH_2C_6H_4\text{-}2\text{-}OCH_3]$. Therefore, the methoxy oxygen of $[-OC_6H_4\text{-}2\text{-}OCH_3]$ is a better Lewis base than that of $[-OCH_2C_6H_4\text{-}2OCH_3]$.

The distance between aluminum and the methoxy oxygen in the *iso*-butyl aluminum derivative, **6**, with 2.800(3) Å is somewhat longer than that of methyl congener, **5**, with 2.625(3) Å. In addition, the distance between aluminum and the phenoxy oxygen of **3** with 2.999(3) Å is also longer than that of $[(\mu\text{-}O(CH_2)_2OPh)AlMe_2]$ with 2.761(3) Å. The lengthening of the Al–O distance emerged by changing the Me to the Bu^i group, results from both more steric hindrance and better electron donor of ^{i}Bu than Me group.

Though ^{27}Al-NMR spectroscopic studies have been widely used to determine the coordination number on Al in solution, it is interfered by the presence of Al impurity in NMR tubes. An interesting result is observed in ^{13}C-NMR spectroscopic studies. The chemical shift for C-2 in **1** or **2** (four-coordinated aluminum) was observed in ca. 5 ppm downfield compared to that in $PhOCH_2OCH_2OH$. However, C-2 in **a** or **3** (four-coordinated aluminum) emerged in ca. 1.5 ppm upfield compared to $PhOCH_2OCH_2OH$. A similar result was observed for the $MeOC_6H_4CH_2OH$ system. The ^{13}C-NMR spectra of $PhOCH_2CH_2OH$ and $MeOC_6H_4CH_2OH$ with **1**–**3**, **5**, **6** and **a** [10] are compared in Table 9. Therefore, ^{13}C-NMR of the carbon adjacent to ethereal oxygen can be used as a model to the interaction between ethereal oxygen and aluminum.



Scheme 5.

Table 9
The comparison of ^{13}C-NMR spectra (in ppm)

	$ROCH_2CH_2O$ (Δ)	$ROCH_2CH_2O$ (Δ)	C.N.
$PhOCH_2CH_2OH$	69.13	61.34	–
1	74.22 (5.09)	58.66 (−2.88)	5
2	74.12 (4.99)	59.03 (−2.31)	5
a[a]	67.59 (−1.54)	60.46 (−0.88)	4
3	67.67 (−1.46)	61.61 (0.27)	4
	$CH_3OC_6H_4$ (Δ)	$C_6H_4CH_2O$ (Δ)	–
$MeOC_6H_4CH_2OH$	55.20	61.75	
5	54.88 (−0.32)	60.87 (−0.88)	4
6	55.00 (−0.20)	61.05 (−0.70)	4

[a] Reference [9].

4. Conclusion

The coordination number of the Al center is determined by both electronic and steric effects of ligand and Al center. Though a bulky ligand attaching on Al would keep oxygen away, the steric effect only plays as a minor role in these cases. The electronic effect can be attributed to the basicity of oxygen donor and the acidity of aluminum center. ^{13}C-NMR spectra can be used as a model to indicate the bonding mode between ethereal oxygen and aluminum.

5. Supplementary materials

For **1**–**6**, tables give full details of the crystal data, data collection, structure solution parameters, atomic coordinates of all atoms, bond distances, bond angles, anisotropic thermal parameters of nonhydrogen atoms, and isotropic thermal parameters of hydrogen atoms.

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