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Aluminum alkyls with intramolecularly coordinated oxygen

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Organoaluminum alkyls L^1AlMe_2 (1), L^2AlMe_2 (2) and $L^2Al^iBu_2$ (3) with O,C,O-chelating ligands L^1 and L^2 [$L^1 = 2,6\text{-}(MeOCH_2)_2C_6H_3$ and $L^2 = 2,6\text{-}(^tBuOCH_2)_2C_6H_3$] were prepared. The compounds have been characterized by elemental analysis, ^1H, ^{13}C, ^{27}Al NMR spectroscopy and X-ray diffraction analysis (3). Solution NMR studies indicated the four coordinated aluminum atom and dissociation/association dynamic process in solution of 1–3. The X-ray diffraction analysis of 3 showed that the aluminum atom is [4 + 1] coordinated with the *trans*-trigonal bipyramidal geometry. The reactivity of 2 was investigated. Reactions of 2 with MeOH and I_2 resulted in aluminum alkoxide [$L^2Al(OMe)_2$ (4)] and iodides [$L^2AlI_2\cdot$ THF (5) and L^2AlI_2 (6)], respectively, characterized by elemental analysis, IR and ^1H, ^{13}C and ^{27}Al NMR spectroscopy. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: aluminum; O,C,O-chelating ligands; NMR spectroscopy

INTRODUCTION

Stabilization of alumininum alkyls through the Al...Y (where, Y = N, P, S or O) intramolecular coordination is currently of interest.[1–9] This arises as the commercial aluminum compounds (triethylaluminum, diethylaluminum chloride), used as cocatalysts in Ziegler–Natta ethylene or propylene polymerization,[10,11] are sensitive to traces of air and moisture, and are difficult to handle. Schumann and co-workers synthesized a large variety of the sulfur-, nitrogen- and oxygen-stabilized aluminum alkyls providing certain stability towards oxygen and moisture.[12,13] The oxygen–intramolecularly coordinated organoaluminum compounds are the active cocatalysts in ethylene or propylene polymerization; some of them are even more active than the industrially used aluminum compounds.[14,15]

Recently, we have synthesized novel potentially terdentate O,C,O-chelating ligands $[2,6\text{-}(ROCH_2)_2C_6H_3]^-$ with increasing steric hindrance of R (Me, ^{i}Pr, ^{t}Bu), which have been used for hypercoordination of organolithium, organoaluminum and organotin(IV) compounds (Scheme 1).[16]

On the basis of these findings, we have decided to use the O,C,O-chelating ligands for the preparation of intramolecularly coordinated dialkylaluminum compounds (**1**–**3**) as eventual co-catalysts in ethylene or propylene polymerization. We have also used **2** as a precursor for the preparation of other organoaluminum derivatives with O,C,O-chelating ligands (**4**–**6**).

EXPERIMENTAL

X-ray crystallographic study

Colorless crystals of **3** suitable for X-ray structure determination were obtained via crystallization from *n*-hexane solution at −30 °C. Data for a crystal of **3**, 0.12 × 0.20 × 0.60 mm, were collected on a KappaCCD diffractometer using MoK$_\alpha$ radiation ($\lambda = 0.71073$ Å) at 150(±2) K. The absorption effect was neglected ($\mu = 0.099$ mm^{-1}). The structure was solved by the direct methods (SIR97) and refined by a full-matrix least-squares procedure based on F^2 (SHELXL97). H atoms were fixed into idealized positions (riding model) and assigned temperature factors $H_{iso}(H) = 1.2\,U_{eq}$(pivot atom); for the methyl moiety a multiple of 1.5 was chosen.

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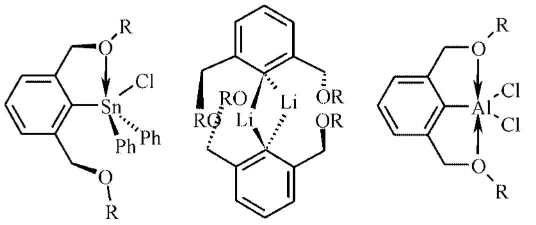


Scheme 1.

Crystallographic data for **3**: $C_{24}H_{43}AlO_2$, $M = 390.56$, monoclinic space group $P2_1/c$, $a = 9.4760(2)$ Å, $b = 8.7830(1)$ Å, $c = 29.3130(5)$ Å, $\beta = 98.2590(9)°$, $Z = 4$, $V = 2414.35(7)$ Å^3, $D_c = 1.074$ g cm^{-3}. $R(F) = 0.053$ for 4076 observed $[I > 2\sigma(I)]$ diffractions and $wR(F^2) = 0.138$ for all 4732 diffractions. CCDC deposition no. 256 896.

Materials and measurements

All manipulations were carried out under a dry, oxygen-free argon atmosphere using the standard Schlenk-tube technique. All solvents were purified and dried by standard procedures and distilled prior to use. The ^{1}H, ^{11}B, ^{13}C and ^{27}Al NMR spectra were recorded on Bruker AMX 360 and Bruker 500 Avance spectrometers respectively, using 5 mm tuneable broadband probes. Appropriate chemical shifts in ^{1}H and ^{13}C NMR spectra were calibrated on the residual peaks of the solvents [benzene-d_6: $\delta(^1H) = 7.16$ ppm and $\delta(^{13}C) = 128.39$ ppm; toluene-d_8: $\delta(^1H) = 2.09$ ppm and $\delta(^{13}C) = 20.40$ ppm]. The ^{11}B and ^{27}Al NMR chemical shifts were related according to the external standard $B(OMe)_3$ and $[Al(H_2O)_6]^{3+}$. Microanalyses were carried out with a Fison EA 1108 instrument in the Microanalytical Laboratory at the University of Pardubice. Infrared data were obtained on a Perkin Elmer 684 using KBr and are reported in cm^{-1}. The synthesis of the starting O,C,O ligands and the corresponding organolithium complexes was performed according to the literature.[16]

Synthesis of $[2,6\text{-}(MeOCH_2)_2C_6H_3]AlMe_2$ (1)

The 1 M hexane solution of Me_2AlCl (5.5 ml, 5.5 mmol) was added to the diethylether solution (30 ml) of $[2,6\text{-}(MeOCH_2)_2C_6H_3]Li$ (0.9 g, 5.5 mmol) at −78 °C. The reaction mixture was stirred for an additional 12 h at room temperature, than the white precipitate was filtered off and washed with 20 ml of hexane. The combined extracts were evaporated to dryness *in vacuo* to give **1**, as a colorless oil. Yield: 1.1 g (90%). b.p.: 65–70 °C/20 Pa. Anal. calc. for $C_{12}H_{19}O_2Al$ (222.27 g mol^{-1}): C, 64.85; H, 4.98. Found: C, 64.69; H, 4.82. Molecular weight determination (cryosc. in benzene): theor. 222.27 g mol^{-1}; exp. 218.28 g mol^{-1}. ^{1}H NMR (360 MHz, C_6D_6, 300 K): δ (ppm) −0.41 (s, 6H, AlCH_3), 3.22 (s, 6H, OCH_3), 4.47 (s, 4H, CH_2O), 7.11 (d, 2H, Ar-*H*3,5), 7.19 (t, 1H, Ar-*H*4). ^{13}C NMR (90.6 MHz, C_6D_6, 300 K): δ (ppm) −9.1 ($AlCH_3$), 57.2 (OCH_3), 74.9 (CH_2O), 127.7 (Ar-C4), 128.0 (Ar-C3,5), 137.5 (Ar-C2,6), Ar-C1 not detected. ^{27}Al NMR (93.8 MHz, C_6D_6, 300 K): δ (ppm) 185, $\nu_{1/2} = 11$ kHz.

Synthesis of $[2,6\text{-}(^tBuOCH_2)_2C_6H_3]AlMe_2$ (2)

The 1 M hexane solution of Me_2AlCl (4.1 ml, 4.1 mmol) was added to the stirred hexane solution (30 ml) of $\{2,6\text{-}[^tBuOCH_2]_2C_6H_3\}Li$ (1.1 g, 4.1 mmol) at room temperature. The reaction mixture was stirred for additional 12 h, the white precipitate was filtered off and washed with 20 ml of hexane. The combined extracts were evaporated to dryness *in vacuo* to provide **2**, as a colorless oil. Yield: 1.12 g (89%). b.p.: 70–74 °C/20 Pa. Anal. calc. for $C_{18}H_{31}O_2Al$ (306.43 g mol^{-1}): C, 70.56; H, 10.20. Found: C, 70.38; H, 10.05. Molecular weight determination (cryosc. in benzene): theor. 306.43 g mol^{-1}; exp. 312.12 g mol^{-1}. ^{1}H-NMR (360 MHz, C_6D_6, 300 K): δ (ppm) −0.39 (s, 6H, Al*Me*), 1.22 (s, 18H, CH_3), 4.55 (s, 4H, CH_2O), 6.95 (d, 2H, Ar-*H*3,5), 7.19 (t, 1H, Ar-*H*4). ^{13}C NMR (90.6 MHz, C_6D_6, 300 K): δ (ppm) −8.5 ($AlCH_3$), 27.7 [$OC(CH_3)_3$], 67.3 (CH_2O), 72.9 [$OC(CH_3)_3$], 120.7 (Ar-C4), 125.3 (Ar-C3,5), 144.7 (Ar-C2,6), Ar-C1 not detected. ^{27}Al NMR (93.8 MHz, C_6D_6, 300 K): δ (ppm) 160, $\nu_{1/2} = 12$ kHz

Synthesis of $[2,6\text{-}(^tBuOCH_2)_2C_6H_3]Al^iBu_2$ (3)

A similar procedure to that used for **2** was used. $^iBu_2AlCl$ (0.4 g, 2.3 mmol) and $[2,6\text{-}(^tBuOCH_2)_2C_6H_3]Li$ (0.6 g, 2.3 mmol) provided **3** as a white powder. Yield: 0.84 g (93%). M.p.: 130–135 °C. Anal. calc. for $C_{24}H_{43}O_2Al$ (390.59 g mol^{-1}): C, 73.80; H, 11.10. Found: C, 73.40; H, 11.00. Molecular weight determination (cryosc. in benzene): theor. 390.59 g mol^{-1}; exp. 380.6 g mol^{-1}. ^{1}H-NMR (360 MHz, C_6D_6, 300 K): δ (ppm) 0.10 [d, 4H, $AlCH_2CH(CH_3)_2$], 0.77 [d, 12H, $AlCH_2CH(CH_3)_2$], 1.00 (s, 18H, CH_3), 1.69 [h, 2H, $AlCH_2CH(CH_3)_2$], 4.38 (s, 4H, CH_2O), 6.75 (d, 2H, Ar-*H*3,5), 7.00 (t, 1H, Ar-*H*4). ^{13}C NMR (90.6 MHz, C_6D_6, 300 K): δ (ppm) 26.1 [$AlCH_2CH(CH_3)_2$], 27.1 [$AlCH_2CH(CH_3)_2$], 27.7 [$OC(CH_3)_3$], 28.5 [$AlCH_2CH(CH_3)_2$], 68.3 (CH_2O), 78.3 [$OC(CH_3)_3$], 121.4 (Ar-C3,5), 126.9 (Ar-C4), 144.5 (Ar-C2,6), Ar-C1 not detected. ^{27}Al NMR (93.8 MHz, C_6D_6, 300 K): δ (ppm) 174, $\nu_{1/2} = 10$ kHz.

Synthesis of $[2,6\text{-}(^tBuOCH_2)_2C_6H_3]Al(OMe)_2$ (4)

The methanol (84 µl, 2.3 mmol) was added to the stirred pentane solution (10 ml) of **2** (0.4 g, 1.3 mmol) at −30 °C. The reaction mixture was stirred for 2 h and solvent was removed *in vacuo* to provide **4** as a white powder. Yield: 0.4 g (91%). M.p.: 165–170 °C. Anal. calc. for $C_{18}H_{31}O_4Al$ (338.43 g mol^{-1}): C, 63.88; H, 9.23. Found: C, 63.70; H, 9.11. Molecular weight determination (cryosc. in benzene): theor. 338.43 g mol^{-1}; exp. 315.6 g mol^{-1}. ^{1}H-NMR (360 MHz, C_6D_6, 300 K): δ (ppm) 0.40 (s, 6H, AlOCH_3), 1.16 (s, 18H, CH_3), 4.35 (s, 4H, CH_2O), 7.27 (t, 1H, Ar-*H*4), 7.34 (d, 2H, Ar-*H*3,5). ^{13}C NMR (90.6 MHz, C_6D_6, 300 K): δ (ppm) 1.8 ($AlOCH_3$), 28.1 [$OC(CH_3)_3$], 64.6 (CH_2O), 73.3 [$OC(CH_3)_3$], 126.5 (Ar-C3,5), 126.8 (Ar-C4), 140.9 (Ar-C2,6), Ar-C1 not detected. IR (KBr, cm^{-1}): 2995 (s), 2900 (s), 2870 (s), 2850(s), 1450(m), 1303(s), 1277(s), 1270(s), 1239(s), 1225(s), 1112(s), 1109(s, br), 990(s), 931(s), 800(s), 765(s), 736(s).

Synthesis of $[2,6\text{-}(^t\text{BuOCH}_2)_2\text{C}_6\text{H}_3]\text{AlI}_2\cdot\text{THF}$(5)

The THF solution (30 ml) of I_2 (0.17 g, 0.6 mmol) was added to the stirred pentane solution (10 ml) of **2** (0.1 g, 0.3 mmol) at room temperature. The reaction mixture was stirred for 5 h and solvents were removed *in vacuo* to provide **5** as yellow powder. Yield: 0.18 g (90%). M.p.: 250 °C-decomp. Anal. calc. for $C_{20}H_{33}O_3I_2Al$ (602.27 g mol^{-1}): C, 39.89; H, 5.52. Found: C, 39.69; H, 5.39. Molecular weight determination (cryosc. in benzene): theor. 602.27 g mol^{-1}; exp. 590.6 g mol^{-1}. ^{1}H-NMR (360 MHz, C_6D_6, 300 K): δ (ppm) 1.15 (s, 9H, CH_3), 1.17 (s, 9H, CH_3), 1.46 (m, 4H, THF), 3.71 (m, 4H, THF), 4.30 (s, 2H, CH_2O), 4.45 (s, 2H, CH_2O), 6.97–7.43 (bs, 3H, Ar). ^{13}C NMR (90.6 MHz, C_6D_6, 300 K): δ (ppm) 25.9 (Al-THF), 28.0, 28.1 [$OC(CH_3)_3$], 64.6 (Al-THF), 69.1, 69.7 (CH_2O), 73.3, 73.8 [$OC(CH_3)_3$], 126.5, 127.9 (Ar-C3,5), 126.8, 128.6 (Ar-C4), 140.9, 142.7 (Ar-C2,6), Ar-C1 not detected. ^{27}Al NMR (93.8 MHz, C_6D_6, 300 K): δ (ppm) 120, $\nu_{1/2} = 6.3$ kHz. IR (KBr, cm^{-1}): 2895 (s), 2850 (s), 2700 (s), 1440 (m), 1283 (s), 1186 (s), 1156 (s), 1100 (s), 918 (s), 805 (s, br), 647 (s), 505 (s, br).

Synthesis of $[2,6\text{-}(^t\text{BuOCH}_2)_2\text{C}_6\text{H}_3]\text{AlI}_2$ (6)

The hexane suspension (30 ml) of I_2 (0.17 g, 0.6 mmol) was added to the stirred hexane solution (20 ml) of **2** (0.1 g, 0.3 mmol) at room temperature. The reaction mixture was stirred for 20 h and solvent was removed *in vacuo*. The residue was washed with mixture of hexane–THF (1 : 1, 10ml) three times to provide **6** as an yellow powder. Yield: 0.15 g (95%). M.p.: 260 °C-decomp. Anal. calc. for $C_{16}H_{25}O_2I_2Al$ (530.17 g mol^{-1}): C, 36.25; H, 4.75. Found: C, 36.35; H, 4.85. IR (KBr, cm^{-1}): 2950 (s), 2850 (s), 1470 (m), 1283 (s), 1190 (s), 1150 (s), 950 (s), 888 (s), 875 (s, br), 770 (s), 752 (s), 647 (s, br), 520 (s, br).

RESULTS AND DISCUSSION

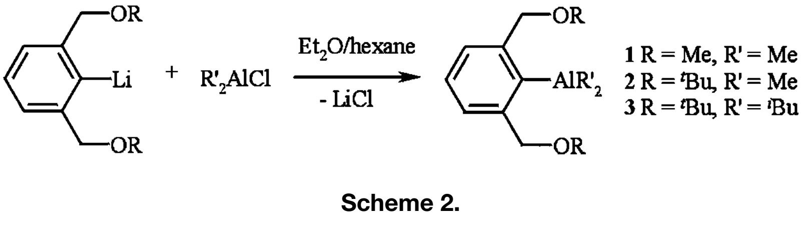
Synthesis and characterization of 1–3

Dialkylaluminum compounds containing Al-O intramolecular interaction are usually synthesized by the reaction of dialkylaluminum chlorides with lithium salt of appropriate oxygen containing ligand.[17] The reaction of Me_2AlCl and $^iBu_2AlCl$ with 2,6-bis(methoxymethyl)phenyllithium or 2,6-bis(*tert*-butoxymethyl)phenyllithium, respectively, in diethyl ether at −78–20 °C or in hexane at 20 °C yields the oxygen-containing dialkylaluminum compounds $[2,6\text{-}(\text{MeOCH}_2)_2\text{C}_6\text{H}_3]\text{AlMe}_2$ (**1**), $[2,6\text{-}(^t\text{BuOCH}_2)_2\text{C}_6\text{H}_3]\text{AlMe}_2$ (**2**) and $[2,6\text{-}(^t\text{BuOCH}_2)_2\text{C}_6\text{H}_3]\text{Al}^i\text{Bu}_2$ (**3**) (Scheme 2) as a volatile colorless oil (**1, 2**) or white crystals (**3**).

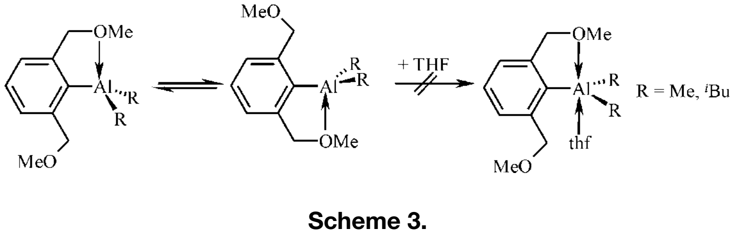
The newly prepared compounds **1**–**3** are monomers (from cryoscopy measurements) soluble in polar (THF or diethyl ether), aromatic (benzene, toluene) as well as in non-polar solvents (hexane). They are sensitive to air and moisture, but in comparison to commercially available Me_3Al or $^iBu_3Al$ only to a moderate degree. Benzene-d_6 solutions (1 ml) of compounds **1**–**2** (100 mg) were completely hydrolyzed within 2 h and of **3** after 6 days on air.

The aluminum chemical shift values [$\delta(^{27}\text{Al}) = 180$ ppm (**1**), 160 ppm (**2**) and 178 ppm (**3**)] fall to the region typical for tetra-coordinated aluminum [$\delta(^{27}\text{Al}) = 125$–180 ppm].[18–23] All ^{1}H NMR signals of **1**–**3** benzene-d_6 solutions at 300 K appear in the expected areas and reveal proposed signal patterns. The ^{1}H NMR spectra of **1**–**3** toluene-d_8 solutions show the broadening of CH_2 and CH_3 protons of CH_2OR 'arms' from the O,C,O-chelating ligands at 170 K. This is a result of dissociation/association dynamic process in toluene-d_8 solutions of **1**–**3** (Scheme 3).[24] The process is typical for organometallic compounds containing Y,C,Y-chelating so called 'pincer' ligands. The process is rapid and cannot be retarded in toluene solutions of **1**–**3** either by the temperature decrease (no decoalescence at 170 K) or by the addition of Lewis base (THF) to **1**–**3** (Scheme 3).

This is in agreement with the four coordinated aluminum atoms in **1**–**3**. The absence of isobutyl group signal splitting in **3** is in accordance with the proposed dynamic process as well. This signal splitting (due to diastereotopic methylene protons) was observed in previously reported diisobutylaluminum complexes containing ligands with the donor atom at room



Scheme 2.



Scheme 3.

temperature as the result of hindered rotation of the isobutyl groups.[14,25,26–27]

The crystal structure of 3

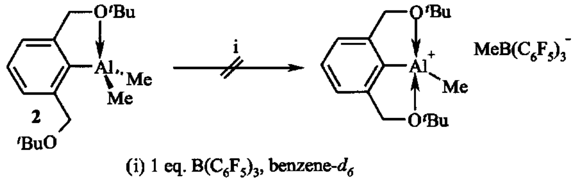
The solid-state structure of **3** is shown in Fig. 1, together with the view along the Al–C1–C4 axis. The aluminum atom is coordinated by three carbon atoms and one oxygen atom from the O,C,O-chelating ligand. The Al–C values (see Fig. 1) fit the region typical for Al–C bonds (the range found in CCDC is 1.964–2.014 Å). The Al–O2 distance [2.1237(±15) Å] indicates the strong coordination of this oxygen atom to the aluminum atom, thus forming the five-membered ring. This distance is comparable to those found in other aryl/alkyl aluminum compounds containing Al–O intramolecular interaction.[12–14,28–32] The Al–O1 distance [2.6137(±15) Å] is a shorter than the sum of van der Waals radii for aluminum and oxygen atoms (3.45 Å)[33,34] and indicates that the second oxygen atom is bound only weakly, resulting in [4 + 1], coordinated aluminum atom. However, the shape of the aluminum coordination polyhedron is *trans*-trigonal bipyramid, due to the weak Al–O1 interaction, having three carbon atoms in an equatorial plane [the sum of C–Al–C bonding angles is 356.98(±8)°] and both oxygen atoms from O,C,O-chelating ligand in axial positions.

The *trans*-trigonal bipyramidal geometry has also been found in the other trialkyl/aryl-aluminum compounds containing two donor atoms Y (Y = N, O), as well.[35–40] However, these aluminum analogs of **3** contain two similar Al–Y distances in contrast to two different Al–O bond lengths found in **3**. This is most probably the result of steric bulk in the vicinity of the aluminum atom caused by the presence of two aluminum-bound ^{i}Bu groups and two ^{t}Bu groups originated from O,C,O-chelating ligand.

Reactivity of compound 2

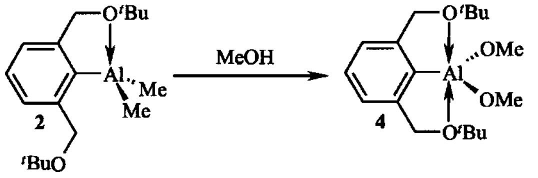
In order to investigate the chemical behavior of the Al–O coordinated aluminum alkyls, we have decided to investigate the reactivity of one of these compounds, **2**. We have focused on three reactions: (i) the reaction with the strong Lewis acid $B(C_6F_5)_3$ for Me^- abstraction at the aluminum metal center; (ii) the reaction with CH_3OH for organoaluminum alkoxide preparation; (iii) the reaction with I_2 for organoaluminum iodide synthesis (see the Experimental section).

The reaction of **2** with $B(C_6F_5)_3$ was performed as a NMR tube experiment in benzene-d_6 solution [see equation (1)], but the decomposition was observed immediately after the addition of $B(C_6F_5)_3$:



(1)

The reaction of **2** with MeOH resulted in the aluminum alkoxide **4** [equation (2)]:



(2)

The ^{1}H NMR spectrum of benzene-d_6 solution of **4** exhibits the only one set of signals at 300 K. The ^{1}H NMR spectroscopy at various temperatures (range 300–170 K) proved the existence of the symmetrical arrangement of the central aluminum atom in **4**, because no decoalescence of the signals of CH_2O^tBu groups was observed.

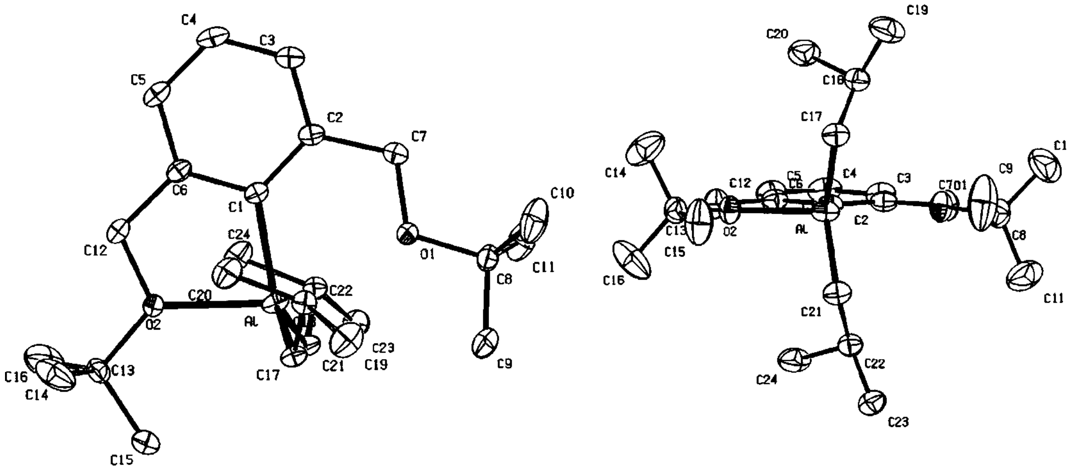
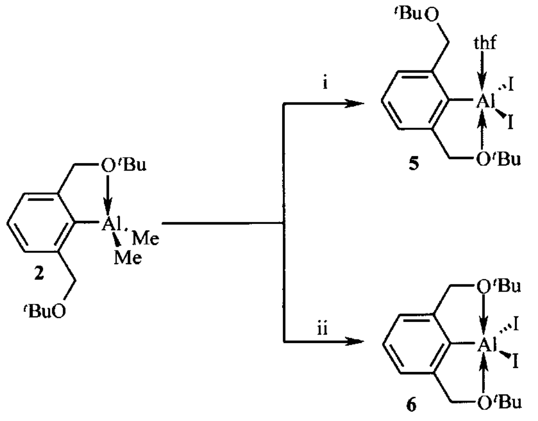


Figure 1. The view of one of the molecules in the structure of **3** and the view along the Al–C1–C4 axis. Displacement ellipsoids are drawn on a 50% probability level; H atoms are omitted for clarity. Selected bond distances (Å) and angles (deg) for **3**: Al–C1, 1.9616(19); Al–C17, 1.987(2); Al–C21, 1.986(2); Al–O1, 2.6137(15); Al–O2, 2.1237(15); C1–Al–C17, 116.53(8); C1–Al–C21, 117.34(8); C17–Al–C21, 123.11(9); C1–Al–O2, 81.68(7); C21–Al–O2, 102.84(8).

The reaction of **2** with I_2 in THF led to **5** [equation (3)].[41,42]



(3)

(i) 2 eq. I_2, THF; (ii) 2 eq. I_2, hexane

The ^{1}H and ^{13}C NMR data show the presence of non-equivalent CH_2O^tBu groups and the presence of one coordinated THF molecule. The value of the ^{27}Al chemical shift of **5** [$\delta(^{27}Al) = 120$ ppm] falls to the region of five coordinated aluminum and is comparable with those found in organoaluminum halides containing a Y,C,Y-chelating ligand.[28–32] The non-equivalence of the CH_2O^tBu groups is retained even at higher temperatures, where no coalescence of signals was observed at 350 K in toluene-d_8 solution of **5**. The same reaction in hexane resulted in yellow insoluble powder characterized as compound **6** (IR and elemental analysis). The attempt to solute compound **6** in THF leading to compound **5** failed. This can be result of two strong Al–O interactions in **6** precluding the coordination of THF molecule.

CONCLUSION

The organoaluminum alkyls containing O,C,O-chelating ligand have been prepared. The X-ray diffraction analysis showed that the aluminum atom is [4 + 1] coordinated with the *trans*-trigonal bipyramidal geometry in **3**. Solution NMR studies indicated the four coordinated aluminum atom and dissociation/association dynamic process in solution of **1–3**. Compound **2** was used for the preparation of the other derivatives with the O,C,O-chelating ligand (**4, 5** and **6**).

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REFERENCES

1. Gruter GJM, van Klink GPM, Akkerman OS, Bickelhaupt F. *Chem. Rev.* 1995; **95**: 2405.
2. Olazabal CA, Gabbaï FP, Cowley AH, Carrano CJ, Mokry LM, Bond M. *Organometallics* 1994; **13**: 421.
3. Cowley AH, Gabbaï FP, Atwood DA, Carrano CJ, Mokry LM, Bond MR. *J. Am. Chem. Soc.* 1994; **116**: 1559.
4. Contreras L, Cowley AH, Gabbaï FP, Jones R, Carrano CJ, Bond MR. *J. Organometall. Chem.* 1995; **489**: C1.
5. Cowley AH, Jones RA, Mardones MA, Ruiz J, Atwood JL, Bott S. *Angew. Chem.Int. Edn Engl.* 1990; **29**: 1150.
6. Schumann H, Hartmann U, Wassermann W, Dietrich A, Görlitz FH, Pohl L, Hostalek M. *Chem. Ber.* 1990; **19**: 3407.
7. Khan M, Steevensz RC, Tuck DG, Noltes JG, Corfield PWR. *Inorg. Chem.* 1980; **19**: 3407.
8. Coggin DK, Fanwick PE, Green MA. *J. Chem. Soc., Chem. Commun.* 1993; 1127.
9. Hair GS, Battle SL, Decken A, Cowley AH, Jones RA. *Inorg. Chem.* 2000; **39**: 27.
10. Ziegler K, Holzkamp E, Breil H, Martin H. *Angew. Chem.* 1955; **67**: 426.
11. Natta G, Pino P, Corradini P, Mantica E, Mazzanti G, Moraglio G. *J. Am. Chem. Soc.* 1955; **77**: 1708.
12. Schumann H, Wassermann BC, Heymer B, Keitsch M, Girsdies F. *Z. Anorg. Allg. Chem.* 2001; **627**: 1828.
13. Schumann H, Wassermann BC, Schutte S, Heymer B, Nickel S, Seuβ TD, Wernik S, Demtschuk J, Girgdies F, Weimann R. *Z. Anorg. Allg. Chem.* 2000; **626**: 2081.
14. Schumann H, Dechert S, Schutte S, Hyeon JY, Hummert M, Wassermann BC, Kaminsky W, Eisenhardt A, Köhler K, Eichhorn J. *Organometallics* 2003; **22**: 1391.
15. Eisenhardt A, Heuer B, Kaminsky W, Köhler K, Schumann H. *Adv. Synth. Catal.* 2003; **345**: 1299.
16. Jambor R, Dostál L, Růžička A, Císařová I, Brus J, Holeček J. *Organometallics* 2002; **19**: 3996.
17. Bahr G, Muller GE. *Chem. Ber.* 1955; **88**: 251.
18. Benn R, Janssen E, Lehmkuhl H, Rufinska A. *J. Organometall. Chem.* 1987; **333**: 155.
19. Benn R, Rufinska A. *Angew. Chem.* 1986; **96**: 851; *Angew. Chem.Int. Edn Engl.* 1986; **25**: 861.
20. Benn R, Rufinska A, Lehmkuhl H, Janssen E, Kruger C. *Angew. Chem.* 1983; **95**: 808.
21. *Angew. Chem. Int. Edn Engl.* 1983; **22**: 779.
22. Schumann H, Wassermann B, Schutte S, Heymer B, Nickel S, Seuβ TD, Wernik S, Demtschuk J, Girgsdies F, Weimann R. *Z. Anorg. Allg. Chem.* 2000; **626**: 2081.
23. Akitt JW. *Prog. NMR Spectrosc.* 1989; **21**: 1.
24. Handwerker H, Leis C, Probst R, Bassinger P, Grohmann A, Kiprof P, Herdtweek F, Blümel J, Auner N, Zybill C. *Organometallics* 1993; **12**: 2162.
25. Schumann H, Hartmann U, Wassermann BC. *Polyhedron* 1990; **9**: 353.
26. Gilbertson RD, Haley MM, Weakley TJR, Weiss H-C, Boese R. *Organometallics* 1998; **17**: 3105.
27. Francis JA, Bott SG, Barron AR. *J. Chem. Soc., Dalton Trans.* 1998; 3305.
28. Lin Ch-H, Ko B-T, Wang Fa-Ch, Lin Ch-Ch, Kuo Ch-Y. *J. Organometall. Chem.* 1999; **575**: 67.
29. Schumann H, Girgsdies F, Dechert S, Gottfriedsen J, Hummert M, Schutte S, Pickardt J. *Z. Anorg. Allg. Chem.* 2002; **628**: 2625.
30. Francis JA, McMahon CN, Bott SG, Barron AR. *Organometallics* 1999; **18**: 4399.
31. Hendershot DG, Barber M, Kumar R, Oliver JP. *Organometallics* 1991; **10**: 3302.
32. Lewinski J, Justyniak I, Horeglad P, Tratkiewicz E, Zachara J, Ochal Z. *Organometallics* 2004; **23**: 4430.
33. Pauling L. *The Nature of the Chemical Bond and The Structure of Molecules and Crystals*. Oxford University Press: Oxford, 1948.
34. Bondi A. *J. Phys. Chem.* 1964; **68**: 441.
35. Müller J, Schröder R, Wang R. *Eur. J. Inorg. Chem.* 2000; **153**.
36. Müller J, Englert U. *Chem. Ber.* 1995; **128**: 493.

37. Müller G, Lachmann J, Rufinska A. *Organometallics* 1992; **11**: 2970.
38. Böker Ch., Noltemeyer M, Gornitzka H, Kneisel BO, Teichert M, Irmer RH, Meller A. *Main Group Metall. Chem.* 1998; **21**: 565.
39. Contreras L, Cowley AH, Gabbaï FP, Jones RA, Carrano CJ, Bond MR. *J. Organometall. Chem.* 1995; **489**: C1.
40. Stender M, Segerer U, Sieler J, Hawkins EH. *Z. Anorg. Allg. Chem.* 1995; **624**: 85.
41. Schiefer M, Reddy ND, Roesky HW, Vidovic D. *Organometallics* 2003; **22**: 3637.
42. Schnitter C, Klimek K, Roesky HW, Albers T, Schmidt H-G, Röpken C, Parisini E. *Organometallics* 1998; **17**: 2249.