



Intramolecular C–H \cdots O hydrogen bond controlling the conformation of heterocycles: synthesis, structure and catalytic reactivity of aluminum aryloxides

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Abstract

The reactions of R_2AlX with one equivalent of 2,2'-methylene-bis-(4,6-di-*tert*-butylphenol) (MDBP- H_2) or 2,2'-methylene-bis-(4-methyl-6-*tert*-butylphenol) (MMBP- H_2) in oxygenated solvent afford monomeric four-coordinated compounds, $XAl(MDBP)(S)$, **1–5** (**1**: $R = Me$, $X = Br$, $S = Et_2O$; **2**: $R = Et$, $X = Cl$, $S = Et_2O$; **3**: $R = Me$, $X = Br$, $S = THF$; **4**: $R = Et$, $X = Cl$, $S = THF$; **5**: $R = X = Et$, $S = Et_2O$) or $XAl(MMBP)(S)$, **6–8** (**6**: $R = X = Et$, $S = Et_2O$; **7**: $R = X = tBu$, $S = Et_2O$; **8**: $R = Et$, $X = Cl$, $S = Et_2O$). Crystal structures of **1**, **2** and **7** demonstrate that the conformation of the eight-membered heterocycles containing aluminum is controlled by an unusual intramolecular C–H \cdots O hydrogen bond. Et_2AlCl or tBu_3Al reacts with one equivalent of 2,2'-ethylidene-bis-(4,6-di-*tert*-butylphenol) (EDBP- H_2) or MDBP- H_2 in toluene giving a dimeric four coordinate compound $[CLAL(\mu-EDBP)]_2$, **9** or $[tBuAl(\mu-MDBP)]_2$, **10**. Some of these compounds have shown great catalytic activities toward the reaction of cyclopentadiene with methacrolein. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Aluminum; Aryloxide; Hydrogen bond; Catalysis

1. Introduction

C–H \cdots X hydrogen bonds have been postulated to stabilize the geometries of many organic and inorganic compounds in the solid state [1]. The importance of C–H \cdots O interactions in aligning molecules of 1,3,5-trinitrobenzene has been examined by Desiraju and coworkers [2]. Eight-membered rings are very important structure components in zeolites [3]. 2,2'-methylene-bis-(4,6-di-*tert*-butylphenol) (MDBP- H_2) and 2,2'-ethylidene-bis-(4,6-di-*tert*-butylphenol) (EDBP- H_2) have the potential to form eight-membered heterocycles. The phosphorus derivatives of MDBP and EDBP have been reported extensively in the literature as stabilizers for polymeric substances [4] and $[(MDBP)AlMe]$ has been synthesized [4c]. The conformations of eight-membered heterocycles have been reviewed by Moore and Anet [5] in which the BC (boat–chair) conformation has been found in the phosphocin ring system [6]. The regioselective and stereose-

lective activities of aluminum alkoxides in organic synthesis are well documented [7]. Our recent interests have been directed towards the preparation and use of aluminum derivatives as Lewis acid for the catalysis of various reactions, such as Diels–Alder reactions [8]. Therefore, we present here the preparation and structural determination of a number of monomeric aluminum aryloxides. Their conformations of the eight-membered heterocycles are controlled by the C–H \cdots O hydrogen bond, which will be reported. The catalytic activities of these compounds toward Diels–Alder reactions will also be described.

2. Experimental

2.1. General

All manipulations were carried out under a dry nitrogen atmosphere. Solvents were dried by refluxing for at least 24 h over sodium/benzophenone (toluene, hexane, diethyl ether, tetrahydrofuran) or phosphorus pentaox-

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ide (CH_2Cl_2) and freshly distilled prior to use. Deuterated solvents (Aldrich) were dried over molecular sieves. AlMe_3 (2.0 M in toluene), AlCl_3 , AlBr_3 , Et_2AlCl (15% in hexane), Et_3Al (15% in hexane), $t\text{Bu}_3\text{Al}$ (0.58 M in hexane), methacrolein, 2,4-di-*tert*-butylphenol, 2,2'-ethylidene-bis-(4,6-di-*tert*-butylphenol) and 2,2'-methylene-bis-(4-methyl-6-*tert*-butylphenol) were purchased and used without further purification. 2,2'-methylene-bis-(4,6-di-*tert*-butylphenol) was prepared according to literature procedures [9]. Cyclopentadiene was freshly distilled before use. Melting points were determined with a Buchi 535 digital melting point apparatus. ^1H - and ^{13}C -NMR spectra were recorded on a Varian Mercury-400 (400 MHz), a Varian VXR-300S (300 MHz) or a Gemini-2000 (200 MHz) 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 Equinox 55 spectrometer.

2.1.1. (Diethyl ether)-bromo- $\{2,2'$ -methylene-bis(4,6-di-*tert*-butylphenato) $\}$ aluminum(III) (1)

To an ice-cold solution of AlBr_3 (0.54 g, 2 mmol) in toluene, AlMe_3 (2.0 M in toluene, 2.0 ml, 4 mmol) was added. The solution was stirred at 0°C for 20 min and was then transferred to an ice-cold ether solution containing 2,2'-methylene-bis(4,6-di-*tert*-butylphenol) (2.55 g, 6.0 mmol). This mixture was stirred for another 4 h and dried in vacuo to afford a white powder. Yield: 3.33 g (92%). Found: C, 65.31; H, 8.64. Anal. Calc. for $\text{C}_{33}\text{H}_{52}\text{AlO}_3\text{Br}$: C, 65.66; H, 8.68%. ^1H -NMR (CDCl_3 , ppm): δ 7.29 (d, 2H, Ph, $J_{\text{H-H}} = 2.4$ Hz), 7.16 (d, 2H, Ph, $J_{\text{H-H}} = 2.4$ Hz), 4.50 (br, 4H, $\text{CH}_2(\text{Et}_2\text{O})$), 3.93 (d, 1H, $J_{\text{H-H}} = 14.0$ Hz, CH_2 , closed to Al), 3.55 (d, 1H, $J_{\text{H-H}} = 14.0$ Hz, CH_2 , away from Al), 1.55 (br, 6H, $\text{CH}_3(\text{Et}_2\text{O})$), 1.41 (s, 18H, $t\text{Bu}$), 1.30 (s, 18H, $t\text{Bu}$). ^{13}C -NMR (CDCl_3 , ppm): 151.2, 141.1, 137.7, 129.4, 125.0, 122.4, (Ph), 69.9 (OCH_2CH_3), 33.4 (CH_2), 35.1, 34.1 ($t\text{Bu}$), 31.6, 30.2 (CH_3), 13.6 (OCH_2CH_3). IR (KBr, cm^{-1}): 2959.7(s), 2869.2(s), 1764.7(m), 1481.8(s), 1442.7(s), 1391.1(s), 1361.7(s), 1284.8(m), 1240.1(s), 934.0(s). M.p. 209°C (dec).

2.1.2. (Diethyl ether)-chloro- $\{2,2'$ -methylene-bis(4,6-di-*tert*-butylphenato) $\}$ aluminum(III) (2)

To an ice-cold solution (0°C) of 2,2'-methylene-bis(4,6-di-*tert*-butylphenol) (1.736 g, 4.0 mmol) in ether (20 ml), a Et_2AlCl (5.0 ml, 15% in hexane) solution was added slowly. After all of the latter solution was added, the mixture was stirred for 3 h and then dried in vacuo to give a white powder. Yield: 2.01 g (90%). Found: C, 70.81; H, 9.31. Anal. Calc. for $\text{C}_{33}\text{H}_{52}\text{AlO}_3\text{Cl}$: C, 70.88; H, 9.37%. ^1H -NMR (CDCl_3 , ppm): δ 7.31 (d, 2H, Ph, $J_{\text{H-H}} = 2.6$ Hz), 7.18 (d, 2H, Ph, $J_{\text{H-H}} = 2.6$ Hz), 4.55 (q, 4H, $\text{CH}_2(\text{Et}_2\text{O})$), 3.95 (d, 1H, $J_{\text{H-H}} = 13.8$ Hz, CH_2 , closed to Al), 3.55 (d, 1H, $J_{\text{H-H}} = 13.8$ Hz, CH_2 , away

from Al), 1.57 (t, 6H, $\text{CH}_3(\text{Et}_2\text{O})$), 1.42 (s, 18H, $t\text{Bu}$), 1.31 (s, 18H, $t\text{Bu}$). ^{13}C -NMR (CDCl_3 , ppm): 151.5, 141.2, 137.8, 129.6, 125.1, 122.5 (Ph), 69.9 (OCH_2CH_3), 33.2 (CH_2), 35.0, 34.1 ($t\text{Bu}$), 31.6, 30.0 (CH_3), 13.4 (OCH_2CH_3). IR (KBr, cm^{-1}): 2962.1(s), 2869.6(s), 1763.6(m), 1481.5(s), 1442.2(s), 1391.0(s), 1361.4(s), 1292.2(m), 1262.7(s), 932.9(s). M.p. 212°C (dec).

2.1.3. (Tetrahydrofuran)-bromo- $\{2,2'$ -methylene-bis(4,6-di-*tert*-butylphenato) $\}$ aluminum(III) (3)

To an ice-cold solution (0°C) of 2,2'-methylene-bis(4,6-di-*tert*-butylphenol) (0.848 g, 2.0 mmol) in THF (20 ml), a Me_2AlBr (0.66 mmol of AlBr_3 in toluene was added into 1.32 mmol of Me_3Al and then stirred for 30 min) solution was added slowly. After all of the solution was added, the mixture was stirred for 2.5 h and then dried in vacuo. The residue was extracted with 20 ml of THF and filtered. The filtrate was then concentrated to ca. 5 ml and cooled to 4°C to furnish colorless crystals. Yield: 1.10 g (92%). Found: C, 65.73; H, 8.56. Anal. Calc. for $\text{C}_{33}\text{H}_{50}\text{AlO}_3\text{Br}$: C, 65.88; H, 8.38%. ^1H -NMR (CDCl_3 , ppm): δ 7.27 (d, 2H, Ph, $J_{\text{H-H}} = 2.2$ Hz), 7.16 (d, 2H, Ph, $J = 2.2$ Hz), 4.36 (m, 4H, OCH_2CH_2), 3.96 (d, 1H, CH_2 , $J = 17.6$ Hz), 3.57 (d, 1H, CH_2 , $J = 17.6$ Hz), 2.16 (m, 4H, OCH_2CH_2); 1.41 (s, 18H, $t\text{Bu}$); 1.29 (s, 18H, $t\text{Bu}$). ^{13}C -NMR (CDCl_3 , ppm): δ 151.5, 141.0, 137.7, 129.2, 125.0, 122.3 (Ph), 70.7 (OCH_2CH_2), 35.1, 34.07, 31.6, 30.1 ($t\text{Bu}$), 33.8 (CH_2), 25.4 (OCH_2CH_2). IR (KBr, cm^{-1}): 2830.4(s), 1723.1(m), 1410.7(s), 1380.1(s), 1341.5(s), 1235.4(s), 1187.2(s), 1124.6(s), 1089.7(s), 1013.4(s), 975.3(s). M.p. 173°C (dec).

2.1.4. (Tetrahydrofuran)-chloro- $\{2,2'$ -methylene-bis(4,6-di-*tert*-butylphenato) $\}$ aluminum(III) (4)

To an ice-cold solution (0°C) of 2,2'-methylene-bis(4,6-di-*tert*-butylphenol) (0.848 g, 2.0 mmol) in THF (20 ml), a Et_2AlCl (2.8 ml, 15% in hexane, 2.4 mmol) solution was added slowly. After all of the solution was added, the mixture was stirred for 2.5 h and then dried in vacuo. The residue was extracted with 20 ml of THF and filtered. The filtrate was then concentrated to ca. 5 ml and cooled to 4°C to furnish colorless crystals. Yield: 1.00 g (90%). Found: C, 70.89; H, 9.00. Anal. Calc. for $\text{C}_{33}\text{H}_{50}\text{AlO}_3\text{Cl}$: C, 71.13; H, 9.04%. ^1H -NMR (CDCl_3 , ppm): δ 7.29 (d, 2H, Ph, $J_{\text{H-H}} = 2.6$ Hz), 7.16 (d, 2H, Ph, $J = 2.6$ Hz), 4.54 (m, 4H, OCH_2CH_2), 3.95 (d, 1H, CH_2 , $J = 14.4$ Hz), 3.55 (d, 1H, CH_2 , $J = 14.4$ Hz), 2.23 (m, 4H, OCH_2CH_2), 1.40 (s, 18H, $t\text{Bu}$); 1.29 (s, 18H, $t\text{Bu}$). ^{13}C -NMR (CDCl_3 , ppm): δ 151.5, 141.0, 137.8, 129.3, 125.0, 122.3 (Ph), 71.97 (OCH_2CH_2), 35.2, 34.1, 31.7, 30.0 ($t\text{Bu}$), 33.7 (CH_2), 25.4 (OCH_2CH_2). IR (KBr, cm^{-1}): 2854.9(s), 1763.2(m), 1453.6(s), 1389.7(s), 1356.5(s), 1267.9(s), 1201.3(s), 1175.8(s), 1137.2(s), 1041.4(s), 992.1(s). M.p. 177°C (dec).

2.1.5. (Diethyl ether)-ethyl- $\{2,2'$ -methylene-bis(4,6-di-*tert*-butylphenato) $\}$ aluminum(III) (5)

To an ice-cold solution (0°C) of 2,2'-methylene-bis(4,6-di-*tert*-butylphenol) (0.42 g, 1.0 mmol) in ether (10 ml), an AlEt₃ (1.4 ml, 15% in hexane) solution was added slowly. After all of the solution was added, the mixture was stirred for 2.5 h and then dried in vacuo. The residue was extracted with 15 ml of ether and filtered. The filtrate was then concentrated to ca. 8 ml and cooled to -20°C to furnish colorless crystals. Yield: 0.49 g (89%). Found: C, 75.74; H, 10.1. Anal. Calc. for C₃₅H₅₇AlO₃: C, 76.04; H, 10.39%. ¹H-NMR (CDCl₃, ppm): 7.10–7.30 (m, 4H, Ph), 4.30 (br, 4H, CH₂(Et₂O)), 4.05 (d, 1H, *J*_{H-H} = 13.6 Hz, CH₂), 3.42 (d, 1H, *J*_{H-H} = 13.6 Hz, CH₂), 1.45 (br, 6H, CH₃(Et₂O)), 1.38 (s, 18H, ^tBu), 1.29 (s, 18H, ^tBu), 1.17 (t, 3H, CH₃(EtAl)), 0.13 (q, 2H, CH₂(EtAl)). ¹³C-NMR (CDCl₃, ppm): 152.7, 139.9, 137.6, 130.1, 125.1, 122.0 (Ph), 67.4 (OCH₂CH₃), 35.0 (CH₂), 34.0, 33.4, 31.6, 29.7 (^tBu), 13.4 (OCH₂CH₃), 8.4 (CH₃CH₂Al), -2.6 (CH₃CH₂Al). IR (KBr, cm⁻¹): 2961.7(s, br), 1633.6(w), 1480.5(s), 1261.6(s), 1097.4(s), 1023.1(s), 800.8(s). M.p. 193°C (dec).

2.1.6. (Diethyl ether)-ethyl- $\{2,2'$ -methylene-bis(4-methyl-6-*tert*-butylphenato) $\}$ aluminum(III) (6)

To an ice-cold solution (0°C) of 2,2'-methylene-bis(4-methyl-6-*tert*-butylphenol) (0.34 g, 1.0 mmol) in ether (10 ml), an AlEt₃ (1.4 ml, 15% in hexane) solution was added slowly. After all of the solution was added, the mixture was stirred for 2.5 h and then dried in vacuo. The residue was extracted with 15 ml of ether and filtered. The filtrate was then concentrated to ca. 8 ml and cooled to -20°C to furnish colorless crystals. Yield: 0.39 g (84%). Found: C, 74.40; H, 9.81. Anal. Calc. for C₂₉H₄₁AlO₃: C, 74.32; H, 9.68%. ¹H-NMR (CDCl₃, ppm): 6.80–7.10 (m, 4H, Ph), 4.30 (br, 4H, CH₂(Et₂O)), 4.00 (d, 1H, *J*_{H-H} = 13.6 Hz, CH₂), 3.35 (d, 1H, *J*_{H-H} = 13.6 Hz, CH₂), 2.24 (s, 6H, CH₃Ph), 1.44 (br, 6H, CH₃(Et₂O)), 1.36 (s, 18H, ^tBu), 1.17 (t, 3H, CH₃(EtAl)), 0.13 (q, 2H, CH₂(EtAl)). ¹³C-NMR (CDCl₃, ppm): 152.6, 138.3, 130.5, 128.8, 126.7, 125.6 (Ph), 67.7 (OEt₂), 34.8 (CH₂), 33.0, 29.8 (^tBu), 20.9 (CH₃), 13.8 (OEt₂), 8.7 (EtAl), -2.4 (EtAl). IR (KBr, cm⁻¹): 2962.4(s, br), 1478.2(s), 1443.5(s), 1391.3(s), 1303.6(s), 879.7(s, br), 802.3(m). M.p. 192°C (dec).

2.1.7. (Diethyl ether)-isobutyl- $\{2,2'$ -methylene-bis(4-methyl-6-*tert*-butylphenato) $\}$ aluminum(III) (7)

To an ice-cold (0°C) solution of 2,2'-methylene-bis(4-methyl-6-*tert*-butylphenol) (0.68 g, 2 mmol) in ether (50 ml), (^tBu)₃Al (0.58 M in hexane, 4.0 ml, 2.3 mmol) was added slowly. After all of the latter solution was added, the mixture was stirred for 2 h and then was dried under vacuum. The residue was extracted with 50 ml of diethyl ether and concentrated to ca. 20 ml and

cooled to 4°C. Colorless crystals were obtained after 24 h. Yield: 0.91 g (91%). Found: C, 74.52; H, 9.89. Anal. Calc. for C₃₁H₄₉AlO₃: C, 74.96; H, 9.94%. ¹H-NMR (CDCl₃, ppm): δ 7.30 (d, 2H, Ph, *J* = 2.2 Hz), 6.89 (d, 2H, Ph, *J* = 2.2 Hz), 4.35 (br, 4H, OCH₂CH₃), 4.02 (d, 1H, CH₂, *J* = 14.2 Hz), 3.38 (d, 1H, CH₂, *J* = 14.2 Hz); 2.23 (s, 6H, CH₃), 2.01(m, 1H, AlCH₂CH(CH₃)₂), 1.43 (t, 6H, OCH₂CH₃), 1.37 (s, 18H, C(CH₃)₃), 1.02 (d, 6H, AlCH₂CH(CH₃)₂, *J* = 7.0 Hz), 0.24 (d, 2H, AlCH₂CH(CH₃)₂, *J* = 7.0 Hz) ¹³C-NMR (CDCl₃, ppm): 152.7, 138.3, 130.4, 128.8, 126.7, 125.6 (Ph), 67.6 (OCH₂CH₃), 33.1, 32.6 (^tBu), 34.8 (-CH₂-), 20.8 (PhCH₃), 13.5 (OCH₂CH₃), 29.8 (AlCH₂CH(CH₃)₂), 28.4 (AlCH₂CH(CH₃)₂), 25.4 (AlCH₂CH(CH₃)₂). IR (KBr, cm⁻¹): 2952.3(br, m), 2861.4(br, m), 1475.5(br, m), 1438.8(br, m), 1389.7(s), 1306.4(w), 1278.9(w), 1149.4(m), 1011.8(s), 926.8(br, w), 892.2(s). M.p. 196–200°C (dec).

2.1.8. (Diethyl ether)-chloro- $\{2,2'$ -methylene-bis(4-methyl-6-*tert*-butylphenato) $\}$ aluminum(III) (8)

To an ice-cold solution (0°C) of 2,2'-methylene-bis(4-methyl-6-*tert*-butylphenol) (1.76 g, 4.0 mmol) in ether (20 ml), an Et₂AlCl (5.0 ml, 15% in hexane) solution was added slowly. After all of the solution was added, the mixture was stirred for 3 h and then dried in vacuo to give a pale yellow powder. Yield: 1.50 g (85%). Found: C, 67.77; H, 8.46. Anal. Calc. for C₂₇H₄₀AlO₃Cl: C, 68.27; H, 8.49%. ¹H-NMR (CDCl₃, ppm): δ 7.07 (d, 2H, Ph, *J* = 2.2 Hz), 6.95 (d, 2H, Ph, *J* = 2.2 Hz), 4.49 (br, 4H, CH₂(Et₂O)), 3.91 (d, 1H, *J*_{H-H} = 14.2 Hz, CH₂), 3.48 (d, 1H, *J*_{H-H} = 14.2 Hz, CH₂), 2.26 (s, 6H, CH₃Ph), 1.53 (t, 6H, CH₃(Et₂O)), 1.40 (s, 18H, ^tBu). ¹³C-NMR (CDCl₃, ppm): 151.6, 139.0, 130.0, 128.9, 128.1, 126.2 (Ph), 70.2 (OEt₂), 34.7 (CH₂), 32.8, 29.8 (^tBu), 20.7 (CH₃), 13.8 (OEt₂). IR (KBr, cm⁻¹): 2950.2(s), 2914.6(sh), 2869.5(m), 1477.6(s), 1439.1(s), 1303.7(s), 1278.0(s), 1005.2(m), 929.6(m), 769.5(m). M.p. 216°C (dec).

2.1.9. Chloro- $\{2,2'$ -ethylidene-bis(4,6-di-*tert*-butylphenato) $\}$ aluminum(III) (9)

To an ice-cold solution (0°C) of 2,2'-ethylidene-bis(4,6-di-*tert*-butylphenol) (1.76 g, 4.0 mmol) in hexane (30 ml), a Et₂AlCl (5.0 ml, 15% in hexane) solution was added slowly. After all of the latter solution was added, the mixture was stirred for 3 h and then dried in vacuo. The residue was dissolved in hot toluene (30 ml). The hot toluene extraction was allowed to cool to room temperature (r.t.) affording colorless crystals. Yield: 1.60 g (86%). Found: C, 72.16; H, 8.81. Anal. Calc. for C₃₀H₄₄AlClO₂: C, 72.19; H, 8.89%. ¹H-NMR (CDCl₃, ppm): δ 7.16–7.46 (m, 4H, Ph), 4.67 (q, 1H, CH(CH₃), *J* = 7.2 Hz); 1.83 (d, 3H, CH(CH₃), *J* = 6.8 Hz); 1.49, 1.35, 1.31, 1.24 (s, 36H, C(CH₃)₃); ¹³C-NMR (CDCl₃,

ppm): δ 149.1, 148.1, 142.5, 141.6, 139.7, 137.5, 137.0, 133.4, 124.9, 124.7, 121.8, 120.2 (Ph), 36.4, 35.0, 34.7, 34.6, 33.13, 31.9, 31.3, 30.6 (*t*Bu), 33.06 (CHCH₃), 22.0 (CHCH₃). IR (KBr, cm⁻¹): 2961.9(s), 2907.9(sh), 2870.1(m), 1600.0(w), 1474.8(s), 1443.8(s), 1361.8(s), 1305.3(s), 1236.8(m), 1086.8 (m). M.p. 119°C (dec).

2.1.10. Isobutyl- $\{2,2'$ -methylene-bis(4,6-di-*tert*-butyl-phenato) $\}$ aluminum(III) (**10**)

To an ice-cold (0°C) solution of 2,2'-methylene-bis(4,6-di-*tert*-butyl-phenol) (0.85 g, 2 mmol) in toluene (40 ml), (*t*Bu)₃Al (0.58 M in hexane, 4.0 ml, 2.0 mmol) was added slowly. After all of the latter solution was added, the mixture was stirred for 2 h and was then dried under vacuum to give a white powder. The residue was extracted with 40 ml of hot toluene and then concentrated to ca. 30 ml and cooled to 25°C. Colorless crystals were obtained after 24 h. Yield: 0.96 g (95%). Found: C, 78.77; H, 9.86. Anal. Calc. for C₆₆H₁₀₂Al₂O₄· $\frac{1}{2}$ C₇H₈: C, 78.78; H, 10.08%. ¹H-NMR (CDCl₃): δ 7.24–7.14 (m, 6.5H, Ph and PhCH₃), 4.50 (d, 1H, *J* = 14.0 Hz), 3.62 (d, 1H, *J* = 14.0 Hz), 2.36 (s, 3H, PhCH₃), 2.08 (m, 1H, AlCH₂CH(CH₃)₂), 1.40 (s, 18H, C(CH₃)₃), 1.32 (s, 18H, C(CH₃)₃), 0.84 (d, 6H, AlCH₂CH(CH₃)₂, *J* = 6.6 Hz), 0.38 (d, 2H, AlCH₂CH(CH₃)₂, *J* = 6.6 Hz). ¹³C-NMR (CDCl₃, ppm): 151.2, 147.2, 144.1, 140.1, 137.3, 132.9, 130.3, 128.6, 126.7, 125.3, 124.8, 122.2, (Ph and PhCH₃), 37.0, 35.9, 35.0, 34.3, 34.2, 32.6, 31.2, 30.1 (*t*Bu), 31.6 (PhCH₃), 29.0 (CH₂), 25.9, 24.6, 21.5 (Al*t*Bu). IR (KBr, cm⁻¹): 2940.1(br), 2871.0(br), 1473.5(br), 1415.3(br), 1362.4(s), 1292.2(br), 1243.4(s), 1201.6(s), 1134.3(s), 1097.6(s), 929.6(br), 882.3(s). M.p. 125–127°C (dec).

2.2. X-ray crystallographic studies

Suitable crystals of **1**, **2**, **7** and **9** were sealed in thin-walled glass capillaries under a 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 at least 25 randomly selected reflections in the 2θ range of 4–28°. 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 [10]. All non-H atoms and hydrogen atoms attached to the carbon bridging two phenyl rings were located from successive Fourier maps. Other H atoms were refined using a riding model [10,11]. Anisotropic thermal parameters were used for all non-H atoms, and fixed isotropic parameters were used for H atoms. The crystallographic data of **1**, **2**, **7** and **9** are summarized in Table 1.

2.3. Typical experiment for catalytic reactions

To a solution of **3** (0.02 g, 0.04 mmol) in CDCl₃ (1 ml) was added methacrolein (0.034 ml, 0.4 mmol) followed by the addition of cyclopentadiene (0.036 ml, 0.48 mmol). The reaction mixture was stirred for 10 min at r.t. Conversion yield and *exo:endo* ratio were determined by ¹H-NMR spectroscopic studies based on the integration in the aldehyde region.

3. Results and discussion

3.1. Syntheses and spectroscopic studies

The reactions of R₂AlX with one equivalent of 2,2'-methylene-bis(4,6-di-*tert*-butylphenol) (MDBP-H₂) in an oxygenated solvent afford monomeric four-coordinated compounds, XAl(MDBP)(S), **1–5** (**1**: R = Me, X = Br, S = Et₂O; **2**: R = Et, X = Cl, S = Et₂O; **3**: R = Me, X = Br, S = THF; **4**: R = Et, X = Cl, S = THF; **5**: R = X = Et, S = Et₂O) or with 2,2'-methylene-bis(4-methyl-6-*tert*-butylphenol) (MMBP-H₂) in diethyl ether yield XAl(MMBP)(S) **6–8** (**6**: R = X = Et, S = Et₂O; **7**: R = X = *t*Bu, S = Et₂O; **8**: R = Et, X = Cl, S = Et₂O) in moderate to high yield as shown in Scheme 1. ¹H-NMR spectra of **1–8** are listed in Table 2. The spectra of **1–8** illustrate that the C-7 (carbon bridging two phenyl rings) protons of these compounds are chemically nonequivalent (AB pattern) in which one proton is bending away from Al and another is closed to Al. However, the observation of two singlet peaks for these four *tert*-butyl groups in the NMR spectra of **1–5** and two equivalent peaks of both *tert*-butyl and methyl substituents in the NMR spectra of **6–8** requires that a σ plane of symmetry pass through the C-7 methylene carbon and the aluminum atom. The ¹H-NMR spectrum of **5** demonstrates two doublet resonances at δ 4.05 and 3.42 ppm with the magnitude of the two-bond geminal coupling constant of ²*J*_{HCH} = 13.6 Hz indicating nonequivalence of the C-7 methylene protons. It is similar to the result observed for the previously reported trivalent phosphorus compounds with the same conformation [12] and [(MDBP)AlMe] [13]. In order to distinguish these two methylene protons (H_a and H_b) on the methylene group as shown in Scheme 2, a nuclear Overhauser effect difference spectroscopy of **5** is performed, which demonstrates two positive hydrogen signals of H(5)/H(9) (7.28 ppm) and of H_a (4.05 ppm) and a negative hydrogen signal of H(14) (4.30 ppm, ether) upon irradiation of H_b (3.42 ppm) indicating that H_a is closed to the Al center and H_b is away from Al. A negative signal for methylene protons may indicate the fluctuation of Et₂O in solution, which is consistent with the results observed in the VT-NMR spectroscopic studies of compound **5**. The unexpected down field of

Table 1
Crystallographic data of complexes **1**, **2**, **7** and **9**

	1 ·½Et ₂ O	2 ·½Et ₂ O	7	9 ·C ₇ H ₈
Formula	C ₃₅ H ₅₇ AlBrO _{3.5}	C ₃₅ H ₅₇ AlClO _{3.5}	C ₃₁ H ₄₉ AlO ₃	C ₃₇ H ₅₂ AlClO ₂
<i>F</i> _w	640.7	596.2	496.7	591.3
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	15.917(3)	15.960(3)	9.286(1)	18.093(5)
<i>b</i> (Å)	19.165(2)	19.079(2)	22.601(2)	9.815(3)
<i>c</i> (Å)	25.255(4)	25.281(4)	14.997(2)	19.795(6)
β (°)	100.91(2)	100.79(2)	98.91(2)	99.61(2)
<i>V</i> (Å ³)	7565(2)	7563(2)	3109.5(8)	3466(2)
<i>Z</i>	8	8	4	4
<i>D</i> _{calc} (Mg m ⁻³)	1.125	1.047	1.061	1.133
Absorption coefficient (mm ⁻¹)	1.140	0.154	0.092	0.165
2θ Range (°)	4–45	4–48	3.5–45	3.5–43
Scan type	2θ–θ	2θ–θ	2θ–θ	2θ–θ
Reflections collected	10193	12186	4277	4080
Observed reflections	4689 (<i>F</i> > 3.0σ(<i>F</i>))	4622 (<i>F</i> > 5.0σ(<i>F</i>))	2981 (<i>F</i> > 4.0σ(<i>F</i>))	2493 (<i>F</i> > 4.0σ(<i>F</i>))
No. of refined parameters	730	730	316	397
<i>R</i> ^a for significant reflections	0.0714	0.0721	0.0587	0.0689
<i>R</i> _w ^b for significant reflections	0.0728	0.0776	0.0649	0.0720
Goodness-of-fit ^c	1.30	1.83	1.85	1.86

$$^a R = \frac{|\sum(|F_o - F_c|)/\sum|F_o||}{\sum|F_o|}$$

$$^b R_w = \frac{|\sum w(|F_o - F_c|)/\sum w|F_o||}{\sum w|F_o|}, w = 1/[\sigma^2(F) + 0.002F^2] \text{ for } \mathbf{1}, w = 1/[\sigma^2(F) + 0.001F^2] \text{ for } \mathbf{2}, \mathbf{7} \text{ and } \mathbf{9}.$$

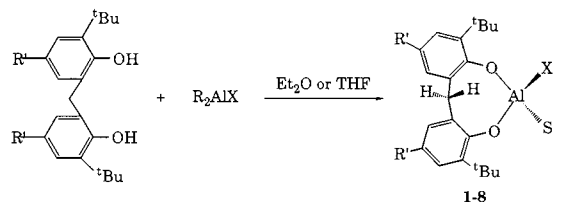
$$^c \text{Goodness-of-fit} = [\sum w(|F_o| - |F_c|)^2 / (N_{ref} \ln s - N_{params})]^{1/2}.$$

H_a relative to H_b is believed resulting from the interaction of H(7a) with the oxygen atom of Et₂O/THF. The result is verified by a short C–H···O distance in crystallographic studies. R₂AlX reacts with one equivalent of EDBP-H₂ or MDBP-H₂ in toluene giving a dimeric four coordinate compound [CLAL(μ-EDBP)]₂, **9** or [tBuAl(μ-MDBP)]₂, **10** as shown in Scheme 3. ¹H-NMR spectra of **9**–**10** show four sets of tBu group signals indicating nonequivalence of tBu groups. The result is consistent with the dimerism of these compounds, which has been verified by single-crystal structure determination.

3.2. Molecular structures of **1**, **2**, **7** and **9**

The molecular structures of **1** and **2** are shown in Fig. 1. The selected bond distances and bond angles of **1** and **2** are summarized in Table 3 and Table 4, respectively. Compound **1** crystallizes in the space group *P*2₁/*n*. There are two independent molecules with similar geometry in an asymmetric unit. The geometry around Al(1) is a distorted tetrahedral with the Al–O(1) (alkoxy oxygen) distance of 1.690(6), Al(1)–O(2) distance of 1.678(6), Al(1)–O(3) (etheral oxygen) distance of 1.832(9) and Al(1)–Br(1) distance of 2.263(3) Å. The distance of O(3)–H(7a) 2.347 and O(6)–H(47a) 2.423 Å and the angles of 171.2 and 151.6°, respectively. Al(1), O(3), C(34), C(35) are almost coplanar with the deviation of 0.0387 Å. The total angle around O(3) of 359.4° and the coplanarity of Al(1)O(3)C(34)C(35) indicate a

sp² hybridization feature of O(3). It is interesting to note that a weak hydrogen bonding may exist between the etheral oxygen and one of the C-7 protons for two reasons. First, the distances of O(3)–H(7a), 2.347 and O(6)–H(47a), 2.423 Å are smaller than the summation

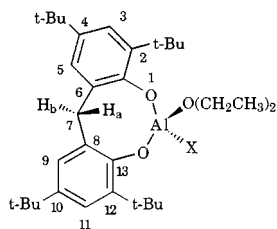


- 1**: X = Br, R = Me, R' = tBu, S = Et₂O; **2**: X = Cl, R = Et, R' = tBu, S = Et₂O
3: X = Br, R = Me, R' = tBu, S = THF; **4**: X = Cl, R = Et, R' = tBu, S = THF
5: X = R = Et, R' = tBu, S = Et₂O; **6**: X = R = Et, R' = Me, S = Et₂O;
7: X = R = tBu, R' = Me, S = Et₂O; **8**: X = Cl, R = Et, R' = Me, S = Et₂O

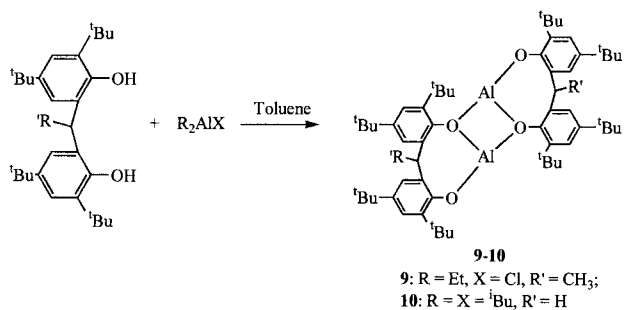
Scheme 1.

Table 2
¹H-NMR data (in ppm) for compounds **1**–**8**

	CH ₂ (closed to Al)	CH ₂ (away from Al)	CH ₃ (methyl)	CH ₃ (tBu)
1	3.93(d)	3.55(d)	–	1.41, 1.30
2	3.95(d)	3.55(d)	–	1.42, 1.31
3	3.96(d)	3.57(d)	–	1.41, 1.29
4	3.95(d)	3.55(d)	–	1.40, 1.29
5	4.05(d)	3.42(d)	–	1.45, 1.38
6	4.00(d)	3.35(d)	2.24	1.36
7	4.02(d)	3.38(d)	2.23	1.37
8	3.91(d)	3.48(d)	2.26	1.40



Scheme 2.



Scheme 3.

of the van der Waals radius for O and H [14]. Second, C(7)–H(7a)–O(3) angle of 171.2 and C(47)–H(47a)–O(6) angle of 151.6° are almost linear. Al(1), O(3), Br(1), and C(7) are almost coplanar with a deviation of 0.0024 Å. The conformational properties of eight-membered ring molecules have been reviewed [5]. Five different conformations of eight-membered heterocycles have been reported in which the BC conformation is considered the most stable form in the cyclooctane case as shown in Fig. 2. The BC conformation is chosen in order to explain both the nonequivalence of the C-7 methylene protons and the observation of two equivalent *tert*-butyl substituents. However, a distorted BC conformation is observed in which Al(1) is coplanar with C(1)C(13)O(1)O(2) because of the interaction of H(7a) with O(3) as shown in Fig. 3. The torsion angle between the Al(1)O(3)Br(1)C(7) plane and two phenyl rings is 61.8 and 54.6°, respectively. The difference Fourier maps of **1** reveal the presence of five peaks that are not within bonding distances of aluminum complexes. Examination of the bond distances and peaks leads to a conclusion for the existence of a free ether molecule in an asymmetric unit. The molecular structure of **2** is similar to that of compound **1** except that bromide is replaced by chloride. The geometry around Al(1) is a distorted tetrahedral with an Al–O(1) (alkoxy oxygen) distance of 1.695(5), an Al(1)–O(2) distance of 1.681(5) and an Al(1)–O(3) (ethereal oxygen) distance of 1.830(6) Å. The distances of O(3)–H(7a) and O(6)–H(47a) are 2.407 and 2.393 Å, respectively, indicating the existence of hydrogen bonding.

The ORTEP of **7** is illustrated in Fig. 4. Selective bond distances and bond angles are listed in Table 5. Compound **7** is a distorted tetrahedral around Al with Al–O(1), Al–O(2), Al–O(3) and Al–C(24) having bond distances of 1.717(3), 1.711(3), 1.888(2) and 1.945(4) Å, respectively. All of these distances are somewhat longer than those of **1** and **2**. A comparison of the average bond distances (Å) and bond angles (°) of **1**, **2** and **7** is given in Table 6. The result is consistent with the better

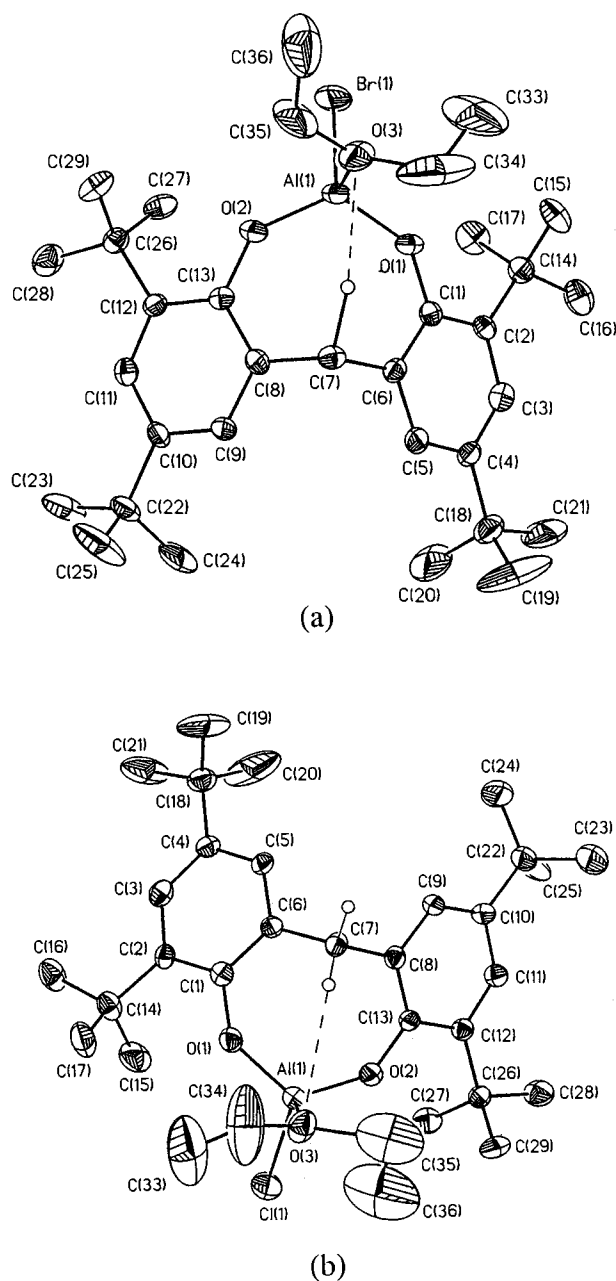


Fig. 1. Molecular structures of (a) [AlBr(MDBP)(Et₂O)] (**1**), (b) [AlCl(MDBP)(Et₂O)] (**2**). Hydrogen atoms except H(7a) are omitted for clarity.

Table 3
Selective bond distances (Å) and bond angles (°) of **1**

Al(1)–Br(1)	2.263(3)	Al(1)–O(1)	1.690(6)
Al(1)–O(2)	1.678(6)	Al(1)–O(3)	1.832(9)
Al(2)–Br(2)	2.279(3)	Al(2)–O(4)	1.693(6)
Al(2)–O(5)	1.682(5)	Al(2)–O(6)	1.849(7)
Br(1)–Al(1)–O(1)	111.3(2)	Br(1)–Al(1)–O(2)	110.4(2)
O(1)–Al(1)–O(2)	119.7(3)	Br(1)–Al(1)–O(3)	103.8(3)
O(1)–Al(1)–O(3)	103.4(3)	O(2)–Al(1)–O(3)	106.6(3)
Al(1)–O(1)–C(1)	142.6(6)	Al(1)–O(2)–C(13)	140.5(5)
Al(1)–O(3)–C(34)	125.6(8)	Al(1)–O(3)–C(35)	121.9(8)
Br(2)–Al(2)–O(4)	111.6(2)	Br(2)–Al(2)–O(5)	110.4(2)
O(4)–Al(2)–O(5)	120.5(3)	Br(2)–Al(2)–O(6)	103.5(3)
O(4)–Al(2)–O(6)	103.7(3)	O(5)–Al(2)–O(6)	105.4(3)
Al(2)–O(4)–C(41)	137.8(5)	Al(2)–O(5)–C(53)	143.7(5)
Al(2)–O(6)–C(74)	125.3(9)	Al(2)–O(6)–C(75)	122.6(8)

Table 4
Selective bond distances (Å) and bond angles (°) of **2**

Al(1)–Cl(1)	2.118(3)	Al(1)–O(1)	1.695(5)
Al(1)–O(2)	1.681(5)	Al(1)–O(3)	1.830(6)
Al(2)–Cl(2)	2.112(4)	Al(2)–O(4)	1.695(6)
Al(2)–O(5)	1.688(5)	Al(2)–O(6)	1.841(7)
Cl(1)–Al(1)–O(1)	112.2(2)	Cl(1)–Al(1)–O(2)	111.0(2)
O(1)–Al(1)–O(2)	119.2(3)	Cl(1)–Al(1)–O(3)	103.6(2)
O(1)–Al(1)–O(3)	103.5(3)	O(2)–Al(1)–O(3)	105.5(3)
Al(1)–O(1)–C(1)	138.8(4)	Al(1)–O(2)–C(13)	144.6(5)
Al(1)–O(3)–C(34)	125.6(8)	Al(1)–O(3)–C(35)	122.5(7)
Cl(2)–Al(2)–O(4)	110.4(2)	Cl(2)–Al(2)–O(5)	112.2(2)
O(4)–Al(2)–O(5)	119.2(3)	Cl(2)–Al(2)–O(6)	103.9(3)
O(4)–Al(2)–O(6)	105.8(3)	O(5)–Al(2)–O(6)	103.7(3)
Al(2)–O(4)–C(41)	140.3(4)	Al(2)–O(5)–C(53)	142.6(5)
Al(2)–O(6)–C(74)	122.0(7)	Al(2)–O(6)–C(75)	125.8(6)

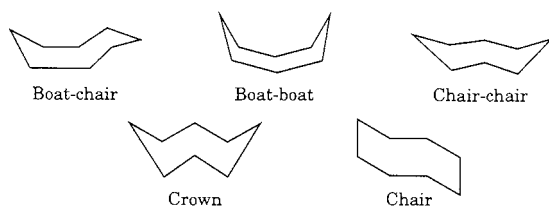


Fig. 2. Possible conformations of eight-membered rings.

electron-withdrawing group of Cl[−] or Br[−] than ^tBu group. The O(3)–H(a) distance of 2.446 Å is within the range for a C–H⋯O hydrogen bond and the angle for C(7)–H(7a)–O(3) of 156.0° is almost linear, also indicating the existence of C–H⋯O hydrogen bonds. The molecular structure of **9** is illustrated in Fig. 5. Selective bond distances and bond angles are listed in Table 7. Complex **9** demonstrates a dimeric feature with the geometry around Al being tetrahedral in which one of

Table 5
Selective bond distances (Å) and bond angles (°) of **7**

Al(1)–O(1)	1.717(3)	Al(1)–O(2)	1.711(3)
Al(1)–O(3)	1.888(2)	Al(1)–C(24)	1.945(4)
O(1)–Al(1)–O(2)	115.8(1)	O(1)–Al(1)–O(3)	100.6(1)
O(2)–Al(1)–O(3)	103.6(1)	O(1)–Al(1)–C(24)	114.6(1)
O(2)–Al(1)–C(24)	110.6(1)	O(3)–Al(1)–C(24)	110.5(1)
Al(1)–O(1)–C(1)	140.1(2)	Al(1)–O(2)–C(13)	146.5(2)
Al(1)–O(3)–C(32)	122.7(2)	Al(1)–O(3)–C(33)	122.5(2)
C(32)–O(3)–C(33)	114.8(3)		

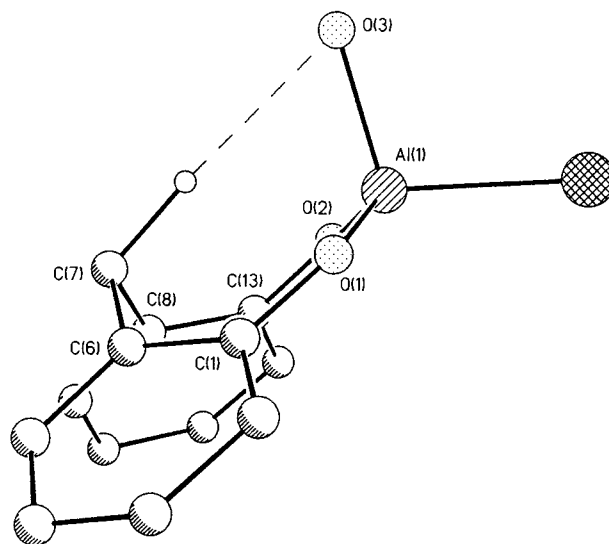


Fig. 3. Coplanarity of Al(1)O(1)O(2)C(13)C(1) is due to the interaction of O(3) with H(7a).

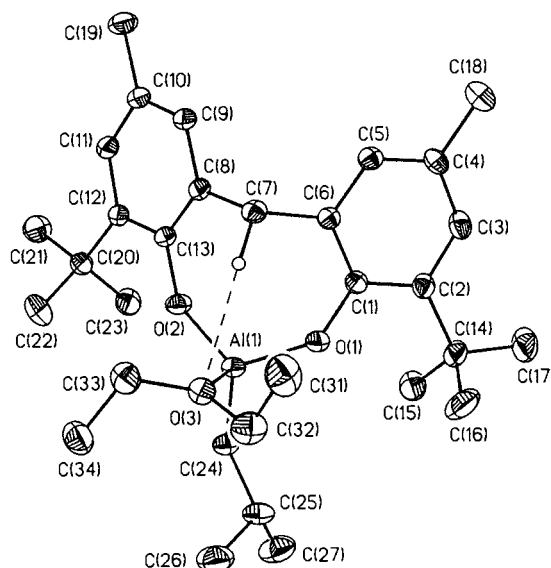


Fig. 4. Molecular structure of [^tBuAl(MMBP)(Et₂O)] (**7**). Hydrogen atoms except H(7a) are omitted for clarity.

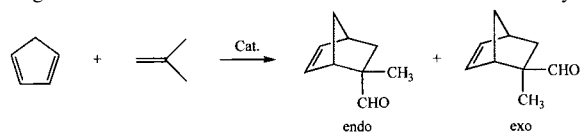
Table 6
Comparison of the average bond distances (Å) and bond angles (°) of **1**, **2** and **7**

Compounds	1	2	7
Al–O (aryloxyde)	1.686(6)	1.690(6)	1.714(3)
Al–O (ethereal)	1.841(9)	1.836(7)	1.888(2)
H–O (ethereal)	2.385	2.400	2.446
C–H–O (ethereal)	161.4	153.0	156.9

Table 7
Selective bond distances (Å) and bond angles (°) of **9**

Al–Cl	2.060(3)	Al–O(1)	1.826(4)
Al–O(2)	1.637(4)	Al–O(1A)	1.817(4)
Cl–Al–O(1)	119.0(2)	Cl–Al–O(2)	108.1(2)
O(1)–Al–O(2)	113.1(2)	Cl–Al–O(1A)	111.0(1)
O(1)–Al–O(1A)	81.1(2)	O(2)–Al–O(1A)	123.1(2)
Al–O(1)–C(1)	121.0(3)	Al–O(2)–C(13)	157.3(4)

Table 8
Regioselective Diels–Alder reactions of methacrolein with cyclopentadiene catalyzed by aluminum aryloxides



Entry	Catalyst	Temperature	Time	Conversion ^a (%)	<i>exo:endo</i> ^a
1	–	r.t.	20 h	7	72:28
2	3	r.t.	10 min	99	84:16
3	3	r.t.	1 h	>99	84:16
4	4	r.t.	10 min	99	82:18
5	4	r.t.	1 h	>99	82:18
6	7	r.t.	10 min	83	91:9
7	7	r.t.	1 h	92	91:9
8	7	0°C	10 min	62	92:8
9	7	0°C	1 h	90	93:7
10	10	r.t.	10 min	83	90:10
11	10	r.t.	1 h	96	90:10
12	10	0°C	10 min	79	90:10
13	10	0°C	1 h	91	90:10

^a Conversion yield and *exo:endo* ratio are determined by ¹H-NMR spectroscopic studies.

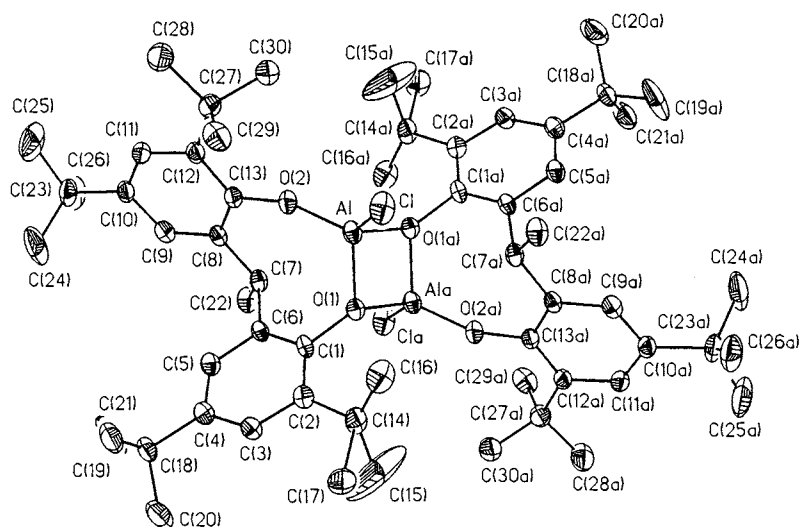


Fig. 5. Molecular structure of $[AlCl(\mu\text{-EDBP})_2]$ (**9**). Hydrogen atoms are omitted for clarity.

the phenoxides is used as a bridging ligand. The distance between Al and the terminal oxygen, Al–O(2) of 1.637(4) Å is shorter than the distance between Al and the bridging oxygens, Al–O(1) and Al–O(1a), of 1.826(4) and 1.817(4) Å, respectively. A disordered toluene molecule is observed in an asymmetric unit.

3.3. Catalytic Diels–Alder reactions

Variable-temperature $^1\text{H-NMR}$ spectroscopic studies demonstrate that ether is fluxional in solution. The fluxionality of solvent is required in the catalytic system. Compounds **3**, **4**, **7** and **10** are active catalysts for the Diels–Alder reaction between methacrolein and cyclopentadiene. The most representative results are summarized in Table 8. A 10% catalyst to methacrolein and 1.2:1 cyclopentadiene:methacrolein was used in all cases. Regioselectivities up to 93:7 of *exo:endo* were observed accompanied by the greatly enhanced reaction rate. The greater catalytic activities of **3–4** than **7** are consistent with the higher acidity of chloride and bromide derivatives than their *t*Bu analogs. The catalytic process is probably starting with the loss of a diethyl ether or THF from aluminum derivatives followed by the addition of methacrolein through the oxygen.

4. Supplementary material

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.

Acknowledgements

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