

# Influence of alkoxy ligands on the Cp–Al bonding mode in $[\text{Cp}_2\text{Al}-\mu\text{-OR}]_2$ from X-ray crystallographic and $^{27}\text{Al}$ -NMR spectroscopic solution studies

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## Abstract

The dicyclopentadienylaluminium alkoxides of general formula  $[\text{Cp}_2\text{Al}-\mu\text{-OR}]_2$  where R = Me, Et, *n*-Bu, *i*-Bu,  $\text{CH}_2t\text{-Bu}$ , *s*-Bu,  $\text{CH}_2\text{Ph}$ ,  $\text{C}_6\text{H}_4\text{-4-}t\text{-Bu}$  (**1–8**) were prepared by reacting CpNa with  $\text{ROAlCl}_2$  at the molar ratio 2:1, respectively (**2–8**) or from the reaction of  $\text{Cp}_3\text{Al}$  with alcohol (**1**). The compounds were characterised by multinuclear NMR ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{27}\text{Al}$ ) method. The molecular structures of compounds **2**, **5** and **6** were determined by X-ray crystallography. The Cp–Al bonding mode in dicyclopentadienylaluminium alkoxides regarding the steric demands of alkoxy groups is discussed based on  $^{27}\text{Al}$ -NMR chemical shifts and structural data obtained. The meaningful correlation between Cp ring-slippage and  $^{27}\text{Al}$ -NMR chemical shifts was observed.

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**Keywords:** Alkoxy ligands; X-ray crystallography; Cp–Al bond mode

## 1. Introduction

Cyclopentadienylaluminium compounds have been investigated for over 40 years [1]. Their structures and bonding are of considerable interest because of the ability of cyclopentadienyl ring to form derivatives with different bonding mode to aluminium atom resulting from low energy barrier to exchange  $\eta^1 \leftrightarrow \eta^2 \leftrightarrow \eta^3 \leftrightarrow \eta^5$  [2]. The spectroscopic investigations in solution can not give clear explanation of Cp–Al bondage [3–10] thus the proper way to examine this area are X-ray measurements or gas phase diffraction studies.

Several cyclopentadienylaluminium alkoxides or phenoxides have been described so far [11–15]. Some of them reveal monomeric structure that results from steric demands of hindered 2,6-di-*tert*-butyl-4-methylphenoxy (BHT) group with cyclopentadienyl rings  $\eta^5$  bonded to aluminium atom [13]. While the other ones,

e.g.  $\text{Cp}_2\text{AlOiPr}$ , were found to be dimeric with alkoxy oxygen bridging atom and Cp ring  $\eta^1$  bonded to aluminium [14,15]. Until now there are no data on dicyclopentadienylaluminium derivatives of tertiary alcohols. In the reaction of *t*-BuOAlCl<sub>2</sub> with excess of cyclopentadienylsodium one of chlorine atoms only is substituted by cyclopentadienyl ligand due to the steric hindrance of *tert*-butoxy group [12]. Attempts to prepare *t*-BuOAlCp<sub>2</sub> from  $\text{Cp}_3\text{Al}$  and *tert*-butyl alcohol were unsuccessful as well [16].

Generally, the structures of alkyl and arylaluminium alkoxides or phenoxides have been investigated widely for years both in solution and solid state [17]. The studies have been undertaken to obtain information concerning the influence of substituents bonded to aluminium atom on valence-angle strain, degree of aggregation, stability of the aggregates, Al–O bond strength, etc.

In this paper we present the analysis of Cp–Al bonding mode in dicyclopentadienylaluminium alkoxides regarding the steric demands of alkoxy groups based on  $^{27}\text{Al}$ -NMR chemical shifts and X-ray crystal-

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lographic data. The eight new dicyclopentadienylaluminum alkoxides were synthesised and characterised by  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectroscopy. The crystal structures of  $[\text{Cp}_2\text{Al}-\mu\text{-OR}]_2$  where  $\text{R} = \text{Et}$  [18],  $\text{CH}_2t\text{-Bu}$ ,  $s\text{-Bu}$  were determined by X-ray diffraction studies.

## 2. Experimental

### 2.1. General procedures

All manipulations were performed using vacuum and Schlenk techniques. All solvents were distilled under argon over potassium benzophenone ketyl (toluene, hexane, benzene and THF). The NMR solvent (benzene- $d_6$ ) was dried over activated 4-Å molecular sieves and deoxygenated in vacuum. Methylaluminum dichloride, purchased as a 1.0-m solution in hexane from Aldrich, was used without purification. Cyclopentadienylsodium was obtained in the reaction of sodium hydride in THF or sodium in xylene with freshly distilled cyclopentadiene. Alcohols were distilled under argon over sodium.

NMR spectra were recorded on Varian VXR-300 (300.13 MHz  $^1\text{H}$ , 74.43 MHz  $^{13}\text{C}$ , 78.206 MHz  $^{27}\text{Al}$ ), Varian VXR-200 (199.971 MHz  $^1\text{H}$ , 50.283 MHz  $^{13}\text{C}$ , 52.106 MHz  $^{27}\text{Al}$ ) and Varian VXR-400 (400.09 MHz  $^1\text{H}$ , 100.60 MHz  $^{13}\text{C}$ , 104.25 MHz  $^{27}\text{Al}$ ). Chemical shifts are reported relative to internal solvent resonances ( $^{13}\text{C}$ ,  $^1\text{H}$ ) and external  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$  ( $^{27}\text{Al}$ ).

### 2.2. Synthesis of $\text{Cp}_3\text{Al}$

A suspension of  $\text{CpNa}$  (15.84 g, 0.18 mol) in toluene (50 ml) was added to a stirred toluene (50 ml) suspension of  $\text{AlCl}_3$  (7.87 g, 0.059 mol) and cooled to  $-50^\circ\text{C}$ . The reaction mixture was warmed up to room temperature (r.t.), then heated up to  $80^\circ\text{C}$  and stirred for 24 h. After decantation of toluene solution and evaporation of solvent in vacuum the product was isolated as the yellow oil with 80% yield.  $^1\text{H}$ -NMR ( $\text{C}_6\text{D}_6$ ):  $\delta = 5.92$  (s, 15H,  $\text{C}_5\text{H}_5$ ).  $^{13}\text{C}$ -NMR ( $\text{C}_6\text{D}_6$ ):  $\delta = 112.12$  ( $\text{C}_5\text{H}_5$ ).  $^{27}\text{Al}$ -NMR ( $\text{C}_6\text{D}_6$ ):  $\delta = 79.62$ . The spectroscopic data is consistent with ones given before by Shapiro et al. [19].

### 2.3. Synthesis of $[\text{Cp}_2\text{Al}-\mu\text{-OMe}]_2$ (1)

$\text{MeOH}$  (0.13 ml, 0.0032 mol) in toluene (50 ml) was added dropwise to a stirred solution of  $\text{Cp}_3\text{Al}$  in toluene (50 ml) (0.71 g, 0.0032 mol) at r.t.. The reaction mixture was heated up to  $80^\circ\text{C}$  and stirred for 3 h. The product was isolated by crystallisation as white solid. Yield 0.48 g, 70%. Anal. Calc. for  $\text{C}_{11}\text{H}_{13}\text{AlO}$  (188.20): C, 70.20; H, 6.96; Al, 14.34. Found: C, 70.43; H, 6.89; Al, 14.05%;  $M_w = 380$  (cryoscopic in benzene),  $n = 2.01$ .  $^1\text{H}$ -NMR ( $\text{C}_6\text{D}_6$ ):  $\delta = 2.65$  (s, 3H,  $\text{CH}_3$ ), 6.04 (s, 10H,  $\text{C}_5\text{H}_5$ ).  $^{13}\text{C}$ -

NMR ( $\text{C}_6\text{D}_6$ ):  $\delta = 50.64$  ( $\text{CH}_3$ ), 111.71 ( $\text{C}_5\text{H}_5$ ).  $^{27}\text{Al}$ -NMR ( $\text{C}_6\text{D}_6$ ):  $\delta = 77.81$  ( $\omega_{1/2} = 1421$  Hz).

### 2.4. Synthesis of $[\text{Cp}_2\text{Al}-\mu\text{-OEt}]_2$ (2)

$\text{EtOH}$  (1 ml, 17 mmol) in hexane (50 ml) was added dropwise to a stirred solution of  $\text{MeAlCl}_2$  (17 ml, 17 mmol) in hexane (75 ml) cooled to  $0^\circ\text{C}$ . During the reaction, methane evolved. The reaction mixture was allowed to warm-up to r.t. and stirred overnight. The formed yellow solution was added to solid  $\text{CpNa}$  (3.79 g, 43 mmol). The reaction mixture was stirred overnight. Hexane solution was decanted and residue twice extracted with hexane (50 ml + 50 ml). The collected hexane solution (ca. 180 ml) was concentrated to 70 ml in vacuum and cooled to  $-15^\circ\text{C}$ . The product precipitated as light-yellow crystalline solid. Yield 1.65 g, 48%. Anal. Calc. for  $\text{C}_{12}\text{H}_{15}\text{AlO}$  (202.23): C, 71.27; H, 7.48; Al 13.34. Found: C, 71.15; H, 7.41; Al, 13.39%;  $M_w = 391$  (cryoscopic in benzene),  $n = 1.94$ .  $^1\text{H}$ -NMR ( $\text{C}_6\text{D}_6$ ):  $\delta = 0.86$  (t,  $J = 7.14$  Hz, 3H,  $\text{CH}_3$ ), 3.13 (q,  $J = 7.14$  Hz, 2H,  $\text{CH}_2$ ), 6.08 (s, 10H,  $\text{C}_5\text{H}_5$ ).  $^{13}\text{C}$ -NMR ( $\text{C}_6\text{D}_6$ ):  $\delta = 16.81$  ( $\text{CH}_3$ ), 61.13 ( $\text{CH}_2$ ), 112.12 ( $\text{C}_5\text{H}_5$ ).  $^{27}\text{Al}$  ( $\text{C}_6\text{D}_6$ ):  $\delta = 84.69$  ( $\omega_{1/2} = 1497$  Hz).

### 2.5. Synthesis of $[\text{Cp}_2\text{Al}-\mu\text{-OnBu}]_2$ (3)

A solution of  $n\text{-BuOH}$  (1 ml, 11 mmol) in hexane (50 ml) was added dropwise to a stirred solution of  $\text{MeAlCl}_2$  (11 ml, 11 mmol) in hexane (50 ml) cooled to  $0^\circ\text{C}$ . A reaction workup similar to the one described above for **2** afforded **3** as light-yellow solid. Yield 1.44 g, 57%. Anal. Calc. for  $\text{C}_{14}\text{H}_{19}\text{AlO}$  (230.28): C, 73.02; H, 8.32; Al, 11.72. Found: C, 73.15; H, 8.39; Al, 12.28%;  $M_w = 455$  (cryoscopic in benzene),  $n = 1.98$ .  $^1\text{H}$ -NMR ( $\text{C}_6\text{D}_6$ ):  $\delta = 0.81$  (t,  $J = 7.35$  Hz, 3H,  $\text{CH}_3$ ), 1.04 (m,  $J = 7.35$  Hz, 2H,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$ ), 1.49 (m,  $J = 7.80$  Hz 2H,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$ ), 3.20 (t,  $J = 8.04$  Hz 2H,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$ ), 6.14 (s, 10H,  $\text{C}_5\text{H}_5$ ).  $^{13}\text{C}$ -NMR ( $\text{C}_6\text{D}_6$ ):  $\delta = 13.81$  ( $\text{CH}_3$ ), 18.87 ( $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$ ), 33.72 ( $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$ ), 65.95 ( $\text{CH}_3\text{CH}_2\text{CH}_2\text{-CH}_2\text{O}$ ), 112.52 ( $\text{C}_5\text{H}_5$ ).  $^{27}\text{Al}$  ( $\text{C}_6\text{D}_6$ ):  $\delta = 85.49$  ( $\omega_{1/2} = 3421$  Hz).

### 2.6. Synthesis of $[\text{Cp}_2\text{Al}-\mu\text{-OiBu}]_2$ (4)

A solution of  $i\text{-BuOH}$  (1 ml, 10.8 mmol) in hexane (50 ml) was added dropwise to a stirred solution of  $\text{MeAlCl}_2$  (10.8 ml, 10.8 mmol) in hexane (50 ml) cooled to  $0^\circ\text{C}$ . A reaction workup similar to the one described for **2** afforded **4** as light-yellow solid. The compound decomposed during X-ray measurements. Yield 1.54 g, 62%. Anal. Calc. for  $\text{C}_{14}\text{H}_{19}\text{AlO}$  (230.28): C, 73.02; H, 8.32; Al, 11.72. Found: C, 72.96; H, 8.20; Al, 11.85%;  $M_w = 436$  (cryoscopic in benzene),  $n = 1.90$ .  $^1\text{H}$ -NMR ( $\text{C}_6\text{D}_6$ ):  $\delta = 0.73$  (d,  $J = 6.80$  Hz, 6H,  $\text{CH}_3$ ), 1.71 (m,  $J = 6.80$

Hz, 1H, CH), 3.13 (d,  $J = 6.80$  Hz, 2H, CH<sub>2</sub>), 6.15 (s, 10H, C<sub>5</sub>H<sub>5</sub>). <sup>13</sup>C-NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta = 19.50$  (CH<sub>3</sub>), 30.60 (CH), 73.12 (CH<sub>2</sub>), 112.79 (C<sub>5</sub>H<sub>5</sub>). <sup>27</sup>Al (C<sub>6</sub>D<sub>6</sub>):  $\delta = 90.44$  ( $\omega_{1/2} = 3440$  Hz).

### 2.7. Synthesis of [Cp<sub>2</sub>Al- $\mu$ -OCH<sub>2</sub>tBu]<sub>2</sub> (**5**)

A solution of *t*-BuCH<sub>2</sub>OH (1.36 g, 15.4 mmol) in hexane (50 ml) was added dropwise to a stirred solution of MeAlCl<sub>2</sub> (15.4 ml, 15.4 mmol) in hexane (50 ml) cooled to 0 °C. A reaction workup similar to the one described for **2** afforded **5** as white solid. Yield 2.71 g, 72%. Anal. Calc. for C<sub>15</sub>H<sub>21</sub>AlO (244.31): C, 73.74; H, 8.66; Al, 11.04. Found: C, 73.59; H, 8.75; Al, 10.87%;  $M_w = 480$  (cryoscopic in benzene),  $n = 1.96$ . <sup>1</sup>H-NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta = 0.79$  (s, 9H, CH<sub>3</sub>), 3.09 (s, 2H, CH<sub>2</sub>), 6.21 (s, 10H, C<sub>5</sub>H<sub>5</sub>). <sup>13</sup>C-NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta = 26.79$  (CH<sub>3</sub>), 32.62 (C), 76.29 (CH<sub>2</sub>), 113.76 (C<sub>5</sub>H<sub>5</sub>). <sup>27</sup>Al (C<sub>6</sub>D<sub>6</sub>):  $\delta = 91.34$  ( $\omega_{1/2} = 4221$  Hz).

### 2.8. Synthesis of [Cp<sub>2</sub>Al- $\mu$ -OsBu]<sub>2</sub> (**6**)

A solution of *s*-BuOH (1 ml, 10.9 mmol) in hexane (50 ml) was added dropwise to a stirred solution of MeAlCl<sub>2</sub> (10.9 ml, 10.9 mmol) in hexane (50 ml) cooled to 0 °C. A reaction workup similar to the one described for **2** afforded **6** as light-yellow solid. Yield 1.60 g, 64%. Anal. Calc. for C<sub>14</sub>H<sub>19</sub>AlO (230.28): C, 73.02; H, 8.32; Al, 11.72. Found: C, 72.91; H, 8.41; Al, 11.38%;  $M_w = 469$  (cryoscopic in benzene),  $n = 2.04$ . <sup>1</sup>H-NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta = 0.53$  (t,  $J = 7.44$  Hz, 3H, CH<sub>3</sub>CH<sub>2</sub>CHCH<sub>3</sub>), 0.95 (d,  $J = 5.79$  Hz, 3H, CH<sub>3</sub>CH<sub>2</sub>CHCH<sub>3</sub>), 1.21 (m, 1H, HCH), 1.58 (m, 1H, HCH), 3.50 (m, 1H, CH), 6.12 (s, 10H, C<sub>5</sub>H<sub>5</sub>). <sup>13</sup>C-NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta = 10.43$  (CH<sub>3</sub>CH<sub>2</sub>CHCH<sub>3</sub>), 21.26 (CH<sub>3</sub>CH<sub>2</sub>CHCH<sub>3</sub>), 31.98 (CH<sub>2</sub>), 75.61 (CH), 113.77 (C<sub>5</sub>H<sub>5</sub>). <sup>27</sup>Al (C<sub>6</sub>D<sub>6</sub>):  $\delta = 104.09$  ( $\omega_{1/2} = 3741$  Hz).

### 2.9. Synthesis of [Cp<sub>2</sub>Al- $\mu$ -OCH<sub>2</sub>Ph]<sub>2</sub> (**7**)

A solution of PhCH<sub>2</sub>OH (1 ml, 9.7 mmol) in toluene (50 ml) was added dropwise to a stirred solution of MeAlCl<sub>2</sub> (9.7 ml, 9.7 mmol) in toluene (50 ml) cooled to –78 °C. During the reaction methane evolved. The reaction mixture was allowed to warm up to r.t., stirred half an hour and then was added to solid CpNa (2.21 g, 25.1 mmol). The mixture was stirred overnight. Toluene solution was decanted and residue twice extracted with toluene (50 ml + 50 ml). The collected toluene solution (ca. 150 ml) was concentrated to 80 ml in vacuum and cooled to –15 °C. The product precipitated as light-yellow solid. Due to the low solubility of the product in deuterated benzene or trichloromethane <sup>13</sup>C- and <sup>27</sup>Al-NMR spectra could not be recorded. Yield 0.56 g, 22%. Anal. Calc. for C<sub>17</sub>H<sub>17</sub>AlO (264.30): C, 77.25; H, 6.48; Al, 10.21. Found: C, 77.52; H, 6.61; Al, 10.34%. <sup>1</sup>H-

NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta = 4.16$  (s, 2H, CH<sub>2</sub>), 5.97 (s, 10H, C<sub>5</sub>H<sub>5</sub>), 7.08–7.33 (m, 5H, C<sub>6</sub>H<sub>5</sub>).

### 2.10. Synthesis of [Cp<sub>2</sub>Al- $\mu$ -OC<sub>6</sub>H<sub>4</sub>-4-*t*Bu]<sub>2</sub> (**8**)

A solution of 4-*t*-BuC<sub>6</sub>H<sub>4</sub>OH (2.25 g, 15 mmol) in toluene (50 ml) was added dropwise to a stirred solution of MeAlCl<sub>2</sub> (15 ml, 15 mmol) in hexane (50 ml) cooled to 5 °C. During the reaction methane evolved. The reaction mixture was allowed to warm to r.t. and stirred overnight. The obtained light-yellow solution was added to solid CpNa (3.19 g, 36.3 mmol) and the reaction mixture was stirred overnight. Toluene–hexane solution was decanted and residue twice extracted with toluene (50 ml + 50 ml). The collected toluene–hexane solution (c.a. 150 ml) was concentrated to 20 ml in vacuum and cooled to –15 °C. The product precipitated as white solid. Yield 1.61 g, 35%. <sup>1</sup>H-NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta = 1.22$  (s, 9H, CH<sub>3</sub>), 6.18 (s, 10H, C<sub>5</sub>H<sub>5</sub>), 7.01 (d,  $J = 8.64$  Hz, 2H, *m*-C<sub>6</sub>H<sub>4</sub>), 7.20 (d,  $J = 8.64$  Hz, 2H, *o*-C<sub>6</sub>H<sub>4</sub>). <sup>13</sup>C-NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta = 31.47$  (CH<sub>3</sub>), 34.06 (C), 112.93 (C<sub>5</sub>H<sub>5</sub>), 121.07, 126.74 (Ar–C, *o*, *m*), 140.74, 148.23 (Ar–C, *p*; Ar–CO). <sup>27</sup>Al (C<sub>6</sub>D<sub>6</sub>): signal is extremely broad and overlapping with probe signal. The product forms clathrates with aromatic solvents.

### 2.11. X-ray structure determination

Single crystals of **2**, **5** and **6** suitable for X-ray diffraction studies were placed in a thin-walled capillaries (Lindemann glass) in an inert atmosphere. The crystallographic data, the summary of data collection and the refinement procedure are presented in Table 1. The measurements for crystals of **2**, **5** were performed on four-circle diffractometer Kuma KM4 and for **6** on Siemens P3 diffractometer.

Data were collected by the  $\omega$ –2 $\theta$  technique at ambient temperature (in case of **2** the study was performed at 100 K). The measured intensities were processed with Lorentz-polarisation effects and crystal decomposition (absorption corrections were not necessary). The structures were solved by direct methods using SHELXS-86 program [20], completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares method against  $F^2$  (SHELXL-97 [21]). All non-hydrogen atoms were anisotropically refined. The positional and isotropic thermal parameters for hydrogen atoms in **2** were refined. The Cp1 ring in **5** was disordered over two rotational positions with refined final s.o.f. equal to 0.59(2) and 0.41(2). The hydrogen atoms in **5** were included in calculated positions and refined isotropically except H(1) and H(6) where positions were also refined. As we found in the refinement process of **6**, the *sec*-butyl group was disordered over two opposite sites that almost mirrored against a plane defined by the central Al<sub>2</sub>O<sub>2</sub> ring. The disorder was

Table 1  
Summary of crystal data for compounds **2**, **5** and **6**

|                                                                           | <b>2</b>                                                        | <b>5</b>                                                        | <b>6</b>                                                        |
|---------------------------------------------------------------------------|-----------------------------------------------------------------|-----------------------------------------------------------------|-----------------------------------------------------------------|
| Empirical formula                                                         | C <sub>24</sub> H <sub>30</sub> Al <sub>2</sub> O <sub>2</sub>  | C <sub>30</sub> H <sub>42</sub> Al <sub>2</sub> O <sub>2</sub>  | C <sub>28</sub> H <sub>38</sub> Al <sub>2</sub> O <sub>2</sub>  |
| Formula weight                                                            | 404.44                                                          | 488.60                                                          | 460.54                                                          |
| Temperature (K)                                                           | 100.0(3)                                                        | 293(2)                                                          | 293(3)                                                          |
| Radiation                                                                 | Mo–K $\alpha$ ( $\lambda$ = 0.71073 Å), graphite-monochromated  | Mo–K $\alpha$ ( $\lambda$ = 0.71073 Å), graphite-monochromated  | Mo–K $\alpha$ ( $\lambda$ = 0.71073 Å), graphite-monochromated  |
| Crystal system                                                            | Monoclinic                                                      | Triclinic                                                       | Monoclinic                                                      |
| Space group                                                               | <i>P</i> 2 <sub>1</sub> / <i>n</i> (no. 14)                     | <i>P</i> 1̄ (no. 2)                                             | <i>P</i> 2 <sub>1</sub> / <i>n</i> (no. 14)                     |
| <i>Z</i>                                                                  | 2                                                               | 1                                                               | 2                                                               |
| Unit cell dimensions                                                      |                                                                 |                                                                 |                                                                 |
| <i>a</i> (Å)                                                              | 9.052(2)                                                        | 8.646(2)                                                        | 8.945(1)                                                        |
| <i>b</i> (Å)                                                              | 9.682(2)                                                        | 9.337(2)                                                        | 9.393(1)                                                        |
| <i>c</i> (Å)                                                              | 12.285(2)                                                       | 9.387(2)                                                        | 12.399(2)                                                       |
| $\alpha$ (°)                                                              | 90                                                              | 70.81(3)                                                        | 90                                                              |
| $\beta$ (°)                                                               | 93.71(3)                                                        | 88.05(3)                                                        | 103.33(1)                                                       |
| $\gamma$ (°)                                                              | 90                                                              | 70.57(3)                                                        | 90                                                              |
| <i>V</i> (Å <sup>3</sup> )                                                | 1074.4(4)                                                       | 672.5(3)                                                        | 1340.8(3)                                                       |
| <i>D</i> <sub>calc</sub> (Mg m <sup>−3</sup> )                            | 1.250                                                           | 1.206                                                           | 1.141                                                           |
| Absorption coefficient (mm <sup>−1</sup> )                                | 0.152                                                           | 0.133                                                           | 0.130                                                           |
| Number of reflections collected                                           | 2031                                                            | 3403                                                            | 5464                                                            |
| Number of unique reflections                                              | 1896 ( <i>R</i> <sub>int</sub> = 0.0176)                        | 3213 ( <i>R</i> <sub>int</sub> = 0.0369)                        | 2367 ( <i>R</i> <sub>int</sub> = 0.0286)                        |
| Data/restraints/parameters                                                | 1896/0/187                                                      | 3213/30/226                                                     | 2367/9/185                                                      |
| Goodness-of-fit on <i>F</i> <sup>2</sup> <sup>a</sup>                     | 1.027                                                           | 1.044                                                           | 1.008                                                           |
| Reflections with <i>I</i> > 2 $\sigma$ ( <i>I</i> )                       | 1399                                                            | 2366                                                            | 1483                                                            |
| Final <i>R</i> indices ( <i>I</i> > 2 $\sigma$ ( <i>I</i> )) <sup>b</sup> | <i>R</i> <sub>1</sub> = 0.0286, <i>wR</i> <sub>2</sub> = 0.0762 | <i>R</i> <sub>1</sub> = 0.0428, <i>wR</i> <sub>2</sub> = 0.1173 | <i>R</i> <sub>1</sub> = 0.0445, <i>wR</i> <sub>2</sub> = 0.1060 |
| <i>R</i> indices (all data) <sup>b</sup>                                  | <i>R</i> <sub>1</sub> = 0.0576, <i>wR</i> <sub>2</sub> = 0.0859 | <i>R</i> <sub>1</sub> = 0.0678, <i>wR</i> <sub>2</sub> = 0.1309 | <i>R</i> <sub>1</sub> = 0.0808, <i>wR</i> <sub>2</sub> = 0.1179 |
| Largest difference peak and hole (e Å <sup>−3</sup> )                     | +0.263 and −0.196                                               | +0.289 and −0.282                                               | +0.166 and −0.121                                               |

<sup>a</sup> Goodness-of-fit *S* = {[*w*(*F*<sub>o</sub><sup>2</sup> − *F*<sub>c</sub><sup>2</sup>)/(*n* − *p*)]<sup>1/2</sup> where *n* is the number of reflections and *p* is the total number of parameters refined.

<sup>b</sup> *R*<sub>1</sub> =  $\Sigma||F_o| - |F_c||/\Sigma|F_o|$ , *wR*<sub>2</sub> = {[ $\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)]$ ]<sup>1/2</sup>.

modelled in terms of two sets of *s*-Bu groups with refined occupancy factors 0.62(1) and 0.38(1). In case of **6** H-atoms were placed in calculated positions with assigned thermal parameters [*U*(H) = 1.2 × *U*<sub>eq</sub>(C)] and [*U*(H) = 1.5 × *U*<sub>eq</sub>(C)] for methyl and disordered groups.

### 3. Results and discussion

#### 3.1. Synthesis

The dicyclopentadienylaluminium alkoxides [Cp<sub>2</sub>Al-μ-OR]<sub>2</sub> (where R = Et (**2**), *n*-Bu (**3**), *i*-Bu (**4**), CH<sub>2</sub>*t*-Bu (**5**), *s*-Bu (**6**), CH<sub>2</sub>Ph (**7**), Ph-*p*-*t*-Bu (**8**)) were obtained by the method described previously [14] according to Eq. (1) from the reaction of ROAlCl<sub>2</sub> and CpNa in hexane or toluene–hexane mixture at ambient temperature.



The dichloroaluminium alkoxides were obtained in the reaction of MeAlCl<sub>2</sub> with alcohol (Eq. (2)).



The reaction products were not isolated and used directly in the syntheses of dicyclopentadienylaluminium derivatives **2**–**8**.

[Cp<sub>2</sub>Al-μ-OMe]<sub>2</sub> (**1**) was obtained from the reaction of Cp<sub>3</sub>Al and methyl alcohol in toluene at 80 °C according to Eq. (3).



#### 3.2. Properties and NMR analysis

The dicyclopentadienylaluminium alkoxides (**1**–**8**) were isolated as white or light-yellow solids by crystallisation from hexane, toluene or a toluene–hexane mixture. The compounds are air and moisture sensitive. In presence of a slight amount of oxygen brown solids are formed. Compounds **2**–**6** are soluble in common hydrocarbon solvents—hexane, toluene. Derivative **7** is practically insoluble in hexane, hardly soluble in toluene. Compounds **1** and **8** are insoluble in hexane, soluble in toluene. All obtained compounds are soluble in THF. Compounds **1**–**8** do not redistribute in presence of THF and do not form stable electron-donor complexes with

this solvent. After dissolving in THF and removal of the solvent in vacuum the  $^1\text{H}$ -NMR spectra of **1–8** showed no THF signals. Compound **8** was found to form clathrates with aromatic solvents (benzene, toluene, and mesitylene). The NMR spectra of the  $\text{CDCl}_3$  solution of crystals **8** showed characteristic patterns of the aromatic solvents. In benzene solution the compounds **1–6** were found to be dimers what was determined by cryoscopic molecular weight investigations. We could not measure the molecular weight of **7** and **8** due to low solubility of **7** and inability to get **8** without the aromatic solvent.

The  $^1\text{H}$ -NMR of **1–8** and  $^{13}\text{C}$ -NMR spectra of **1–6**, **8** in deuterated benzene showed signal patterns characteristic for alkoxy groups (**1–7**) or *tert*-butyl group on phenyl ring (**8**) in high field region and one signal of the cyclopentadienyl ligands in low one. In the low field region the characteristic signal pattern of *para* substituted phenyl ring (**8**) was detected as well. The spectroscopic data are consistent with the proposed chemical formulae of the obtained compounds. We were not able, however, to determine the nature of Cp bonding to aluminium atom in solution from NMR spectra. Rapid rotation of the cyclopentadienyl rings gives a single resonance in  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectrum for the cyclopentadienyl hydrogens and carbons. This behaviour is consistent with the calculated barrier of less than  $3\text{ kcal mol}^{-1}$  for 1,2-migration of the metal centre about a cyclopentadienyl ring [2]. Similar dynamic behaviour was reported for other cyclopentadienyl compounds [11,12,14].

$^{27}\text{Al}$ -NMR chemical shifts of **1–6** vary within range 78–104 ppm and can be regarded as corresponding to four-coordinate aluminium centre [14]. The spectra of **7** and **8** could not be measured due to poor solubility (**7**) or overlapping with probe signal (**8**).

### 3.3. Molecular and crystal structure

The X-ray structure analysis of **2**, **5** and **6** revealed the presence of alkoxy-bridged centrosymmetric dimers in the solid state (Figs. 1–3). Some selected geometrical data are given in Table 2. The structural data for  $[\text{Cp}_2\text{Al}-\mu\text{-O}i\text{-Pr}]_2$  (**9**) [14] are included in Table 2 for comparison. The  $\text{Al}_2(\mu\text{-O})_2$  central ring is planar with almost identical bond lengths and bond angles values in all structures (Table 2).

In each reported dimer one of the Al–O bond is shorter of about  $0.02\text{ \AA}$  than the second one. (This differentiation could not be noticed in **5** due to substantial disorder observed). The reason of this could be the presence of the weak secondary, agostic type interactions between metal and the hydrogen of alkoxy  $\alpha$ -carbon atom [22,23]. The mean  $\text{Al}\cdots\text{H}(11)$  contact is  $2.87\text{ \AA}$ .

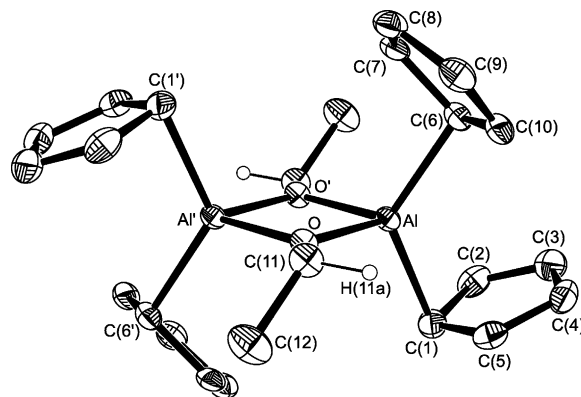


Fig. 1. An ORTEP [24] diagram of **2** showing 50% probability of thermal ellipsoids. Hydrogen atoms are omitted for clarity.

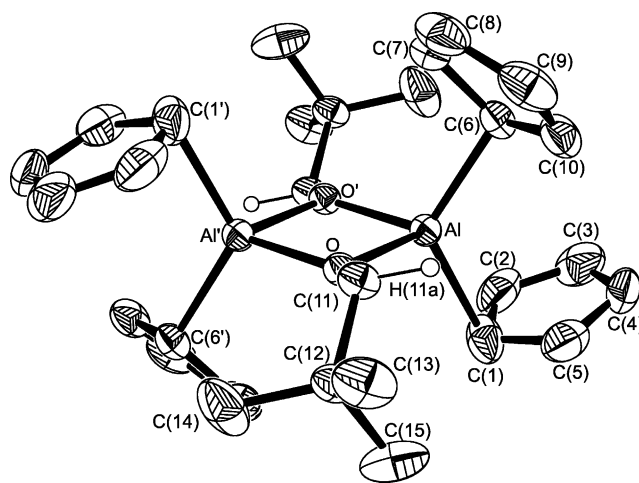


Fig. 2. An ORTEP [24] diagram of **5** showing 30% probability of thermal ellipsoids. Hydrogen atoms are omitted for clarity.

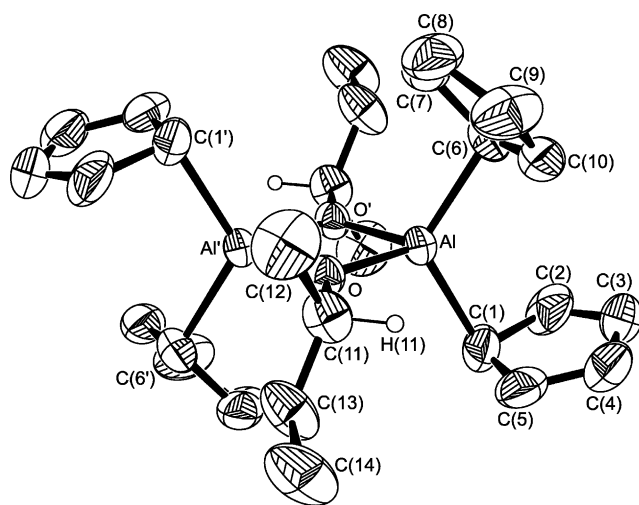


Fig. 3. An ORTEP [24] diagram of **6** showing 30% probability of thermal ellipsoids. Hydrogen atoms are omitted for clarity.

The spatial arrangement of Cp rings with respect to  $\text{Al}_2(\mu\text{-O})_2$  plane is presented for compared structures in

Table 2  
Selected bond lengths (Å) and bond angles (°) compounds **2**, **5**, **6** and **9**<sup>a</sup>

|                      | <b>2</b>  | <b>5</b>              | <b>6</b>  | <b>9</b> <sup>b</sup> [14] |
|----------------------|-----------|-----------------------|-----------|----------------------------|
| <i>Bond lengths</i>  |           |                       |           |                            |
| Al–O                 | 1.822(1)  | 1.821(1)              | 1.821(2)  | 1.821(1)                   |
| Al–O'                | 1.841(1)  | 1.816(1)              | 1.837(2)  | 1.837(1)                   |
| Al–C(6)              | 2.006(2)  | 1.985(2)              | 2.006(3)  | 2.003(2)                   |
| Al–C(1)              | 2.041(2)  | 1.98(1)               | 2.010(3)  | 2.022(2)                   |
| Al...C(2)            | 2.468(2)  | 2.37(1)               | 2.722(3)  | 2.709(2)                   |
| O–C(11)              | 1.448(2)  | 1.431(2)              | 1.475(3)  | 1.473(2)                   |
| Cp1 ring slippage    | 1.278(4)  | 1.384(4) <sup>c</sup> | 1.811(5)  | 1.747(5)                   |
| <i>Bond angles</i>   |           |                       |           |                            |
| O–Al–O'              | 80.48(6)  | 81.27(6)              | 80.79(7)  | 80.85(5)                   |
| C(6)–Al–C(1)         | 124.79(7) | 121.6(3)              | 119.3(2)  | 118.66(9)                  |
| O–Al–C(6)            | 113.37(7) | 112.53(7)             | 112.0(1)  | 115.20(8)                  |
| O'–Al–C(6)           | 113.07(7) | 111.64(7)             | 116.2(1)  | 114.50(9)                  |
| O–Al–C(1)            | 110.65(7) | 106.4(4)              | 110.0(2)  | 111.96(8)                  |
| O'–Al–C(1)           | 105.49(7) | 116.0(5)              | 112.1(1)  | 109.63(8)                  |
| Al–O–Al'             | 99.52(6)  | 98.73(6)              | 99.21(7)  | 99.15(5)                   |
| Cg1–C(1)–Al          | 92.1(1)   | 95.8(11) <sup>c</sup> | 108.7(1)  | 106.7(1)                   |
| Cg2–C(6)–Al          | 112.5(1)  | 118.8(1)              | 114.6(1)  | 113.8(1)                   |
| T1 (Cg1–C(1)–Al–Al') | 179.7(1)  | 177.1(8) <sup>c</sup> | –165.3(2) | –167.4(1)                  |
| T2 (Cg2–C(6)–Al–Al') | 47.0(1)   | 51.6(2)               | 61.6(2)   | 50.2(2)                    |

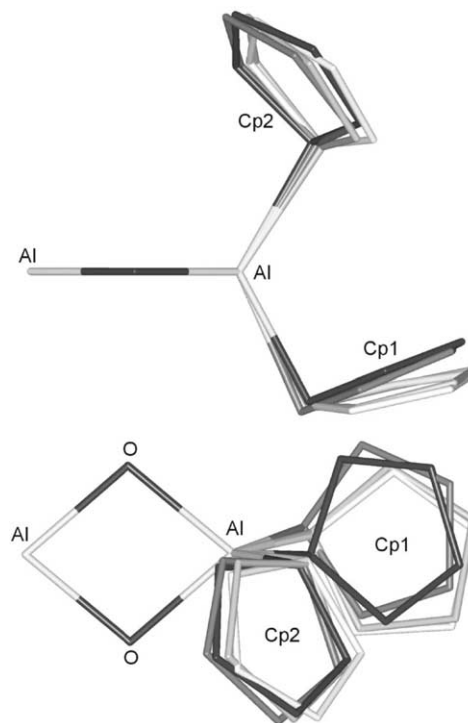
<sup>a</sup> Atoms labelled with prime belong to the centrosymmetric counterparts of the dimeric unit.

<sup>b</sup> The literature values are presented according to the atom numbering scheme used in this work.

<sup>c</sup> The mean value for two disordered positions of the Cp1 ring.

**Fig. 4.** As shown, Cp1 rings are in *anti* while Cp2 in *syn* position. The relevant orientation of Cp rings towards the central  $\text{Al}_2(\mu\text{-O})_2$  core depends on the nature of alkoxy ligand. The different displacement of Cp1 and Cp2 rings regarding the type of substituents on  $\alpha$ -carbon atom of the alkoxy ligand is observed. This displacement is described by torsion angles  $\text{Cg1}-\text{C}(1)-\text{Al}-\text{Al}'$  ( $T1$ ) and  $\text{Cg2}-\text{C}(6)-\text{Al}-\text{Al}'$  ( $T2$ ), where Cg1 and Cg2 denote Cp-ring centroids. The deviation of the Cp1 ring from the parallel orientation to the central plane is negligible for primary alcohol's derivatives ( $T1$  close to  $180^\circ$  for **2** and **5**) and significant for secondary ones ( $T1$  equal approximately  $-166^\circ$ ). It is noteworthy that although Cp2 rings are in *syn* position to the  $\text{Al}_2\text{O}_2$  core they are located on the side of the bulkiest substituent. As a result Cp2 rings are considerable swung from the central position ( $T2=0^\circ$ ) and the values of  $T2$  varies from  $47.0(1)^\circ$  in **2** to  $61.6(2)^\circ$  in **6**.

The cyclopentadienyl groups are bonded to Al atom in the  $\eta^1$  manner. In all cases there is one short aluminium atom – ring carbon atom distance range from 1.985(2) to 2.066(2) Å. The Al–C(2) contacts of 2.468(2) and 2.37(1) Å for compounds **2** and **5**, respectively, are falling in the bonding distance range for cyclopentadienylaluminium compounds [25]. The analysis of ring C–C bond lengths revealed however



**Fig. 4.** The Cp rings spatial arrangement towards  $\text{Al}_2(\mu\text{-O})_2$  plane in four-coordinate dicyclopentadienylaluminium alkoxides. Top: side view perpendicular to the Al–Al vector; bottom: view on the molecular  $\text{Al}_2\text{O}_2$  mean plane. The positions of atoms in the central ring are superimposed. The dark grey colours correspond to primary alcohols derivatives **2** and **5**, the lighter to compound **6** and **9**. The alkyl groups of all substituents bonded to the oxygen atoms are omitted for clarity.

their alteration consistent with  $\eta^1$  hapticity. For example in case of **2** (the structure was determined at 100 K) there are two short distances C(2)–C(3) and C(4)–C(5) of 1.375(3) and 1.378(3) Å, two long bonds C(1)–C(2) and C(1)–C(5) 1.434(3) and 1.432(3) Å, respectively, and the remaining C(3)–C(4) of 1.394(3) Å.

The analysis of angles between ring centroids Cg1, Cg2, carbons C(1), C(6) and aluminium atom revealed the different nature of  $\eta^1$  bonding in studied compounds. The angles  $\text{Cg1}-\text{C}(1)-\text{Al}$  in **2** and **5** are close to  $90^\circ$  what points  $\eta^1(\pi)$  type interactions. The remaining angles values (see Table 2) are above  $105^\circ$  what shows  $\eta^1(\sigma)$  Cp–Al bond character [26].

Due to various Cp–Al  $\eta^1(\sigma)$  or  $\eta^1(\pi)$  character and diversified Cp rings orientation versus central  $\text{Al}_2\text{O}_2$  core there are significant differences in ring-slippage of Cp1 and Cp2 [27]. Although Cp1 ring is in *anti* position it is closer to aluminium atom than Cp2 ring. For all compounds the Cp1 ring-slippage values range from 1.28 to 1.82 Å and they are much less than ones of Cp2 (above 2.0 Å). The shorter Cp1 ring-slippage values corresponds to  $[\text{Cp}_2\text{Al}-\mu\text{-OR}]_2$  derivatives of primary alcohols (Table 2).

We found the  $^{27}\text{Al}$ -NMR chemical shift of aluminium atom in the studied aluminium compounds also depends

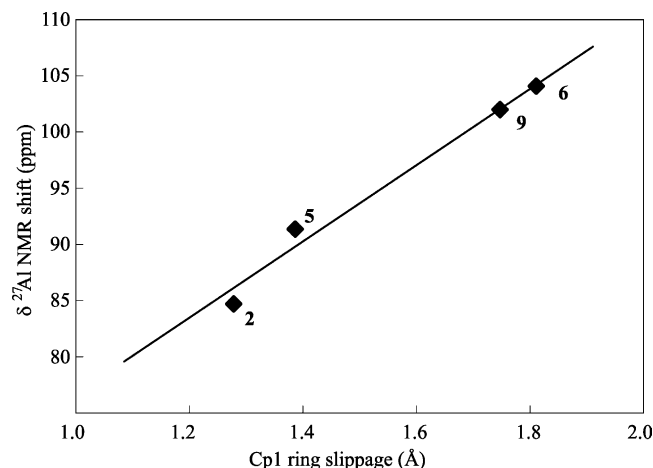


Fig. 5. Plot of the  $^{27}\text{Al}$  chemical shift vs. the Cp1 cyclopentadienyl ring slippage in four-coordinate dicyclopentadienylaluminium alkoxides.

on alcohol's order. The observed  $^{27}\text{Al}$ -NMR spectra for  $[\text{Cp}_2\text{Al}-\mu\text{-OR}]_2$  derivatives of primary alcohols **2–5** showed signals at the range 84–91 ppm. For secondary ones **6, 9** the signals of aluminium atom are shifted downfield (102–104 ppm). It shows that in  $[\text{Cp}_2\text{Al}-\mu\text{-OR}]_2$  compounds derived from primary alcohols the cyclopentadienyl rings cause higher electron density around aluminium atom than in secondary ones. The more alkyl substituents are located on  $\alpha$ -carbon atom of alkoxy ligand the weaker aluminium atom shielding of Cp ring is observed.

We found that the chemical shift of  $^{27}\text{Al}$ -NMR signals correlates with X-ray structural parameter Cp1 ring-slippage values (Fig. 5). The correlation factor is equal to 0.98. According to this relation it is possible to determine Cp–Al bonding mode in  $[\text{Cp}_2\text{Al}-\mu\text{-OR}]_2$  compounds on the basis of the  $^{27}\text{Al}$ -NMR chemical shift without diffraction studies. For example, compounds **3** and **4** showed signals of aluminium atoms at 85 ppm and 90 ppm, respectively. It implies one of the Cp ring to be  $\eta^1(\sigma)$  bonded to Al atom and second one  $\eta^1(\pi)$ . In case of compound **1** where  $^{27}\text{Al}$ -NMR spectra showed signals at 78 ppm one of the cyclopentadienyl rings is probably  $\eta^{1.5}$  or  $\eta^2$  bonded to aluminium atom and second one  $\eta^1$ .

#### 4. Conclusion

We affirmed the agreement of the data obtained for solution and solid state phases of analysed  $[\text{Cp}_2\text{Al}-\mu\text{-OR}]_2$  compounds. The  $^{27}\text{Al}$ -NMR chemical shift correlates well with Cp ring slippage—the X-ray structural parameter. Based on these results we showed the influence of substituents on  $\alpha$ -carbon atom of alkoxy

ligand on the Cp bonding mode. In the derivatives of secondary alcohols both Cp rings are  $\eta^1(\sigma)$  bonded to aluminium atom while in ones of primary alcohols exhibits  $\eta^1(\sigma)$  and  $\eta^1(\pi)$  Cp–Al bonding mode. For  $[\text{Cp}_2\text{Al}-\mu\text{-OMe}]_2$  we postulate that the one of cyclopentadienyl ring is  $\eta^{1.5}$  or  $\eta^2$  and the second one  $\eta^1$  bonded to the aluminium atom.

#### 5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 178972–178974 for compounds **2, 5** and **6**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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