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# $Cp*AlR_2$ compounds (R = Me, Et, <sup>i</sup>Bu): synthesis and structure of novel aluminium organyls with a pentamethylcyclopentadienyl substituent as well as structure of analogous $Cp'AlR_2$ compounds (Cp' = Cp, MeCp; R = Me, Et)

Markus Scherer<sup>1</sup>, Thomas Kruck<sup>\*</sup>

Institut für Anorganische Chemie der Universität zu Köln, Greinstraße 6, 50939 Köln, Germany Received 26 July 1995; in revised form 24 August 1995

#### Abstract

The novel organoaluminium compounds  $(C_5Me_5)AIR_2$  (R = Me, Et, <sup>i</sup>Bu) have been prepared by the reaction of  $(C_5Me_5)K$  with dialkylaluminium chlorides. The <sup>1</sup>H, <sup>13</sup>C, <sup>27</sup>Al NMR and mass spectra of the new compounds are reported and discussed. It is shown that  $(C_5Me_5)AIR_2$  compounds are characterized by  $\eta^3$ -coordinated  $(C_5Me_5)$  ligands. The new complexes are exclusively monomeric. However, the known derivatives with unsubstituted or monosubstituted Cp systems like Cp'AIR<sub>2</sub> (Cp' = Cp, MeCp; R = Me, Et) show an equilibrium between monomeric and dimeric species in benzene solution. Such compounds have been investigated by <sup>27</sup>Al NMR for the first time. The Cp' rings in monomeric species are bound in an  $\eta^2$ -symmetry, whereas the dimeric, alkyl-bridged molecules show  $\sigma$ -coordinated Cp' systems. In order to obtain a compound, which shows a monosubstituted Cp ligand and furthermore is exclusively monomeric the novel complex (<sup>t</sup>BuCp)Al(<sup>i</sup>Bu)<sub>2</sub> was synthesized. As expected, the <sup>27</sup>Al NMR spectrum of this compound is consistent with an  $\eta^2$ -coordinated ring system too.

Keywords: Organoaluminium compounds; (Cyclopentadienyl)aluminium complexes; Pentamethylcyclopentadienyl ligand

#### 1. Introduction

The chemistry of (pentamethylcyclopentadienyl)aluminium compounds has attracted much interest in recent years. The synthesis of  $(C_5Me_5)_4Al_4$  by Schnöckel and coworkers [1] is surely a highlight of this decade in preparative organometallic chemistry. An alternative synthetic method for  $(C_5Me_5)_4Al_4$  was developed by Roesky and coworkers [2] starting from  $(C_5 - Me_5)AlCl_2$  [3], a complex first described in 1992. Surprisingly, however, there are no reports of (pentamethylcyclopentadienyl)aluminium complexes with the formula  $(C_5Me_5)AlR_2$  (R = alkyl ligand). This lack of such reports is even more surprising considering the fact that CpAlEt<sub>2</sub>, the first ever reported (cyclopentadienyl) aluminium compound, has been known since 1961 [4]. In 1982 Paine and coworkers [5] attempted to prepare  $(C_5Me_5)AlMe_2$  by reaction of  $[Me_2AlCl]_2$  with either  $(C_5Me_5)MgCl$  or  $(C_5Me_5)Li$ . Instead of  $(C_5Me_5)Al-Me_2$ , however, they obtained the chlorine containing complex  $(C_5Me_5)AlClMe$  via an as yet undetermined mechanism. Here we wish to communicate the first successful synthesis of  $(C_5Me_5)AlR_2$  (R = Me, Et or <sup>i</sup>Bu) compounds. The novel complexes were made by metathesis reaction of  $[R_2AlCl]_2$  (R = Me, Et or <sup>i</sup>Bu) with  $(C_5Me_5)K$  in either *n*-pentane or benzene.

#### 2. Results and discussion

It is apparent from the results that the use of  $(C_5Me_5)K$  instead of  $(C_5Me_5)MgCl$  or  $(C_5Me_5)Li$  plays an important role for the synthesis of the compounds described herein. The new complexes are air-sensitive, colourless liquids, which can easily be isolated by distillation. Cryoscopic molecular weight determinations in benzene show only monomeric species. <sup>27</sup>Al NMR shifts of known compounds like  $(C_5Me_5)_4Al_4$  [1], AlCp<sub>3</sub> [6] or Cp<sub>2</sub> AlMe [7] indicate the coordination mechanism

<sup>\*</sup> Corresponding author.

<sup>&</sup>lt;sup>1</sup>Present address: Department of Chemistry and Biochemistry, University of Texas, Austin, TX 78712, USA.

to f Chemistry and Biochemistry, 78712 USA

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Fig. 1. Synthesis of  $(C_5Me_5)AlR_2$  compounds  $(R = Me, Et, {}^{i}Bu)$ .

between the aluminium atom and the cyclopentadienyl ring. Therefore, we decided to carry out <sup>27</sup>Al NMR experiments with the novel ( $C_5Me_5$ )AlR<sub>2</sub> complexes too. For each of the new compounds **3a-c** we found <sup>27</sup>Al NMR signals between 71.6 and 72.7 ppm. These data are consistent with a coordination number of 5 for the aluminium atom [8–10]. Consequently, the ( $C_5Me_5$ ) ligands in these complexes must be coordinated in an  $\eta^3$ -symmetry, illustrated schematically in Fig. 2.

Roesky and coworkers' [3]  $(C_5Me_5)AlCl_2$  shows another binding situation. The cyclopentadienyl systems in this dimeric, chlorine-bridged complex are  $\eta^5$ -coordinated, whereas Paine and coworkers' [5]  $(C_5Me_5)Al$ -ClMe shows an  $\eta^3$ -bound  $(C_5Me_5)$  ligand. Nevertheless, it may be concluded that the coordination mechanism between the  $(C_5Me_5)$  ring and the aluminium atom depends ultimately on the remaining ligands of the complex.

Because of their highly fluxional behaviour, <sup>1</sup>H NMR spectra of the new compounds show only a singlet for the methyl protons of the  $(C_5Me_5)$  rings. For the same reason, the carbon atoms of the  $(C_5Me_5)$ -methyl groups, as well as those of the  $C_5$  ring, each appear as only one signal in <sup>13</sup>C NMR spectra. The dynamic behaviour observed in these complexes is caused by rearrangements of the aluminium atom around the cyclopentadiene ring [11]. Finally, mass spectra of each of the complexes reported here show  $(C_5Me_5)AlR^+$  as parent peaks. Further, no  $AlR_2^+$  fragment ions are observed in any of the spectra. Thus, it may be concluded that a fragmentation of the aluminium–alkyl bond is favoured over cleavage of the Al–Cp bond.

As described above, (cyclopentadienyl)aluminium compounds show various geometries between the metal atom and the ring system. However, this propensity to form a variety of differing coordination geometries led



Fig. 2. Cp-Al binding situation in  $(C_5Me_5)AIR_2$  compounds  $(R = Me, Et, {}^iBu)$ .

to numerous structural ambiguities. For example, AlCp<sub>3</sub>, a compound first described in 1961, was proposed to exclusively form  $\sigma$ -coordinated Cp groups [12]. However, <sup>27</sup>Al NMR investigations ( $\delta$ (<sup>27</sup>Al) of AlCp<sub>3</sub> 88 ppm) allowed Benn et al. [6] to propose the coordination number 5 for the aluminium atom and the formula ( $\eta^3$ -Cp)Al( $\eta^1$ -Cp)<sub>2</sub> for this compound.

Below, we wish to report on binding geometries of CpAIR<sub>2</sub> complexes containing unsubstituted, respectively monosubstituted Cp rings. In the case of CpAlMe,, infrared spectroscopy of the solid compound suggested an  $\eta^5$  Cp-Al interaction [13], whereas electron diffraction analysis of gaseous CpAlMe2 was found to be most consistent with an  $\eta^2$ -configuration [14]. Further, Haaland and coworkers [15] reported that vibrational spectra in nonpolar solvents were more consistent with  $\eta^2$ - or  $\eta^3$ -structures. Lastly, an X-ray structure of CpAlMe<sub>2</sub> determined by Oliver and coworkers [16] revealed that the solid compound consists of infinite chains which are composed of dimethylaluminium groups bridged by  $\eta^{1}$ -bound Cp rings. Considering the low rotational barriers between different geometries [17]. it seems that the Cp-Al configuration of individual compounds also depends strongly on their state of aggregation.

For CpAlR<sub>2</sub> complexes with methyl or ethyl groups as alkyl ligands there exists an equilibrium between monomeric and dimeric (alkyl-bridged) species in benzene solution (e.g. the degree of association in CpAlEt<sub>2</sub> decreases from 1.95 in a 0.56 M solution to 1.22 in a 0.065 M solution) [4].

As <sup>1</sup>H and <sup>13</sup>C NMR measurements are not useful to determine the Cp–Al binding geometry [18] we decided to investigate the binding situation of Cp'AlR<sub>2</sub> complexes (Cp' = Cp, MeCp) in solution by <sup>27</sup>Al NMR studies. Aluminium organyls with coordination number 3 usually lead to  $\delta$ (<sup>27</sup>Al) signals at about 250 ppm, whereas shifts at about 150 ppm are attributed to aluminium complexes with coordination number 4 [6]. Assuming a proposal of Giannini and Cesca [4] who predicted an  $\eta^1$ -Cp–Al binding mechanism for monomeric as well as dimeric CpAlEt<sub>2</sub>, one would expect to observe a signal between 250 and 150 ppm caused by an equilibrium between CpAlEt<sub>2</sub> and [CpAlEt<sub>2</sub>]<sub>2</sub>. Interestingly, however, all complexes listed in Table 1 show <sup>27</sup>Al NMR signals at about 150 ppm.

Table 1 <sup>27</sup>Al NMR shifts of Cp'AlR<sub>2</sub> compounds (C<sub>6</sub>D<sub>6</sub>, 25°C)

	$\delta(^{27}\text{Al})$ (ppm)	$v_{1/2}$ (Hz)
CpAlMe <sub>2</sub>	149.8	959
(MeCp)AlMe <sub>2</sub>	152.6	986
CpAlEt,	145.5	1437
(MeCp)AlEt <sub>2</sub>	142.4	1396



R ≈ Me, Et

Fig. 3. Equilibrium behaviour of  $(C_5H_5)AlR_2$  (R = Me, Et) in benzene solution.

No signals at lower fields are observed. This must be attributed to a coordination number of 4 for the aluminium atom in monomeric as well as in dimeric species [19]. A coordination number of 4 is realized in monomeric complexes by forming  $\eta^2$ -Cp-Al geometries, and in dimeric compounds by forming  $\sigma$ -bound Cp rings. Therefore, an equilibrium between these two forms leads to a change in the Cp-Al binding situation (see Fig. 3). Considering the low energy barriers between  $\eta^1$ -Cp-Al and  $\eta^2$ -Cp-Al configurations [17], this behaviour is not surprising.

To preclude the equilibrium formation of dimeric species we synthesized the novel Cp-Al complex 4, which has more bulky substituents (see Fig. 4). In contrast to the solid CpAlMe<sub>2</sub> or CpAlEt<sub>2</sub> we obtained a colourless liquid. Cryoscopic molecular weight determination in benzene solution shows no association tendencies. As observed in the above-described complexes, we obtained a <sup>27</sup>Al NMR signal at 147.1 ppm, indicating a coordination number of 4 for the aluminium atom. This result suggests an  $\eta^2$ -Cp-Al geometry in this exclusively monomeric complex (see Fig. 4) and thus also confirms our <sup>27</sup>Al NMR results with Cp'AlR<sub>2</sub> (Cp' =  $C_5H_5$ , MeCp; R = Me, Et) compounds. In spite of its bulky substituents, 4 still shows fluctional behaviour between the aluminium atom and the Cp system. This is indicated by the <sup>1</sup>H and <sup>13</sup>C NMR signals of the ring ligand.

Our results are also consistent with those of Haaland and coworker [14] from the electron diffraction analysis determination of the  $\eta^2$ -Cp-Al structure in monomeric CpAlMe<sub>2</sub>. Furthermore, Cp<sub>2</sub>AlMe, a compound first described in 1994, also shows  $\eta^2$ -coordinated Cp rings



Fig. 4. Structure of  $({}^{1}BuC_{5}H_{4})Al({}^{1}Bu)_{2}$ .

[7]. The results of these groups in combination with our data from <sup>27</sup>Al NMR studies of several CpAlR<sub>2</sub> compounds strongly suggest that an  $\eta^2$ -geometry is favoured in monomeric Cp-Al compounds with unsubstituted or monosubstituted Cp systems.

#### 3. Experimental

All experiments were carried out under nitrogen using standard inert gas techniques. Solvents (*n*-pentane, benzene, toluene) were distilled from Na/K melt. Elemental analyses were carried out on a Hereaus CHN– O-Rapid. The NMR spectra were recorded on a Bruker AC 200 spectrometer at room temperature: <sup>1</sup>H (200.1 MHz) ext. TMS, <sup>13</sup>C{<sup>1</sup>H} (50.3 MHz) ext. TMS, <sup>27</sup>Al{<sup>1</sup>H} (52.2 MHz) ext. Al(acac)<sub>3</sub> and the mass spectra on a Finnigan-MAT spectrometer. ( $C_5Me_5$ )K was prepared in the usual way from  $C_5Me_5$ H and K in toluene. Dialkylaluminium chlorides were obtained commercially (Aldrich) and used without purification.

# 3.1. Dimethyl( $\eta^3$ -pentamethylcyclopentadienyl)aluminium(III) (**3a**)

A solution of 3.40 g (18.5 mmol) **2a** in 30 ml of benzene was added slowly with stirring to a mixture of 7.31 g (42 mmol) **1** and 120 ml benzene. After 5 h stirring at room temperature the precipitated KCl was filtered off and the solvent removed in vacuum. The product was isolated by distillation (80°C, 0.3 mm Hg) to give 5.20 g (27 mmol, 73%) **3a** as a colourless oil. At temperatures below 10°C the liquid product crystallizes to a low melting solid.

Melting point 23–28°C. <sup>1</sup>H NMR ( $C_6D_6$ ):  $\delta = -0.81$ (s, 6H, AlCH<sub>3</sub>), 1.80 (s, 15H,  $C_5CH_3$ ); <sup>13</sup>C(<sup>1</sup>H) NMR ( $C_6D_6$ ):  $\delta = -8.2$  (br, AlCH<sub>3</sub>), 10.3 ( $C_5CH_3$ ), 114.2 ( $C_5CH_3$ ); <sup>27</sup>Al(<sup>1</sup>H) NMR ( $C_6D_6$ ):  $\delta = 71.6$  ( $\nu_{1/2} \approx 1040$ Hz); MS (EI), m/e (%): 192 (8) [M<sup>+</sup>], 177 (100) [M<sup>+</sup>-CH<sub>3</sub>], 136 (31) [ $C_5Me_5H^+$ ]. Anal. Found: C, 73.64; H, 11.88.  $C_{12}H_{12}$ Al. Calc.: C, 74.95; H, 11.01%. Molecular weight (cryoscopic in benzene) 195.

## 3.2. Diethyl( $\eta^3$ -pentamethylcyclopentadienyl)aluminium(III) (**3b**)

At 0°C a solution of 4.44 g (18.5 mmol) **2b** in 30 ml of *n*-pentane was added dropwise to a mixture of 7.31 g (42 mmol) **1** and 120 ml *n*-pentane. After 20 h stirring at room temperature KCl was filtered off and the solvent removed in vacuum. The dark red crude product was purified by distillation (84°C, 0.3 mm Hg) to give 6.35 g (29 mmol, 78%) of pale yellow **3b**.

<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta = -0.17$  (q, <sup>3</sup>J<sub>HH</sub> = 8.2 Hz, 4H, AlCH<sub>2</sub>CH<sub>3</sub>), 1.08 (t, <sup>3</sup>J<sub>HH</sub> = 8.2 Hz, 6H, AlCH<sub>2</sub>CH<sub>3</sub>), 1.84 (s, 15H, C<sub>5</sub>CH<sub>3</sub>); <sup>15</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta = 1.2$  (br, AlCH<sub>2</sub>CH<sub>3</sub>), 9.8 (AlCH<sub>2</sub>CH<sub>3</sub>), 10.4 (C<sub>5</sub>CH<sub>3</sub>), 114.3 (C<sub>5</sub>CH<sub>3</sub>); <sup>27</sup>Al{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta = 72.2 (\nu_{1/2} \approx 976 \text{ Hz})$ ; MS (EI), m/e (%): 220 (4) [M<sup>+</sup>], 191 (100) [M<sup>+</sup>-C<sub>2</sub>H<sub>5</sub>], 136 (36) [C<sub>5</sub>Me<sub>5</sub>H<sup>+</sup>]. Anal. Found: C, 72.56; H, 11.24. C<sub>14</sub>H<sub>25</sub>Al. Calc.: C, 76.33; H, 11.44%. Molecular weight (cryoscopic in benzene) 231.

# 3.3. Diisobutyl( $\eta^3$ -pentamethylcyclopentadienyl)aluminium(III) (**3c**)

Synthesis of **3c** analogous to that of **3b**, starting from **2c**. 65% yield of a pale yellow liquid (b.p. 93°C, 0.3 mm Hg).

<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta = -0.12$  (d, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, 4H, AlCH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>), 1.13 (m, 2H, AlCH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>), 1.01 (d, <sup>3</sup>J<sub>HH</sub> = 6.5 Hz, 12H, AlCH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>), 1.87 (s, 15H, C<sub>5</sub>CH<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta = 28.4$ (AlCH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>), 26.4 (AlCH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>), 10.7 (C<sub>5</sub>CH<sub>3</sub>), 114.5 (C<sub>5</sub>CH<sub>3</sub>); <sup>27</sup>Al{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta =$ 72.7 ( $\nu_{1/2} \approx 983$  Hz); MS (EI), m/e (%): 276 (0.2) [M<sup>+</sup>], 219 (100) [M<sup>+</sup>-C<sub>4</sub>H<sub>9</sub>], 162 (2) [M<sup>+</sup>-2C<sub>4</sub>H<sub>9</sub>], 136 (27) [C<sub>5</sub>Me<sub>5</sub>H<sup>+</sup>]. Anal. Found: C, 77.63; H, 11.78. C<sub>18</sub>H<sub>33</sub>Al. Calc.: C, 78.22; H, 12.03%. Molecular weight (cryoscopic in benzene) 283.

# 3.4. Diisobutyl( $\eta^2$ -tertbutylcyclopentadienyl)aluminium (III) (4)

We obtained 4 in a metathesis reaction between  $[({}^{i}Bu)_{2}AlCl]_{2}$  and Na( ${}^{i}BuCp$ ) in benzene; experimental as described above (78% yield of a pale yellow liquid; b.p. 81°C, 0.9 mm Hg).

<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta = -0.06$  (m, 4H, AlC H<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>), 1.79 (m, 2H, AlCH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>), 0.97 (d, <sup>3</sup>J<sub>HH</sub> = 6.5 Hz, 12H, AlCH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>), 1.23 (s, 9H, (CH<sub>3</sub>)<sub>3</sub>CC<sub>5</sub>H<sub>4</sub>), 6.04 (m, 4H, (CH<sub>3</sub>)<sub>3</sub>CC<sub>5</sub>H<sub>4</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta = 26.5$  (AlCH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>), 26.2 (AlCH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>), 32.5 ((CH<sub>3</sub>)<sub>3</sub>CC<sub>5</sub>H<sub>4</sub>), 32.2 ((CH<sub>3</sub>)<sub>3</sub>CC<sub>5</sub>H<sub>4</sub>), 105.7/105.3 ((CH<sub>3</sub>)<sub>3</sub>CC<sub>5</sub>H<sub>4</sub>), 32.2 ((CH<sub>3</sub>)<sub>3</sub>CC<sub>5</sub>H<sub>4</sub>), 105.7/105.3 ((CH<sub>3</sub>)<sub>3</sub>CC<sub>5</sub>H<sub>4</sub>); <sup>27</sup>Al{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta = 147.1$  ( $\nu_{1/2} \approx 894$  Hz); MS (EI), *m/e* (%): 262 (1) [M<sup>+</sup>], 205 (100) [M<sup>+</sup>-C<sub>4</sub>H<sub>9</sub>], 148 (2) [M<sup>+</sup>-2C<sub>4</sub>H<sub>9</sub>], 122 (17) [(CH<sub>3</sub>)<sub>3</sub>CC<sub>5</sub>H<sub>4</sub>H<sup>+</sup>]. Anal. Found: C, 76.73; H, 11.57. C<sub>17</sub>H<sub>31</sub>Al. Calc.: C, 77.78; H, 11.82%. Molecular weight (cryoscopic in benzene) 267.

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