

Cp*AlR₂ compounds (R = Me, Et, ⁱBu): synthesis and structure of novel aluminium organyls with a pentamethylcyclopentadienyl substituent as well as structure of analogous Cp'AlR₂ compounds (Cp' = Cp, MeCp; R = Me, Et)

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Abstract

The novel organoaluminium compounds (C₅Me₅)AlR₂ (R = Me, Et, ⁱBu) have been prepared by the reaction of (C₅Me₅)K with dialkylaluminium chlorides. The ¹H, ¹³C, ²⁷Al NMR and mass spectra of the new compounds are reported and discussed. It is shown that (C₅Me₅)AlR₂ compounds are characterized by η³-coordinated (C₅Me₅) ligands. The new complexes are exclusively monomeric. However, the known derivatives with unsubstituted or monosubstituted Cp systems like Cp'AlR₂ (Cp' = Cp, MeCp; R = Me, Et) show an equilibrium between monomeric and dimeric species in benzene solution. Such compounds have been investigated by ²⁷Al NMR for the first time. The Cp' rings in monomeric species are bound in an η²-symmetry, whereas the dimeric, alkyl-bridged molecules show σ-coordinated Cp' systems. In order to obtain a compound, which shows a monosubstituted Cp ligand and furthermore is exclusively monomeric the novel complex (ⁱBuCp)Al(ⁱBu)₂ was synthesized. As expected, the ²⁷Al NMR spectrum of this compound is consistent with an η²-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 (C₅Me₅)₄Al₄ by Schnöckel and coworkers [1] is surely a highlight of this decade in preparative organometallic chemistry. An alternative synthetic method for (C₅Me₅)₄Al₄ was developed by Roesky and coworkers [2] starting from (C₅Me₅)AlCl₂ [3], a complex first described in 1992. Surprisingly, however, there are no reports of (pentamethylcyclopentadienyl)aluminium complexes with the formula (C₅Me₅)AlR₂ (R = alkyl ligand). This lack of such reports is even more surprising considering the fact that CpAlEt₂, the first ever reported (cyclopentadienyl)aluminium compound, has been known since 1961 [4]. In 1982 Paine and coworkers [5] attempted to prepare

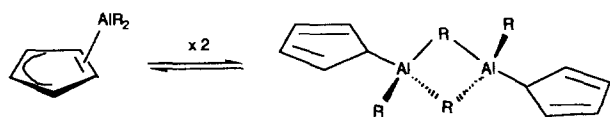
(C₅Me₅)AlMe₂ by reaction of [Me₂AlCl]₂ with either (C₅Me₅)MgCl or (C₅Me₅)Li. Instead of (C₅Me₅)AlMe₂, however, they obtained the chlorine containing complex (C₅Me₅)AlClMe via an as yet undetermined mechanism. Here we wish to communicate the first successful synthesis of (C₅Me₅)AlR₂ (R = Me, Et or ⁱBu) compounds. The novel complexes were made by metathesis reaction of [R₂AlCl]₂ (R = Me, Et or ⁱBu) with (C₅Me₅)K in either *n*-pentane or benzene.

2. Results and discussion

It is apparent from the results that the use of (C₅Me₅)K instead of (C₅Me₅)MgCl or (C₅Me₅)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. ²⁷Al NMR shifts of known compounds like (C₅Me₅)₄Al₄ [1], AlCp₃ [6] or Cp₂AlMe [7] indicate the coordination mechanism

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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 η^2 -Cp-Al geometries, and in dimeric compounds by forming σ -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 η^1 -Cp-Al and η^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 $CpAlMe_2$ or $CpAlEt_2$ 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 ^{27}Al NMR signal at 147.1 ppm, indicating a coordination number of 4 for the aluminium atom. This result suggests an η^2 -Cp-Al geometry in this exclusively monomeric complex (see Fig. 4) and thus also confirms our ^{27}Al NMR results with $Cp'AlR_2$ ($Cp' = C_5H_5$, MeCp; R = Me, Et) compounds. In spite of its bulky substituents, **4** still shows fluxional behaviour between the aluminium atom and the Cp system. This is indicated by the 1H and ^{13}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 η^2 -Cp-Al structure in monomeric $CpAlMe_2$. Furthermore, Cp_2AlMe , a compound first described in 1994, also shows η^2 -coordinated Cp rings

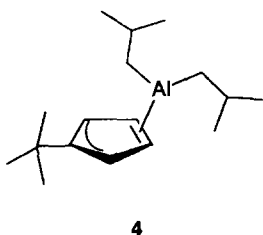


Fig. 4. Structure of $(^1BuC_5H_4)Al(^1Bu)_2$.

[7]. The results of these groups in combination with our data from ^{27}Al NMR studies of several $CpAlR_2$ compounds strongly suggest that an η^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: 1H (200.1 MHz) ext. TMS, $^{13}C\{^1H\}$ (50.3 MHz) ext. TMS, $^{27}Al\{^1H\}$ (52.2 MHz) ext. $Al(acac)_3$ and the mass spectra on a Finnigan-MAT spectrometer. $(C_5Me_5)K$ was prepared in the usual way from C_5Me_5H and K in toluene. Dialkylaluminium chlorides were obtained commercially (Aldrich) and used without purification.

3.1. Dimethyl(η^3 -pentamethylcyclopentadienyl)aluminum(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. 1H NMR (C_6D_6): $\delta = -0.81$ (s, 6H, $AlCH_3$), 1.80 (s, 15H, C_5CH_3); $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta = -8.2$ (br, $AlCH_3$), 10.3 (C_5CH_3), 114.2 (C_5CH_3); $^{27}Al\{^1H\}$ NMR (C_6D_6): $\delta = 71.6$ ($\nu_{1/2} \approx 1040$ Hz); MS (EI), *m/e* (%): 192 (8) [M^+], 177 (100) [$M^+ - CH_3$], 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(η^3 -pentamethylcyclopentadienyl)aluminum(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**.

1H NMR (C_6D_6): $\delta = -0.17$ (q, $^3J_{HH} = 8.2$ Hz, 4H, $AlCH_2CH_3$), 1.08 (t, $^3J_{HH} = 8.2$ Hz, 6H, $AlCH_2CH_3$), 1.84 (s, 15H, C_5CH_3); $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta = 1.2$

(br, AlCH_2CH_3), 9.8 (AlCH_2CH_3), 10.4 (C_5CH_3), 114.3 (C_5CH_3); $^{27}\text{Al}\{^1\text{H}\}$ NMR (C_6D_6): $\delta = 72.2$ ($\nu_{1/2} \approx 976$ Hz); MS (EI), m/e (%): 220 (4) [M^+], 191 (100) [$\text{M}^+ - \text{C}_2\text{H}_5$], 136 (36) [$\text{C}_5\text{Me}_5\text{H}^+$]. Anal. Found: C, 72.56; H, 11.24. $\text{C}_{14}\text{H}_{25}\text{Al}$. Calc.: C, 76.33; H, 11.44%. Molecular weight (cryoscopic in benzene) 231.

3.3. Diisobutyl(η^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).

^1H NMR (C_6D_6): $\delta = -0.12$ (d, $^3J_{\text{HH}} = 7.5$ Hz, 4H, $\text{AlCH}_2\text{CH}(\text{CH}_3)_2$), 1.13 (m, 2H, $\text{AlCH}_2\text{CH}(\text{CH}_3)_2$), 1.01 (d, $^3J_{\text{HH}} = 6.5$ Hz, 12H, $\text{AlCH}_2\text{CH}(\text{CH}_3)_2$), 1.87 (s, 15H, C_5CH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): $\delta = 28.4$ ($\text{AlCH}_2\text{CH}(\text{CH}_3)_2$), 26.4 ($\text{AlCH}_2\text{CH}(\text{CH}_3)_2$), 10.7 (C_5CH_3), 114.5 (C_5CH_3); $^{27}\text{Al}\{^1\text{H}\}$ NMR (C_6D_6): $\delta = 72.7$ ($\nu_{1/2} \approx 983$ Hz); MS (EI), m/e (%): 276 (0.2) [M^+], 219 (100) [$\text{M}^+ - \text{C}_4\text{H}_9$], 162 (2) [$\text{M}^+ - 2\text{C}_4\text{H}_9$], 136 (27) [$\text{C}_5\text{Me}_5\text{H}^+$]. Anal. Found: C, 77.63; H, 11.78. $\text{C}_{18}\text{H}_{33}\text{Al}$. Calc.: C, 78.22; H, 12.03%. Molecular weight (cryoscopic in benzene) 283.

3.4. Diisobutyl(η^2 -tertbutylcyclopentadienyl)aluminium(III) (4)

We obtained **4** in a metathesis reaction between $[(i\text{Bu})_2\text{AlCl}]_2$ and $\text{Na}(t\text{BuCp})$ in benzene; experimental as described above (78% yield of a pale yellow liquid; b.p. 81°C , 0.9 mm Hg).

^1H NMR (C_6D_6): $\delta = -0.06$ (m, 4H, $\text{AlCH}_2\text{CH}(\text{CH}_3)_2$), 1.79 (m, 2H, $\text{AlCH}_2\text{CH}(\text{CH}_3)_2$), 0.97 (d, $^3J_{\text{HH}} = 6.5$ Hz, 12H, $\text{AlCH}_2\text{CH}(\text{CH}_3)_2$), 1.23 (s, 9H, $(\text{CH}_3)_3\text{CC}_5\text{H}_4$), 6.04 (m, 4H, $(\text{CH}_3)_3\text{CC}_5\text{H}_4$); $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): $\delta = 26.5$ ($\text{AlCH}_2\text{CH}(\text{CH}_3)_2$), 26.2 ($\text{AlCH}_2\text{CH}(\text{CH}_3)_2$), 32.5 ($(\text{CH}_3)_3\text{CC}_5\text{H}_4$), 32.2 ($(\text{CH}_3)_3\text{CC}_5\text{H}_4$), 105.7/105.3 ($(\text{CH}_3)_3\text{CC}_5\text{H}_4$); $^{27}\text{Al}\{^1\text{H}\}$ NMR (C_6D_6): $\delta = 147.1$ ($\nu_{1/2} \approx 894$ Hz); MS (EI), m/e (%): 262 (1) [M^+], 205 (100) [$\text{M}^+ - \text{C}_4\text{H}_9$], 148 (2) [$\text{M}^+ - 2\text{C}_4\text{H}_9$], 122 (17) [$(\text{CH}_3)_3\text{CC}_5\text{H}_4\text{H}^+$]. Anal. Found: C, 76.73; H, 11.57. $\text{C}_{17}\text{H}_{31}\text{Al}$. Calc.: C, 77.78; H, 11.82%. Molecular weight (cryoscopic in benzene) 267.

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