

Synthesis, properties and crystal structure of bis(cyclopentadienyl) aluminium complex $[\eta^1-(C_5H_5)_2AlO-^iPr]_2$

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Abstract

The reaction of Cl_2AlO-^iPr with C_5H_5Na affords the isopropoxy-bridged dimer $[\eta^1-(C_5H_5)_2AlO-^iPr]_2$. The compound has been characterized by NMR and its crystal structure determined by X-ray diffraction study.

Keywords: Aluminium; X-ray diffraction; Nuclear magnetic resonance; Cyclopentadienyl

1. Introduction

Cyclopentadienyl compounds of the main-group metals are of interest because of the variety of bonding modes that have been observed. Since the bonding modes influence the properties and reactions of the compounds, it is of importance to determine the nature of the interaction of the cyclopentadienyl groups with metal atoms.

Relatively few data have been given on structural characterisation of aluminium cyclopentadienyl complexes. Several dialkylaluminium and chloroalkylaluminium cyclopentadienyl complexes have only been studied by X-ray crystallography and electron diffraction [1–4]. The known monocyclopentadienylaluminium derivatives are highly fluxional and therefore no conclusive evidence can be drawn on their ground-state structure from IR and NMR spectra [4–7].

From X-ray analysis it has been established that dimethyl(cyclopentadienyl)aluminium in solid state consists of infinitive chains [1]. Dimethylaluminium units are bridged by cyclopentadienyl rings. The one length of the bridge bond anticipates for an electron deficient bond while the other is significantly longer. In the gas phase the compound has been found to be monomeric with cyclopentadienyl ring in η^2 fashion bonded to the aluminium atom [2]. The nature of the Cp–aluminium bond in hydrocarbon solutions of the compound is not clear. In benzene solution the degree of association of the compound is 1.4 [8]. An X-ray crystal structural study of chloro(pentamethylcyclopentadienyl)methyl-

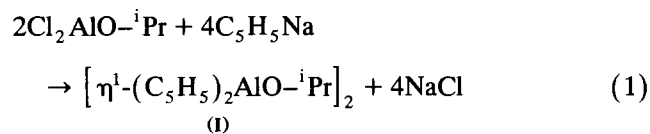
aluminium reveals dimeric units with Al–Cl bridge bonds [4]. The cyclopentadienyl groups are bonded to aluminium atoms in an η^3 manner.

To the best of our knowledge no structural information has been given on bis(cyclopentadienyl)aluminium derivatives. In this paper we describe the synthesis, characterization and a single-crystal X-ray diffraction analysis of the novel bis(η^1 -cyclopentadienyl)isopropoxide dimer $[\eta^1-(C_5H_5)_2AlO-^iPr]_2$.

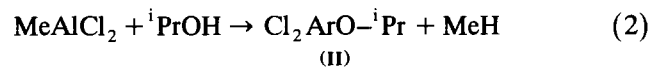
2. Results and discussion

2.1. Synthesis, properties and NMR analysis

The title compound $[\eta^1-(C_5H_5)_2AlO-^iPr]_2$ (**I**) was obtained according to Eq. 1 at ambient temperature from the reaction of Cl_2AlO-^iPr (**II**) with C_5H_5Na (**III**) in toluene or a toluene-tetrahydrofuran (THF) mixture with a high yield.



The isopropoxyaluminium dichloride (**II**) was obtained from reaction of $MeAlCl_2$ with isopropoxy alcohol:



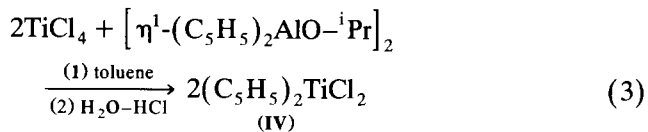
The aluminium compound **II** formed in Eq. (2) was not isolated and used directly in the synthesis of bis(cyclopentadienyl)aluminium derivative **I**. $[\eta^1-(C_5H_5)_2AlO-{}^iPr]_2$ can be isolated as light-yellow crystals by recrystallization from a toluene–hexane mixture. As expected, **I** is quite air sensitive. In the presence of a slight amount of oxygen a brown solid is formed. An elemental analysis of the resulting compound confirms the formation of **I**. In benzene solution the compound was found to be a dimer ($n = 1.96$). The molecular weight was obtained cryometrically.

The 1H and ${}^{13}C$ NMR spectra of **I** in deuterated benzene show signal pattern characteristic of the isopropoxy group in high field region and one signal of the cyclopentadienyl ligands in low one (see Section 3). The spectroscopic data are consistent with the proposed chemical formulation of the obtained compound; however, they did not permit us to determine the nature of the Cp bonding to the aluminium atom in a solution. Attempts to detect a static structure of **I** in toluene at $-70^\circ C$ by 1H NMR revealed no changes in signal pattern and no appreciable alteration in the ring proton atoms signal shape compared with the resonance signal width measured at room temperature. Similar dynamic behaviour has been reported for other cyclopentadienyl-aluminium compounds [4–7]. The equivalence of cyclopentadienyl proton atoms on the NMR time scale may result from rapid changes in aluminium atom-ring hapticity or rapid ring whizzing. The ${}^{27}Al$ NMR measurements of **I** showed a signal at 101.99 ppm.

No stable donor–acceptor complex was found to be

formed in the reaction of **I** with excess of THF or diethyl ether in toluene. Reactions were carried out at room temperature. After removal of the solvents in vacuum the 1H NMR spectra of crystalline residue showed no THF or Et_2O signals but the signals of **I** only.

The reaction of **I** with $TiCl_4$ at room temperature in toluene afforded with a high yield $(C_5H_5)_2TiCl_2$ (**IV**):



The titanium compound **IV** was identified by 1H NMR spectra and elemental analysis (see Section 3).

2.2. Crystal and molecular structure of $[\eta^1-(C_5H_5)_2AlO-{}^iPr]_2$ (**I**)

A perspective view of the molecule with the atom numbering system is shown in Fig. 1.

The X-ray crystal structure analysis revealed the presence of isopropoxy-bridged dimers in a solid state (Fig. 1). The dimer is centrosymmetric and there are no short intermolecular contacts between dimers. Selected atomic bond distances and angles are presented in the Tables 1 and 2 respectively. The cyclopentadienyl groups are bonded to the Al atom in the η^1 manner. Examination of C–C distances in the cyclopentadienyl ring shows that there are two shorter distances (C(12)–C(13), 1.347(4) Å; C(14)–C(15), 1.335(3) Å) with the remain-

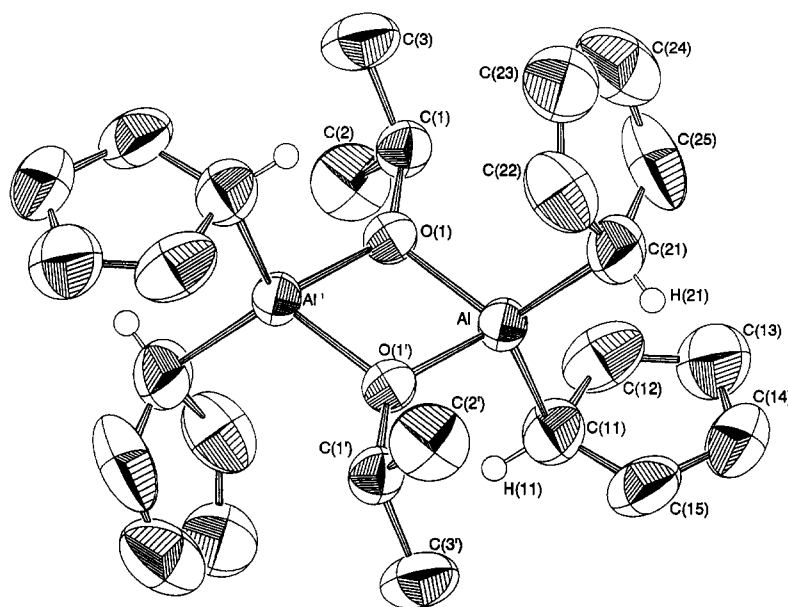


Fig. 1. Structure of **I** with the atom-numbering scheme.

Table 1
Selected bond lengths (Å) for $[\eta^1-(C_5H_5)_2AlO-{}^iPr]_2$

Al–O(1)	1.8212(11)	Al–O(1')	1.8370(11)
Al–C(21)	2.003(2)	Al–C(11)	2.022(2)
C(1)–C(2)	1.493(6)	C(1)–C(3)	1.508(5)
C(11)–C(15)	1.429(3)	C(21)–C(22)	1.434(3)
C(11)–C(12)	1.441(3)	C(21)–C(25)	1.444(4)
C(12)–C(13)	1.347(4)	C(22)–C(23)	1.342(4)
C(13)–C(14)	1.386(4)	C(23)–C(24)	1.378(4)
C(14)–C(15)	1.335(3)	C(24)–C(25)	1.310(4)
O(1)–C(1)	1.473(2)		

Symmetry transformations used to generate equivalent atoms (designated by prime): $-x, -y, -z$.

ing distances as follows: C(11)–C(12), 1.441(3) Å; C(11)–C(15), 1.429(3) Å; C(13)–C(14), 1.386(4) Å. For the second cyclopentadienyl ring bonded to the same aluminium atom the distances are 1.342(4) Å, 1.310(4) Å, 1.434(3) Å, 1.444(4) Å and 1.378(4) Å respectively.

The cyclopentadienyl rings are almost flat; the rms deviations of the ring carbon atoms from mean least-square planes in both cases are 0.02 Å. A small fold of the rings along lines containing C(12), C(15) and C(22), C(25) respectively is observed. The dihedral angle between the C(12), C(11), C(15) plane and the C(12), C(13), C(14), C(15) plane is 5.2(2)°. In the second ring the angle between the same sets of planes is 4.3(2)°. For both cyclopentadienyl rings there is one short aluminium atom–ring carbon atom distance: Al–C(11), 2.022(2) Å; Al–C(21), 2.003(2) Å. These distances fall within the range expected for Al–C bonding interaction in cyclopentadienyl aluminium compounds. The remaining aluminium–carbon ring distances are longer (e.g. Al–C(12), 2.693(2) Å; Al–C(15), 2.709(2) Å; Al–C(22), 2.802(2) Å; Al–C(25), 2.721(2) Å) compared with the accepted range of Al–C bonds and they are considered to be non-bonding distances. These data providing support for an $\eta^1-C_5H_5$ –metal interaction. As

Table 2
Selected bond angles (°) for $[\eta^1-(C_5H_5)_2AlO-{}^iPr]_2$

O(1)–Al–O(1')	80.85(5)	Al–O(1)–Al'	99.15(5)
O(1)–Al–C(21)	115.20(8)	O(1')–Al–C(21)	114.50(9)
O(1)–Al–C(11)	111.96(8)	O(1')–Al–C(11)	109.63(8)
C(21)–Al–C(11)	118.66(9)	C(2)–C(1)–C(3)	112.5(5)
C(1)–O(1)–Al	123.8(2)	C(1)–O(1)–Al'	137.0(2)
O(1)–C(1)–C(2)	109.6(3)	O(1)–C(1)–C(3)	109.2(3)
C(15)–C(11)–Al	102.1(2)	C(25)–C(21)–Al	103.0(2)
C(12)–C(11)–Al	100.74(14)	C(22)–C(21)–Al	108.07(14)
C(15)–C(11)–C(12)	104.4(2)	C(22)–C(21)–C(25)	103.4(2)
C(13)–C(12)–C(11)	108.1(2)	C(23)–C(22)–C(21)	108.1(3)
C(12)–C(13)–C(14)	109.1(2)	C(22)–C(23)–C(24)	109.6(3)
C(15)–C(14)–C(13)	109.3(2)	C(25)–C(24)–C(23)	109.2(3)
C(14)–C(15)–C(11)	108.9(2)	C(24)–C(25)–C(21)	109.5(3)

Symmetry transformations used to generate equivalent atoms (designated by prime): $-x, -y, -z$.

mentioned earlier a cyclopentadienyl ligand is able to interact with aluminium atom in a different manner. It is likely that in **I** the bonding of Cp groups in η^1 fashion is derived from steric hindrance. In the dimeric structure of the studied compound **I**, each aluminium atom is surrounded by four bulky groups. The plane containing C(11), Al, C(21) is perpendicular to the plane of the four-membered Al_2O_2 ring. The Al_2O_2 four-membered ring is planar. The Al–O(1) and Al–O'(1') bond lengths are 1.821(11) Å and 1.837(11) Å respectively. The bond angle of Al–O(1)–Al' is 99.15(5)° and of O(1)–Al–O'(1') is 80.85(5)°. The four-membered ring has been found to be a structural feature of the $Al_2(O-{}^iBu)_6$ [9].

3. Experimental details

3.1. General comments

All the reactions were carried out under dry argon using Schlenk techniques. Solvents were dried by standard methods. CpNa (**III**) was obtained from the reaction of freshly distilled CpH with NaH in THF and used directly in the synthesis of the aluminium compound. NMR spectra were run on Varian VXR-300 (1H , ${}^{13}C$ and ${}^{27}Al$).

3.2. Synthesis of $[\eta^1-(C_5H_5)_2AlO-{}^iPr]_2$

iPrOH (6.42 ml, 84 mmol) was added slowly (0.5 h) to a stirred solution of Cl_2AlMe (9.5 g, 84 mmol) in toluene (100 ml) cooled to $-30^\circ C$. During the reaction, methane slowly evolved. The mixture was allowed to warm to ambient temperature (1 h) and then CpNa (15.0 g, 170 mmol) in THF (100 ml) added. The reaction mixture was stirred for 1 h; the solvent was removed in vacuo. A yellow residue was washed with pentane (30 ml) and dried in vacuo; extracted toluene (150 ml) was

Table 3
Crystal data and structure refinement for $[\eta^1-(C_5H_5)_2AlO^{-1}Pr]_2$.

Empirical formula	$C_{13}H_{17}AlO$
Formula weight	216.25
Temperature (K)	295(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit-cell dimensions	
<i>a</i> (Å)	8.710(2)
<i>b</i> (Å)	10.572(3)
<i>c</i> (Å)	13.193(3)
β (°)	90.25(2)
Volume (Å ³)	1214.9(5)
<i>Z</i>	4
Density (calculated) (Mg m ⁻³)	1.182
Absorption coefficient (mm ⁻¹)	0.139 mm ⁻¹
<i>F</i> (000)	464
Crystal size (mm)	1.20 × 0.45 × 0.35
θ range for data collection (°)	2.5 to 25.0
Index ranges	0 ≤ <i>h</i> ≤ 10, 0 ≤ <i>k</i> ≤ 12, −15 ≤ <i>l</i> ≤ 15
Number of reflections collected	2282
Number of independent reflections	2134 (<i>R</i> _{int} = 0.0135)
Refinement method	Full-matrix least-squares on <i>F</i> ²
Number of data	2117
Number of restraints	6
Number of parameters	224
Goodness of fit on <i>F</i> ²	1.062
Reflections with <i>I</i> > 2σ(<i>I</i>)	1845
Final <i>R</i> indices (<i>I</i> > 2σ(<i>I</i>))	
<i>R</i> ₁	0.0347
<i>wR</i> ₂	0.0965
<i>R</i> indices (all data)	
<i>R</i> ₁	0.0409
<i>wR</i> ₂	0.1012
Extinction coefficient	0.004(2)
Largest difference peak and hole (electrons Å ⁻³)	0.18 and −0.16

Table 4
Atomic coordinates and equivalent isotropic displacement parameters for $[\eta^1-(C_5H_5)_2AlO^{-1}Pr]_2$.

	<i>x</i> (× 10 ⁻⁴)	<i>y</i> (× 10 ⁻⁴)	<i>z</i> (× 10 ⁻⁴)	<i>U</i> _{eq} (× 10 ⁻³ Å ²)	SOF
Al	76(1)	139(1)	1049(1)	45(1)	
O(1)	840(1)	876(1)	−91(1)	45(1)	
C(1)	1909(2)	1955(2)	−79(3)	51(1)	0.890(11)
C(2)	3451(5)	1533(7)	−436(7)	87(2)	0.890(11)
C(3)	1253(8)	3008(4)	−718(6)	83(2)	0.890(11)
C(11)	1696(3)	−857(2)	1807(2)	70(1)	
C(12)	2662(3)	151(2)	2174(2)	82(1)	
C(13)	2316(4)	358(3)	3154(2)	96(1)	
C(14)	1224(3)	−515(2)	3459(2)	89(1)	
C(15)	877(3)	−1273(2)	2681(2)	76(1)	
C(21)	−1387(3)	1209(2)	1843(2)	79(1)	
C(22)	−2552(3)	1661(3)	1162(2)	83(1)	
C(23)	−2263(3)	2883(3)	964(2)	96(1)	
C(24)	−1010(4)	3277(3)	1521(3)	103(1)	
C(25)	−495(3)	2328(3)	2064(2)	99(1)	
C(1A)	2001(20)	1715(17)	−655(29)	64(7)	0.110(11)
C(2A)	3546(23)	1480(28)	−280(28)	38(7)	0.110(11)
C(3A)	1473(39)	3030(19)	−692(28)	42(8)	0.110(11)

*U*_{eq} is defined as one third of the trace of the orthogonalized *U*_{*ij*} tensor.

added. The toluene was evaporated in vacuo to give **I** as a light-yellow solid (yield, 14.7 g (81%)) which was crystallized from toluene–hexane.

Anal. found: C, 72.39; H, 7.98; Al, 12.33; *M*_w (cryometrically in benzene) 423 (*n* = 1.96). $C_{13}H_{17}OAl$ calc.: C, 72.22; H, 7.87; Al, 12.50%; *M*_w = 216. ¹H NMR (C_6D_6): δ 0.89 (d, *J* = 6.3 Hz, 6H, CH₃), 3.68 (sep., *J* = 6.3 Hz, 1H, CH), 6.11 (s, 10H, C₅H₅) ppm. ¹³C NMR (C_6D_6): δ 25.57 (CH₃), 70.19 (CH), 113.72 (C₅H₅) ppm. ²⁷AlNMR (C_6D_6): δ 101.99 ppm.

3.3. Reaction of $[(\eta^1-C_5H_5)_2AlO^{-1}Pr]_2$ (**I**) with $TiCl_4$

A solution of **I** (3.0 g, 13.8 mmol) in toluene (10 ml) was added to a stirred solution of $TiCl_4$ (2.64 g, 13.8 mmol) in toluene at room temperature. The red solution was stirred for 1 h and then a water–HCl mixture (20 ml) (5 : 1) added. More toluene was added, the toluene extract washed with water, dried, filtered and evaporated to dryness to give $(C_5H_5)_2TiCl_2$ as a red solid (yield, 2.61 g (76%)).

¹H NMR ($CDCl_3$): δ 6.57 (s, C₅H₅). Anal. Found: Cl, 28.11; Ti, 19.42. $C_{10}H_{10}Cl_2Ti$ calc.: Cl, 28.51; Ti, 19.27%.

3.4. X-ray structure determination

A transparent light-yellow well-shaped crystal of **I** was placed in a thin-walled capillary tube (Lindemann glass) in an inert atmosphere. The tube was plugged with grease, flame sealed and then mounted on the goniometer head of a four-circle P3 (Siemens AG) diffractometer. The crystallographic data, a summary of

data collection and the refinement procedure are presented in Table 3.

The crystal system, the orientation matrix and the unit-cell parameters were obtained from the least-squares refinement of the angular positions measured for 17 reflections randomly found in the 2θ range between 15 and 31°. The intensities were collected up to $2\theta = 50^\circ$ (maximum $(\sin \theta)/\lambda = 0.60$) in the θ - 2θ mode with the scan range 1.8° plus the $K\alpha_1$ - $K\alpha_2$ separation at various scan speeds. Two check reflections (316) and (224), repeated every 70 reflections, showed a decay of 3.6%. The intensities were adjusted accordingly and corrected for the Lorentz-polarization effect. No absorption correction was applied. The phase problem was solved by direct methods using the SHELXS-86 program [10].

Positional and thermal parameters of the non-hydrogen atoms (first isotropic and then anisotropic) were adjusted by means of several rounds of full-matrix least-squares calculation [11]. The positions of the hydrogen atoms were determined on the subsequent difference Fourier map. We found disorder of isopropyl groups in the studied molecule. The low electron density maximum near the C(1) atom of the isopropyl group indicated that the group could flip between two positions. Because of this, further refinement was carried out for two isopropyl groups, assuming that the occupation factors of both groups added to unity. Owing to partial overlapping of the atoms of the disordered groups, geometrical restraints was introduced and only a secondary carbon atom of the second isopropyl group was refined anisotropically (site occupation factor was refined at a level of 11%). In the later iterations, hydrogen atoms of the second isopropyl group were incorporated at their calculated positions. An extinction correction was included as a variable in the final cycles. Final difference Fourier synthesis contained no unusual

features. The structure was refined against F^2 with $w^{-1} = \delta^2(F_0^2) + (0.0601P)^2 + 0.1562P$ where $P = (F_0^2 + 2F_c^2)/3$. The R values presented in Table 3 are defined as $wR_2 = (\sum w(F_0^2 - F_c^2)^2 / \sum wF_0^4)^{1/2}$ and $R1 = \sum ||F_0| - |F_c|| / \sum |F_0|$.

Atomic coordinates and equivalent isotropic thermal parameters are listed in Table 4.

Tables of hydrogen atom coordinates and anisotropic thermal parameter and a complete list of bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

Acknowledgements

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