Synthesis and Structures of Sterically Crowded Aryloxide-substituted Aluminium Chloride†

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The reaction of $AlCl_3$ with $Li(OR')\cdot Et_2O$ ($R' = C_6H_2Bu^t_3$-2,4,6) in diethyl ether gave $Al(OR')Cl_2\cdot Et_2O$ **1**, a monomeric aryloxide compound of aluminium. Its reaction with 2 equivalents of potassium gave elemental aluminium and $[Al(OEt)(OR')_2]_2$ **2** containing a four-membered Al_2O_2 ring. Compound **1** crystallizes in the monoclinic space group $P2_1/c$ with $a = 10.692(2)$, $b = 21.825(4)$, $c = 11.683(2)$ Å and $\beta = 115.49(3)°$ and compound **2** in the space group $P\bar{1}$ with $a = 10.227(2)$, $b = 10.966(2)$, $c = 18.493(4)$ Å, $\alpha = 101.13(3)$, $\beta = 97.63(3)$ and $\gamma = 115.29(3)°$.

Aluminium alkyl reagents react with phenols to give aluminium aryloxide compounds.[1] In general these compounds exist as dimers or trimers. Only with sterically demanding phenols such as $HOC_6H_3Bu^t_2$-2,6 is the resulting aluminium aryloxide monomeric.[2] These monomeric species are highly regio- and stereo-selective in organic syntheses[3,4] and they have found application in the preparation of new Ziegler–Natta catalysts with high selectivity and stereospecificity in the polymerization of propene.[5–8] To the best of our knowledge, there is only one structurally characterized monomeric compound known, $Al(OR)Cl_2\cdot Et_2O$ ($R = C_6H_2Bu^t_2$-2,6-Me-4)[9]. In this paper we describe a facile route to monomeric $Al(OR')Cl_2\cdot Et_2O$ **1** ($R' = C_6H_2Bu^t_3$-2,4,6) and its chemical behaviour. Reaction of **1** with two equivalents of potassium leads to the formation of $[Al(OEt)(OR')_2]_2$ **2**. Compounds **1** and **2** are characterized by NMR studies and X-ray crystallography.

Results and Discussion

The reaction of $AlCl_3$ with Li-containing compounds often leads to the formation of a mixture of mono-, di- and tri-substituted derivatives. Only with sterically demanding reagents it is possible to synthesize monosubstituted compounds. We were interested in preparing a monosubstituted organoaluminium dichloride with a strong bond between aluminium and the organic substituent and $OC_6H_2Bu^t_3$-2,4,6 (OR′) was selected as the ligand. A few aluminium aryloxides formed from the reaction of $AlMe_3$ and alcohols are known.[1] However only one monomeric example of the type $Al(OR)Cl_2$ is described in the literature, *i.e.* $Al(OR)Cl_2\cdot Et_2O$ ($R = C_6H_2Bu^t_2$-2,6-Me-4), which is prepared by the reaction of 2 equivalents of $SnMe_3Cl$ with $AlMe_2(OR)\cdot Et_2O$ or $AlEt_2(OR)\cdot Et_2O$.[9]

The interaction of $AlCl_3$ with 1 equivalent of $Li(OR')\cdot Et_2O$ results in the nearly quantitative formation of $Al(OR')Cl_2\cdot Et_2O$ **1** [equation (1)]. Compound **1** is an air- and moisture-sensitive

$$AlCl_3 + Li(OR')\cdot Et_2O \longrightarrow \underset{\mathbf{1}}{Al(OR')Cl_2\cdot Et_2O} + LiCl \quad (1)$$

colourless solid but stable under an inert gas atmosphere.

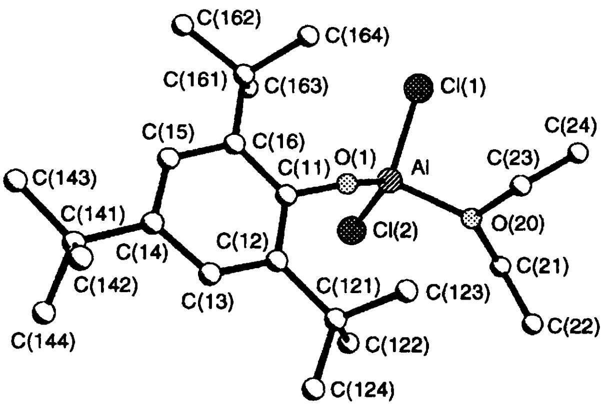

Fig. 1 Molecular structure of $Al(OR')Cl_2\cdot Et_2O$ **1**. Thermal ellipsoids are shown at the 50% level and hydrogen atoms have been omitted for clarity

Table 1 Selected bond lengths (Å) and angles (°) in $Al(OR')Cl_2\cdot Et_2O$ **1**

Al–O(1)	1.699(2)	Al–O(20)	1.861(2)
Al–Cl(1)	2.132(1)	Al–Cl(2)	2.125(1)
O(1)–C(11)	1.383(3)	O(20)–C(21)	1.478(3)
O(20)–C(23)	1.479(3)		
O(1)–Al–O(2)	105.9(8)	O(1)–Al–Cl(2)	117.2(7)
O(20)–Al–Cl(2)	105.0(6)	O(1)–Al–Cl(1)	115.9(7)
O(20)–Al–Cl(1)	100.6(7)	Cl(2)–Al–Cl(1)	110.1(4)
C(11)–O(1)–Al	152.7(2)	C(21)–O(20)–C(23)	115.1(2)
C(21)–O(20)–Al	125.6(2)	C(23)–O(20)–Al	117.5(1)

Crystals of compound **1** were formed from a solution in hexane at 0 °C. Its molecular structure has been determined by X-ray crystallography and is shown in Fig. 1; selected bond lengths and angles are given in Table 1. The structure shows discrete monomeric units of **1**. The Al–Cl bond distances of 2.125(1) and 2.132(1) Å are slightly longer than those in $Al(OR)Cl_2\cdot Et_2O$ [2.104(2) and 2.110(2) Å][9] but within the range of terminal Cl atoms. The other bond lengths and angles are nearly identical to those found in $Al(OR)Cl_2\cdot Et_2O$. The structure demonstrates the effective shielding of the two Bu^t groups.

Recently we reported on the successful reduction of $Al(\eta^5$-$C_5Me_5)Cl_2$ to an aluminium(I) compound[10] and we were therefore interested in extending this type of reaction to compound **1**. However, in general, organoaluminium dichlorides react with

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

reducing agents under disproportionation to give elemental aluminium and di- or tri-substituted derivatives of the type AlL_2Cl and AlL_3, respectively.[11]

The reaction of **1** with 2 equivalents of potassium in toluene leads to a brown oil after removal of solvent. Compound $[Al(OEt)(OR')_2]_2$ **2** was obtained after two months of crystallisation in 8% yield [equation (2)]. Its molecular

$$2\,Al(OR')Cl_2{\cdot}Et_2O + 4K \longrightarrow [Al(OEt)(OR')_2]_2 + 4KCl \quad (2)$$

structure has been determined by X-ray crystallography and is shown in Fig. 2; selected bond lengths and angles are given in Table 2. The central unit in **2** is a four-membered Al_2O_2 ring with an inversion centre within the ring giving a planar ring system. An ethyl group is bound to each oxygen of the ring. Clearly the formation of compound **2** is accomplished under the cleavage of an ether molecule. The Al–O bond lengths [1.839(2) and 1.850(2) Å] and Al–O–Al and O–Al–O bond angles [102.4(1)–77.7(1)°] are within the ranges reported for Al_2O_2 ring systems.[12,13] As expected the Al–O distances from $OC_6H_2Bu^t_3$-2,4,6 are shorter than those within the Al_2O_2 ring, but they are longer than those in **1** or in $AlMe(OR)_2$ [average 1.686(2) Å].[14] The reasons are obviously the higher steric crowding in **2** and the larger Al–O–C angle in **1** [152.7(2)]° compared to **2** [142.3(2)°]. The Al–O–C unit therefore has more sp character in **1** and more sp^2 character in **2**. Consequently the Al–O bond distances in monomeric aluminium compounds are found to be shorter than those in dimeric systems.

The formation of $[Al(OEt)(OR')_2]_2$ **2** from the reaction of $Al(OR')Cl_2{\cdot}Et_2O$ **1** with 2 equivalents of potassium shows that aluminium aryloxides react in the same manner as the corresponding aluminium alkyl and aryl derivatives. Proton NMR studies of the oily residue indicate that it is a mixture of several compounds possibly containing a reduced form of aluminium. Further investigations are underway.

Table 2 Selected bond lengths (Å) and angles (°) in $[Al(OEt)(OR')_2]_2$ **2**

Al(1)–O(1)	1.713(2)	Al(1)–O(2)	1.723(2)
Al(1)–O(3)	1.839(2)	Al(1)–O(3a)	1.850(2)
Al(1)–Al(1a)	2.874(2)	Al(1a)–O(3)	1.850(2)
O(1)–C(11)	1.382(4)	O(2)–C(21)	1.396(4)
O(3)–C(1)	1.460(4)		
O(1)–Al(1)–O(2)	118.6(1)	O(1)–Al(1)–O(3)	105.8(1)
O(2)–Al(1)–O(3)	122.6(1)	O(1)–Al(1)–O(3a)	120.7(1)
O(2)–Al(1)–O(3a)	105.7(1)	O(3)–Al(1)–O(3a)	77.7(1)
Al(1)–O(1)–C(11)	142.3(2)	Al(1)–O(2)–C(21)	142.7(2)
Al(1)–O(3)–C(1)	128.6(2)	Al(1a)–O(3)–C(1)	125.7(2)
Al(1)–O(3)–Al(1a)	102.4(1)		

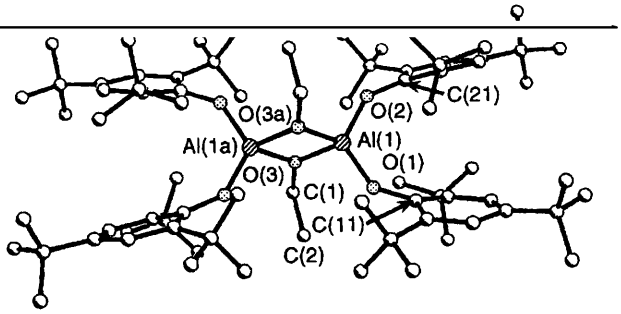

Fig. 2 Molecular structure of $[Al(OEt)(OR')_2]_2$ **2**. Thermal ellipsoids are shown at the 50% level and hydrogen atoms have been omitted for clarity

Table 3 Crystallographic details for $Al(OR')Cl_2{\cdot}Et_2O$ **1** and $[Al(OEt)(OR')_2]_2$ **2** ($R' = C_6H_2Bu^t_3$-2,4,6)

	1	**2**
Empirical formula	$C_{22}H_{39}AlCl_2O_2$	$C_{76}H_{126}Al_2O_6$
M	433.41	118.73
Crystal size/mm	0.60 × 0.50 × 0.50	0.50 × 0.50 × 0.50
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
a/Å	10.692(2)	10.227(2)
b/Å	21.825(4)	10.966(2)
c/Å	11.683(2)	18.493(4)
α/°	—	101.13(3)
β/°	115.49(3)	97.63(3)
γ/°	—	115.29(3)
U/Å^3	2460.9(8)	1785.0(6)
Z	4	1
D_c/Mg m^{-3}	1.170	1.107
μ/mm^{-1}	0.313	0.090
$F(000)$	936	656
2θ range/°	7–45	7–45
Index ranges	$-11 \leqslant h \leqslant 10$	$-10 \leqslant h \leqslant 3$
(partial)	$-23 \leqslant k \leqslant 23$	$-10 \leqslant k \leqslant 11$
	$-11 \leqslant l \leqslant 12$	$-19 \leqslant l \leqslant 19$
Reflections collected	7587	4562
Independent reflections	3220	4553
Data/restraints/parameters	3218/0/245	4549/0/380
Goodness of fit on F^2	0.963	1.014
Final R indices [$I > 2\sigma(I)$]		
$R1$	0.0424	0.0712
$wR2$*	0.1146	0.1846
R indices (all data)		
$R1$	0.0500	0.0833
$wR2$*	0.1265	0.2064
Largest difference peak, hole/e nm^{-3}	538, −393	541, −745

* $wR2 = \{[\Sigma w(F_o^2 - F_c^2)^2]/\Sigma wF_o^4\}^{\frac{1}{2}}$ where $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$ [$P = (F_o^2 + 2F_c^2)/3$] and a = 0.0800, 0.1400, b = 1.7500, 2.1000 for **1** and **2** respectively.

Table 4 Atomic coordinates (× 10^4) for **1**

Atom	*x*	*y*	*z*
Al	−812(1)	632(1)	1941(1)
Cl(1)	1308(1)	839(1)	2439(1)
Cl(2)	−2062(1)	890(1)	31(1)
O(1)	−1400(2)	821(1)	3035(2)
C(11)	−2208(3)	1163(1)	3456(2)
C(12)	−3451(3)	907(1)	3409(2)
C(13)	−4261(3)	1273(1)	3801(2)
C(14)	−3902(3)	1867(1)	4264(2)
C(15)	−2658(3)	2090(1)	4343(2)
C(16)	−1775(3)	1753(1)	3967(2)
C(121)	−3928(3)	246(1)	2952(2)
C(122)	−4253(3)	175(1)	1539(2)
C(123)	−2829(3)	−218(1)	3769(3)
C(124)	−5265(3)	74(1)	3062(3)
C(141)	−4865(3)	2231(1)	4691(3)
C(142)	−4980(4)	1893(2)	5799(3)
C(143)	−4341(3)	2880(1)	5124(4)
C(144)	−6308(3)	2284(1)	3586(3)
C(161)	−395(3)	2044(1)	4109(2)
C(162)	−106(3)	2667(1)	4796(3)
C(163)	−441(3)	2178(1)	2789(2)
C(164)	831(3)	1632(1)	4910(2)
O(20)	−766(2)	−221(1)	1918(2)
C(21)	−1327(3)	−608(1)	768(2)
C(22)	−2144(3)	−1139(1)	899(3)
C(23)	190(3)	−535(1)	3091(2)
C(24)	1413(3)	−823(1)	2984(3)

Experimental

General.—All solvents were dried, distilled and degassed prior to use. Elemental analyses were performed at this institute. Melting points were determined in sealed capillaries and are uncorrected. The IR spectra (4000–300 cm^{-1}) were recorded on a Bio-Rad Digilab FTS-7 instrument as Nujol mulls and ^{1}H and ^{13}C NMR spectra (C_6D_6) on Bruker AM 250 spectrometers. Chemical shifts are given *versus* internal C_6D_5H (δ 7.15, ^{1}H) and C_6D_6 (δ 128, ^{13}C), respectively. Mass spectra [EI (electron impact)] were recorded on Varian MAT CH5 and Finnigan MAT System 8230 spectrometers. The synthesis of Li(OR′)·Et_2O was carried out according to the literature method.[15]

Preparation of Al(OR′)Cl_2·Et_2O **1**.—To a mixture of $AlCl_3$ (1.08 g, 8 mmol) and Li(OR′)·Et_2O (2.74 g, 8 mmol) was added Et_2O (70 cm^3) and the suspension stirred at room temperature for 20 h. Then the solvent was removed *in vacuo* and the resulting yellow solid extracted with hexane (60 cm^3). The solvent was reduced to 35 cm^3 and **1** crystallized at 0 °C in 92% yield (3.19 g), m.p. 118 °C (Found: C, 62.2; H, 9.0. Calc. for $C_{22}H_{39}AlCl_2O_2$: C, 63.2; H, 9.42%). IR (Nujol): ν 1244s, 1147s, 1124vs, 1006vs, 940s, 891vs, 873w, 768vs, 618w, 561s, 522vs, 441vs, 401w and 345s cm^{-1}. NMR: δ_H(250 MHz, 25 °C, C_6D_6, $SiMe_4$), 0.65 (6 H, t, CH_2*Me*, $^3J_{HH}$ 7.0), 1.37 (9 H, s, *p*-Bu^t), 1.64 (18 H, s, *o*-Bu^t), 3.62 (4 H, q, C*H*$_2$Me, $^3J_{HH}$ 7.0 Hz), 7.53 (2 H, s, C_6H_2); δ_C(100 MHz, 25 °C, C_6D_6, $SiMe_4$), 12.8 (Me, OEt), 31.9 (Me, *o*-Bu^t), 32.3 (Me, *p*-Bu^t), 35.0 (C, *p*-Bu^t), 35.9 (C, *o*-Bu^t), 69.6 (CH_2, OEt), 122.9 (*o*-C, C_6H_2O), 139.1 (*p*-C, C_6H_2O), 141.4 (*m*-C, C_6H_2O), 152.9 (OC, C_6H_2O). Mass spectrum (EI): *m*/*z* 358 (M^+ − Et_2O).

Preparation of [Al(OEt)(OR′)$_2$]$_2$ **2**.—To a solution of **1** (6.26 g, 15 mmol) in toluene (70 cm^3) potassium (1.20 g, 31 mmol) was added. The mixture was refluxed for 1.5 h and then filtered. The solvent was removed *in vacuo* very slowly to give colourless crystals of **2** (0.35 g, 8%), m.p. 196 °C (Found: C, 74.8; H, 10.5. Calc. for $C_{76}H_{126}Al_2O_6$: C, 76.72; H, 10.67%). IR (Nujol): ν 1236w, 1118s, 1018vs, 926s, 873vs, 776s, 727w, 630vs, 521w and 447w cm^{-1}. NMR: δ_H(250 MHz, 25 °C, C_6D_6, $SiMe_4$) 1.25 (3 H, t, CH_2*Me*, $^3J_{HH}$ 7.0), 1.39 (18 H, s, *p*-Bu^t), 1.45 (36 H, s, *o*-Bu^t), 4.55 (2 H, q, C*H*$_2$Me, $^3J_{HH}$ 7.0 Hz); δ_C(100 MHz, 25 °C, C_6D_6, $SiMe_4$), 18.2 (Me, OEt), 31.9 (Me, *p*-Bu^t), 33.4 (Me, *o*-Bu^t), 34.7 (C, *p*-Bu^t), 36.3 (C, *o*-Bu^t), 64.8 (CH_2, OEt), 122.8 (*o*-C, C_6H_2O), 138.0 (*p*-C, C_6H_2O), 140.2 (*m*-C, C_6H_2O), 153.9 (OC, C_6H_2O). Mass spectrum (EI): *m*/*z* 1189 (M^+).

Table 5 Atomic coordinates (× 10^4) for **2**

Atom	*x*	*y*	*z*
Al(1)	4 412(1)	9 871(1)	9 223(1)
O(1)	3 821(2)	8 328(2)	8 536(1)
O(2)	4 337(2)	11 265(2)	8 957(1)
O(3)	3 801(2)	9 366(2)	10 059(1)
C(1)	2 387(4)	8 248(3)	10 090(2)
C(2)	2 187(4)	6 814(4)	9 725(2)
C(11)	3 556(3)	7 780(3)	7 762(2)
C(12)	4 530(4)	7 322(3)	7 484(2)
C(13)	4 492(4)	7 098(3)	6 718(2)
C(14)	3 460(4)	7 228(4)	6 204(2)
C(15)	2 375(4)	7 416(4)	6 479(2)
C(16)	2 328(4)	7 651(3)	7 244(2)
C(121)	5 574(4)	6 977(3)	7 988(2)
C(122)	6 892(4)	8 294(4)	8 531(2)
C(123)	6 215(4)	6 176(4)	7 518(2)
C(124)	4 656(4)	5 989(4)	8 424(2)
C(141)	3 548(4)	7 076(5)	5 372(2)
C(142)	3 321(8)	5 623(6)	5 009(2)
C(143)	2 396(6)	7 337(7)	4 923(2)
C(144)	5 088(6)	8 147(7)	5 344(3)
C(161)	840(4)	7 510(4)	7 402(2)
C(162)	−256(4)	5 936(4)	7 150(2)
C(163)	870(4)	8 071(4)	8 218(2)
C(164)	228(4)	8 255(4)	6 939(2)
C(21)	3 701(3)	11 611(3)	8 364(2)
C(22)	4 336(4)	11 794(3)	7 735(2)
C(23)	3 504(4)	11 921(3)	7 112(2)
C(24)	2 178(4)	11 960(3)	7 098(2)
C(25)	1 723(4)	11 990(3)	7 771(2)
C(26)	2 470(3)	11 861(3)	8 419(2)
C(221)	5 931(4)	12 043(3)	7 727(2)
C(222)	7 007(4)	13 305(4)	8 406(2)
C(223)	6 400(4)	12 426(4)	7 016(2)
C(224)	6 147(4)	10 763(4)	7 752(2)
C(241)	1 263(4)	12 074(4)	6 407(2)
C(242)	1 914(6)	11 993(6)	5 726(2)
C(243)	1 212(5)	13 457(4)	6 605(2)
C(244)	−334(5)	10 883(5)	6 201(2)
C(261)	2 025(4)	12 199(3)	9 163(2)
C(262)	848(4)	12 710(4)	9 075(2)
C(263)	1 381(4)	10 967(4)	9 506(2)
C(264)	3 407(4)	13 427(4)	9 725(2)

Crystal Structure Determinations of **1** *and* **2**.—Data were collected at −120 °C on a Stoe AED 2 (revision 6.2) four-circle diffractometer. Monochromated Mo-Kα radiation (λ = 0.710 73 Å) was used and semi-empirical absorption corrections employed. The structures were solved by direct methods (SHELXS 86[16]) and refined against F^2 using SHELXL 92.[17] All non-hydrogen atoms were refined anisotropically. For the hydrogen atoms a riding model was used.

The crystallographic details for compounds **1** and **2** are summarized in Table 3 and atomic coordinates in Tables 4 and 5 respectively.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining band lengths and angles.

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