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Sterically encumbered aluminum aryloxide complexes

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Summary — This work was conducted as part of a broad-based effort to determine the factors that affect cation formation for organometallic aluminum complexes. Previous studies have shown that the cationic complexes $[R_2Al(NH_2{}^tBu)_2]X$ result from the combination of R_2AlX and excess $NH_2{}^tBu$ when X = Br and I. In the present study the effect of replacing one alkyl group with the relatively bulky aryloxide (2,6-di-*tert*-butyl phenoxide = Ph*O) to yield complexes of formula $[Me(Ph^*O)AlX]_2$ (X = Cl (**1**), Br (**2**)) was examined. With excess $NH_2{}^tBu$ only the adduct species formed, $Me(Ph^*O)AlX(NH_2{}^tBu)$ (where X = Cl (**3**), Br (**4**)). In using R_2AlI a different type of reaction occurs and only $Ph^*OAlMe_2(NH_2{}^tBu)$ (**5**) and $[NH_3{}^tBu]I$ are obtained. Of related interest, the compound $Me_2(Ph^*O)Al(THF)$ (**6**) is also reported. The presence of **4** as an adduct species indicates that the inductive effect of the aryloxide prevents cation formation where X = Br, in contrast to the complexes which possess only alkyl. All of the compounds were characterized by mp, ^{1}H NMR, IR, elemental analyses, and in some cases, X-ray crystallography. X-ray data: (**1**) monoclinic, $P2_1/n$, a = 10.604(1), b = 20.776(4), c = 14.752(1) Å, β = 92.450(1)°, V = 3247.1(7) Å^3, Z = 4, with 3245 reflections with $F > 4.0\ \sigma F$, R = 0.0436; (**3**) orthorhombic, $Pna2_1$, a = 16.879(2), b = 12.315(2), c = 10.442(1) Å, V = 2170.5(5) Å^3, Z = 4, with 1270 reflections with $F > 4.0\ \sigma F$, R = 0.0477; (**5**) orthorhombic, $Pna2_1$, a = 17.111(3), b = 12.375(1), c = 10.380(1) Å, V = 2197.7(5) Å^3, Z = 4, with 1226 reflections with $F > 4.0\ \sigma F$, R = 0.0538.

organometallic aluminum complex / $[R_2Al(NH_2{}^tBu)_2]$ / $Me(Ph^*O)AlX(NH_2{}^tBu)$ / $Ph^*OAlMe_2(NH_2{}^tBu)$ / $Me_2(Ph^*O)Al(THF)$ / aryloxy effect / X-ray analysis / ^{1}H NMR

Résumé — Complexes aryloxydes de l'aluminium avec un encombrement stérique important. *Ce travail s'insère dans une étude qui vise à déterminer les facteurs qui interviennent sur la formation de cation des complexes organométalliques de l'aluminium. Des études préliminaires ont montré que les complexes cationiques $[R_2Al(NH_2{}^tBu)_2]$ résultaient de la combinaison de R_2AlX et d'un excès de $NH_2{}^tBu$ quand X = Br et I. Dans la présente étude, l'effet de remplacement d'un groupe alkyl par le relativement encombrant aryloxy (2,6-di-*tert*-butylphenoxy = Ph*O) pour obtenir les complexes de formule $[Me(Ph^*O)AlX]_2$ avec X = Cl (**1**), Br (**2**) a été examiné. Avec un excès de $NH_2{}^tBu$ seuls les adduits $Me(Ph^*O)AlX(NH_2{}^tBu)$ sont obtenus [quand X = Cl (**3**), Br (**4**)]. En utilisant R_2AlI une réaction de type différent intervient et seuls les composés $Ph^*OAlMe_2(NH_2{}^tBu)$ (**5**) et $[NH_3{}^tBu]I$ sont obtenus. Le composé $Me_2(Ph^*O)Al(THF)$ (**6**) a également été décrit. La formation de l'adduit **4** indique que l'effet inductif de l'aryloxy empêche la formation du cation quand X = Br, par comparaison avec les complexes qui ne présentent que des groupes alkyls. Tous les composés ont été caractérisés par leur point de fusion, ^{1}H RMN, IR, analyses élémentaires, et dans certains cas par analyse RX : (**1**) monoclinique,* $P2_1/n$, a = *10,604(1),* b = *20,776(4),* c = *14,752(1) Å,* β = *92,450(1)°,* V = *3247,1(7) Å*^{3}, Z = *4 avec 3245 réflexions et* $F > 4{,}0\ \sigma F$, R = *0,0436; (**3**) orthorhombique,* $Pna2_1$, a = *16,879(2),* b = *12,315(2),* c = *10,442(1) Å,* Z = *4 avec 1226 réflexions et* $F > 4{,}0\ \sigma F$, R = *0,0538.*

complexe cationique de l'aluminium / $[R_2Al(NH_2{}^tBu)_2]$ / $Me(Ph^*O)AlX(NH_2{}^tBu)$ / $Ph^*OAlMe_2(NH_2{}^tBu)$ / $Me_2(Ph^*O)Al(THF)$ / effet inductif des groupes aryloxy / analyse RX / ^{1}H RMN

Introduction

Although the first group 13 cation $[Me_2Ga(NH_3)_2]^+$ was synthesized in 1933 by Kraus and Toonder [1], it was only in 1962 that the compound was correctly postulated to be cationic by Shriver and Parry [2]. Since that time four-coordinate cations have been reported sporadically in the literature. Representative examples include the cations, $[Al(2\text{-}C(SiMe_3)_2C_5H_4N)_2]^+$ [3], $[^tBu_2Al(TMEDA)]^+$ [4], and $[Me_2Ga(NH_2{}^tBu)_2]^+$ [5]. More recently, the synthesis and structural characterization of a series of complexes of general formula, $[R_2Al(NH_2{}^tBu)_2]X$ (where R = alkyl and X = Br and I) [6] and a chiral aluminum cation have appeared [7].

A systematic study into four-coordinate aluminum cations is needed since such compounds may be expected to find as much relevance in organic transformations and catalysis as the traditional neutral derivatives [8]. They may possess enhanced Lewis acidity based upon the positive charge and are less air and moisture

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Table I. Selected bond distances (Å) and angles (deg) for **1**, **3**, **5** and related compounds.

Compound	*Al-O*	*Al-O-C*	*Al-Cl*	*Al-Me*	*O-Al-Cl*	*O-Al-C*	*Ref*
$[Ph^*OAlMeCl]_2$ **1**	1.679(2)	151.7(2)	2.298(2)	1.92(1)	107(2)	127.8(3)	–
$[BHTAlMeCl]_2$	1.672(4)	154.1(3)	2.277(3)	1.920(8)	106.5(1)	127.7(3)	11f
			Al-E	*O-Al-E*	*Al-C(ave)*	*C-Al-C'*	
$Ph^*OAlMeCl(NH_2{}^tBu)$ **3**	1.722(5)	153.8(6)	2.141(4)	110.8(2)	1.965(7)	117.1(3)	–
$Ph^*OAlMe_2(NH_2{}^tBu)$ **5**	1.750(4)	154.1(6)	2.032(6)	99.2(2)	1.98(1)	114(2)	–
$(BHT)AlMe_2(PMe_3)$	1.736(3)	164.5(4)	2.499(3)	104.5(2)	1.970(4)	111.7(3)	11c
$(BHT)AlEt_2(MT)$[a]	1.749(5)	145.6(5)	1.887(6)	101.7(3)	1.96(2)	116.4(4)	11b
$(BHT)AlMe_2(O{=}CPh_2)$	1.731(8)	157.7(8)	1.907(8)	103.1(4)	1.95(2)	113.1(8)	11d
$(BHT)AlCl_2(OEt_2)$	1.700(2)	154.4(2)	1.873(2)	104.1(4)	–	–	11f

[a] MT = methyl toluate.

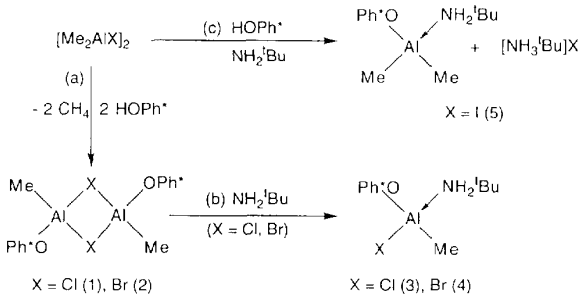
sensitive than the trialkyl aluminum derivatives. Initial work towards this end appears promising. For example, four-coordinate aluminum cations have been postulated to promote certain Diels–Alder reactions [9]. Additionally, the use of six-coordinate cations of the form, $[SalenAl(MeOH)_2]_+$, as propylene oxide oligomerization catalysts has recently been reported [10].

In a recent publication it has been shown that the use of R_2AlX (R = Me, Et) in combination with $NH_2{}^tBu$ results in adduct formation when X = F and $Cl(R_2Al(NH_2{}^tBu)X)$ [6] and in cation formation when X = Br and I ($[R_2Al(NH_2{}^tBu)_2]X$) [6]. In the current manuscript an examination of how changing one alkyl to aryloxide (yielding $R(Ph^*O)AlX$) changes the reactivity of the complex towards cation formation. The aryloxide complexes that are reported are also of fundamental interest in their own right.

Results and discussion

The aryloxy halides, $R(Ph^*O)AlX$, are relatively underrepresented in the literature. The best known examples of this type of compound are those utilizing the 2,6-di-*tert*-butyl-4-methylphenol ligand (in common language this ligand is known as butylated hydroxy toluene or BHT). These are generally of formula, $(BHT)_2AlX$ and $(BHT)AlX_2$ (where X = alkyl or chloride) and coordinated with a Lewis base [11]. For the present work the most convenient introduction of an aryloxide group onto aluminum involves the reaction of the alcohol (2,6-di-*tert*-butyl phenol = Ph^*OH) with the Me_2AlX species. In the cases where X = Cl and Br this leads to the isolation of high yields of the desired products **1** and **2** (scheme 1a). The ^1H NMR spectra of these complexes are very similar. However, the change in halide has the effect of shielding on going from Br (δ 0.07 ppm) to Cl (δ −0.07 ppm). The trend of more electronegative groups to have a stronger shielding effect was also observed in the series of compounds, $Me_2AlX(NH_2{}^tBu)$ where X = F (δ −0.40 ppm), Cl (δ −0.27 ppm) and Br (δ −0.19 ppm) [6b]. It can be attributed to a decrease in the 'effective electronegativity' of the aluminum atom resulting from the presence of the halide [12]. The relative shielding of the aluminum methyl group increases as the electronegativity of the halide increases.

In the solid state compound **1** exists as a halide-bridged dimer, with the alkoxide groups adopting a *trans* orientation to one another (fig 1, tables I–IV).



Scheme 1. General syntheses of compounds **1**–**5**.

It has previously been demonstrated that group 13 complexes possessing both a heteroatom (O, N, P) and a halide will preferentially bridge through the heteroatom if the groups are not too sterically encumbered [13]. This is supported, for example, by the compounds, $[NMe_2(\mu\text{-}NMe_2)GaCl]_2$ [14], $[TMP(\mu\text{-}OEt)GaCl]_2$ (TMP = 2,2,6,6-tetramethylpiperidide) [14], $[(\mu\text{-}Ar^nO)GaCl_2]_2$ (Ar^n = 2,4,6-tris(dimethylaminomethyl)phenyl) [15] and $(\mu\text{-}P(SiMe_3)_2\ GaCl_2)_2$ [16]. In the case of **1** and **2** the steric bulk of the aryloxide prevents this from occurring and the halides bridge.

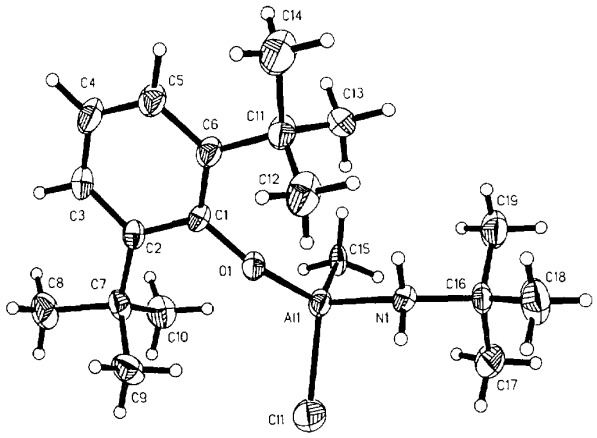


Fig 1. Molecular structure and atom numbering scheme for **1**.

The Al atoms in **1** adopt a geometry approximating T_d. The greatest deviation from ideal values occurs along the O-Al-methyl angle (average = 127.9(3)°).

Table II. Crystal data for $[Ph^*OAlMeCl]_2$ **1**, $[Ph^*OAlMeCl]_2$ **3** and $Ph^*O(Me_2)Al(NH_2{}^tBu)$ **5**.

	1	*3*	*5*
Formula	$C_{30}H_{48}Al_2Cl_2O_2$	$C_{19}H_{35}AlClNO$	$C_{20}H_{38}AlNO$
Formula weight	565.5	355.9	335.5
Crystal system	Monoclinic	Orthorhombic	Orthorhombic
Space group	$P2_1/n$	$Pna2_1$	$Pna2_1$
a (Å)	10.604(1)	16.879(2)	17.111(3)
b (Å)	20.776(4)	12.315(2)	12.375(1)
c (Å)	14.752(1)	10.442(1)	10.380(1)
$\alpha(^\circ)$	–	–	–
$\beta(^\circ)$	92.45(1)	–	–
$\gamma(^\circ)$	–	–	–
V (Å^3)	3247.1(7)	2170.5(5)	2197.7(5)
Z	4	4	4
D_{calc} (g/cm^3)	1.157	1.089	1.014
Crystal size (mm)	$(0.3)^2 \times 0.5$	$(0.4)^2 \times 0.8$	$1.0 \times 0.5 \times 0.2$
Temperature (K)	298	298	298
2θ range(deg)	3.5–45	3.5–45	3.5–45
Scan type	2θ–θ	2θ–θ	2θ–θ
Scan speed(deg/min)	6–60	10–60	10–60
Scan range (deg)	0.40	0.53	0.38
Reflections collected	5383	2041	2064
Independent reflections	4234	1752	1707
Observed reflections	3245	1270	1226
$F > x\sigma(F)$	4	4	4
No of parameters	325	207	207
R	0.0436	0.0477	0.0538
R_w	0.0449	0.0490	0.0528
GOF	1.44	1.30	1.22
Largest difference peak (e/Å^3)	0.29	0.24	0.27

Table III. Selected bond lengths (Å) and angles (deg) for compounds **1**, **3** and **5**.

$[Me(Ph^*O)AlCl]_2$ 1		*$Me(Ph^*O)AlCl(NH_2{}^tBu)$ 3*		*$Ph^*OAlMe_2(NH_2{}^tBu)$ 5*	
Al(1)-Cl(1)	2.298 (2)	Al(1)-Cl(1)	2.141 (4)	Al(1)-N(1)	2.032 (6)
Al(1)-Cl(2)	2.298 (2)	Al(1)-O(1)	1.722 (5)	Al(1)-O(1)	1.750 (4)
Al(1)-O(1)	1.679 (3)	Al(1)-N(1)	1.998 (6)	Al(1)-C(1)	1.981 (8)
Al(1)-C(15)	1.919 (4)	Al(1)-C(15)	1.965 (7)	Al(1)-C(2)	1.985 (9)
Al(2)-Cl(1)	2.299 (2)	O(1)-C(1)	1.365 (8)	N(1)-C(17)	1.539 (8)
Al(2)-Cl(2)	2.296 (2)	N(1)-C(16)	1.533 (9)	O(1)-C(3)	1.360 (7)
Al(2)-O(2)	1.679 (2)				
Al(2)-C(16)	1.924 (4)				
O(1)-C(6)	1.377 (4)				
O(2)-C(17)	1.379 (4)				
Cl(1)-Al(1)-Cl(2)	87.1(1)	Cl(1)-Al(1)-O(1)	110.8(2)	N(1)-Al(1)-O(1)	99.2(2)
Cl(1)-Al(1)-O(1)	105.4(1)	Cl(1)-Al(1)-N(1)	98.2(2)	N(1)-Al(1)-C(1)	110.7(3)
Cl(2)-Al(1)-O(1)	109.9(1)	O(1)-Al(1)-N(1)	101.8(2)	O(1)-Al(1)-C(1)	114.7(3)
Cl(1)-Al(1)-C(15)	112.0(1)	Cl(1)-Al(1)-C(15)	114.4(2)	N(1)-Al(1)-C(2)	101.4(3)
Cl(2)-Al(1)-C(15)	107.1(1)	O(1)-Al(1)-C(15)	117.1(3)	O(1)-Al(1)-C(2)	112.8(3)
O(1)-Al(1)-C(15)	127.8(2)	N(1)-Al(1)-C(15)	112.3(3)	C(1)-Al(1)-C(2)	115.9(4)
Al(2)-Cl(1)-Al(1)	89.4(1)	Al(1)-O(1)-C(1)	153.8(6)	Al(1)-N(1)-C(17)	126.4(5)
Al(2)-Cl(2)-Al(1)	89.5(1)	Al(1)-N(1)-C(16)	126.8(5)	Al(1)-O(1)-C(3)	154.1(6)
Al(1)-O(1)-C(6)	151.7(2)	O(1)-C(1)-C(2)	119.8(5)	O(1)-C(3)-C(4)	121.2(6)
Al(2)-O(2)-C(17)	147.2(2)	O(1)-C(1)-C(6)	119.5(5)	O(1)-C(3)-C(8)	118.0(5)
Cl(1)-Al(2)-Cl(2)	87.2(1)	N(1)-C(16)-C(17)	107.0(6)	N(1)-C(17)-C(18)	107.6(6)
Cl(1)-Al(2)-O(2)	107.6(1)	N(1)-C(16)-C(18)	108.2(7)	N(1)-C(17)-C(19)	108.0(6)
Cl(2)-Al(2)-O(2)	110.8(1)	N(1)-C(16)-C(19)	108.8(6)	N(1)-C(17)-C(20)	108.3(7)
Cl(1)-Al(2)-C(16)	110.0(1)				
Cl(2)-Al(2)-C(16)	105.9(1)				
O(2)-Al(2)-C(16)	127.9(2)				
O(1)-C(6)-C(1)	119.0(3)				
O(1)-C(6)-C(5)	118.9(3)				

Table IV. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) for $[Ph^*OAlMeCl]_2$ **1**.

Atom	x	y	z	U *(eq)*
Al(1)	3972(1)	2810(1)	4257(1)	41(1)
Al(2)	3133(1)	3946(1)	5602(1)	37(1)
Cl(1)	4884(1)	3301(1)	5518(1)	52(1)
Cl(2)	2073(1)	3197(1)	4716(1)	48(1)
O(1)	4447(2)	3238(1)	3369(2)	39(1)
O(2)	2666(2)	3918(1)	6674(2)	37(1)
C(1)	3966(3)	3340(2)	1768(2)	37(1)
C(2)	4432(4)	3372(2)	894(3)	50(1)
C(3)	5700(4)	3354(2)	751(3)	58(2)
C(4)	6556(4)	3319(2)	1476(3)	53(2)
C(5)	6177(3)	3283(2)	2368(2)	39(1)
C(6)	4863(3)	3282(2)	2500(2)	33(1)
C(7)	2546(3)	3373(2)	1886(3)	44(1)
C(8)	2213(4)	3950(2)	2491(3)	51(1)
C(9)	2052(4)	2733(2)	2279(3)	57(2)
C(10)	1781(4)	3470(3)	980(3)	74(2)
C(11)	7186(3)	3259(2)	3152(3)	49(1)
C(12)	7095(4)	2630(2)	3701(3)	62(2)
C(13)	7047(4)	3854(2)	3765(3)	67(2)
C(14)	8537(4)	3279(3)	2805(3)	77(2)
C(15)	3928(4)	1891(2)	4384(3)	59(2)
C(16)	3305(4)	4693(2)	4846(2)	47(1)
C(17)	2240(3)	4254(2)	7407(2)	34(1)
C(18)	3139(4)	4483(2)	8069(2)	40(1)
C(19)	2668(4)	4827(2)	8792(3)	60(2)
C(20)	1393(4)	4925(3)	8872(3)	72(2)
C(21)	539(4)	4682(2)	8238(3)	57(2)
C(22)	931(3)	4339(2)	7481(2)	38(1)
C(23)	−55(3)	4081(2)	6786(3)	39(1)
C(24)	−1420(4)	4203(2)	7055(3)	57(2)
C(25)	76(4)	4425(2)	5862(3)	53(1)
C(26)	73(4)	3345(2)	6677(3)	53(2)
C(27)	4558(4)	4369(2)	8016(2)	40(1)
C(28)	4850(4)	3645(2)	8002(3)	51(1)
C(29)	5081(4)	4708(2)	7180(2)	48(1)
C(30)	5314(4)	4652(2)	8842(3)	59(2)

This acts to reduce the steric repulsion between the phenyl *tert*-butyl groups and the Al-methyl. The absence of steric congestion within **1** is apparent in the relatively short Al-O bond distances (average = 1.679(3)°). The Al-methyls adopt a *trans* orientation around the central Al_2Cl_2 four-membered ring. It is common for the atoms within the four-membered rings to adopt widened the E-Al-E′ angles and narrowed E-Cl-E′ angles. This minimizes the repulsion between the groups on the respective aluminum atoms. However, in the present case these approximate 90° fairly closely. That the sum of these angles do not total to 360° is an indication that the four-membered ring is not planar and in a 'butterfly' configuration.

When excess $NH_2{}^tBu$ is added to **1** and **2** the adduct complexes, **3** and **4** are formed (scheme 1b). In each, the Al-Me ^1H NMR chemical shift is insignificant (δ −0.09 and 0.03 ppm, respectively) when compared to **1** and **2**. These groups integrate in a 1:3 ratio with the *tert*-butyl amine group. The molecular structure, as determined by X-ray crystallography, confirms the adduct formation for **3** (fig 2, tables I–III and V). Compared to **1** the structure is now monomeric with the aluminum atom in a distorted T_d array. The greatest deviation from this geometry occurs for the O(1)-Al(1)-C(15) angle (117.1(3)°). The N(1)-Al(1)-C(15) and Cl(1)-Al(1)-C(15) angles are of marginally lesser value, 112.3(3)° and 114.4(2)°. The fact that all of the angles not incorporating carbon take more narrow values is a manifestation of Bent's rule [17]. That is, the more electronegative constituents around aluminum contain more *p* character in the bonding and consequently adopt more acute angles (compared to the less electronegative constituents).

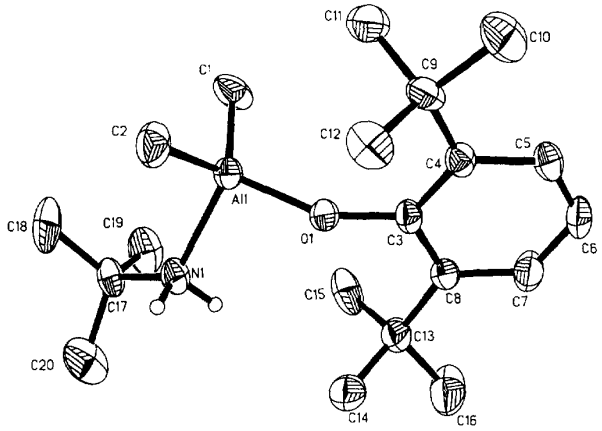


Fig 2. Molecular structure and atom numbering scheme for **3**.

Table V. Atomic coordinates ($\times 10^5$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^4$) for $Me(Ph^*O)ClAl(NH_2{}^tBu)$ **3**.

Atom	x	y	z	U *(eq)*
Al(1)	65524(12)	19416(15)	84498	440(7)
Cl(1)	55843(13)	22383(18)	71717(42)	863(11)
O(1)	69802(24)	6991(33)	81417(58)	420(18)
N(1)	73350(30)	29604(37)	76653(66)	423(20)
C(1)	72505(37)	−3051(47)	84800(95)	383(23)
C(2)	67054(39)	−11794(49)	86294(89)	409(25)
C(3)	70104(47)	−21592(56)	90603(88)	521(31)
C(4)	78009(51)	−23037(59)	93425(104)	651(36)
C(5)	83184(45)	−14725(55)	91353(101)	571(32)
C(6)	80578(39)	−4587(53)	87047(89)	481(29)
C(7)	58179(43)	−10866(56)	82988(96)	492(28)
C(8)	53927(43)	−22130(54)	83779(115)	754(37)
C(9)	57276(52)	−7451(73)	68953(90)	650(35)
C(10)	53821(43)	−3414(66)	91921(98)	617(33)
C(11)	86879(41)	4305(59)	84181(135)	644(34)
C(12)	86169(47)	8469(73)	70539(115)	769(42)
C(13)	86052(51)	13486(62)	94164(110)	744(39)
C(14)	95438(40)	145(66)	85732(156)	1159(62)
C(15)	63303(42)	22944(52)	102494(70)	387(25)
C(16)	74617(47)	41573(56)	80122(90)	502(30)
C(17)	66719(47)	47075(58)	79072(122)	906(50)
C(18)	80620(56)	46243(69)	70989(113)	896(43)
C(19)	77988(60)	42222(70)	93449(109)	815(43)

The Al-O bond distance (1.722(5) Å) is somewhat longer than that demonstrated for **1**. Al-N bond dis-

tances in general do not differ greatly for covalent and coordinate covalent complexes (as in the present case). Thus, a distance of 1.998(6)° is standard for both types of complexes. The overall morphology of this complex is very similar to that of $(MesO)_2GaCl(NH_2{}^tBu)$, for which the Ga-N bond distance is 1.998(3) Å [18].

In the case of **3** the formation of an adduct follows the precedent of the bis alkyl complexes, $R_2AlX(NH_2{}^tBu)$ (where X = F and Cl). However, for **4** the isolation of the adduct rather than the cation is in contrast to what occurs for the reaction of R_2AlBr with excess *tert*-butyl amine. The fact that cations are not formed in this reaction may be attributed to a combination of two factors: (1) the steric bulk of the aryloxide impedes a potential 5-coordinate transition state; and (2) the inductive effect of the aryloxide acts to strengthen the Al-Br bond and increase the energy needed to dissociate it.

It was apparent from the above results that the most likely starting material to a cationic aluminum complex would be the one containing the iodide atom, Me(Ph*O)AlI. Unfortunately there is no precedent in the literature for this type of complex. However, it seemed reasonable to assume that the same type of preparation used to make **1** and **2** could be used here. Following this procedure led to the isolation of a solid that was composed of a mixture of products as evidenced by the ^1H NMR. There are no iodide bridged structures know for the group 13 elements. Thus, the formation of iodide-bridged dimers analogous to **1** and **2** may not be possible. In order to achieve the cations, then, the putative Me(Ph*O)AlI was prepared in situ and then combined with *tert*-butyl amine. This procedure led to a quantitative yield of $I[NH_3{}^tBu]$ and a lesser amount of $Me_2AlOPh^*(NH_2{}^tBu)$ **5**. From these products it was apparent that the initial alkane elimination to form the Me(Ph*O)AlI was not occurring. Thus, the observed products may be the result of adduct formation ($Me_2AlI(HOPh^*)$ followed by elimination of ammonium iodide after addition of $NH_2{}^tBu$. Conducting this reaction through a range of temperatures (from −78 to 25 °C) had no effect on the ultimate products.

The ^1H NMR data for **5** shows equivalent Al-Me groups with a chemical shift of δ −0.26 ppm. This compares closely to that seen for **6** (δ −0.32 ppm). (Compound **6** was prepared in a comparatively routine fashion by the addition of the phenol to $AlMe_3$ in toluene followed by addition of THF.) The connectivity for **5** is confirmed by the X-ray data (fig 3, tables I–III and VI). In the structure the Al atom is bound in a distorted T_d array. Despite the steric bulk of the $NH_2{}^tBu$ and Ph*O groups they adopt a relatively narrow N-Al-O angle (99.2(3)°) in keeping with Bent's rule [12]. Correspondingly, the C-Al-C angle is widened (115.9(4)°). To reduce contact between the ^{t}Bu and Ph*, these groups adopt an *anti* configuration to one another. This leads to relatively broadened angles about the nitrogen (Al(1)-N(1)-C(17), 126.4(5)°) and oxygen (Al(1)-O(1)-C(3), 154.1(6)°) atoms. These values are similar to what was observed in **3**.

The Al-O bond length in **5** (1.750(4) Å) also compares closely with that observed for **3** (1.722(5) Å). However, taken with the same distance in **1** (1.679(2) Å) a general trend may be observed. The bond distances decrease with the increase in electronegativity of the substituents on Al. Moreover, the Al-O distance in **5** compares closely to that observed for $(BHT)AlMe_2(PMe_3)$ [11c]. These relatively short distances (Al-O distances are generally of the order of 1.8–2.0 Å) [19] are in keeping with the presence of π-bonding between the aryloxide ligand and aluminum atom. This appears to be a central feature of four-coordinate aluminum aryloxide complexes in general [11c].

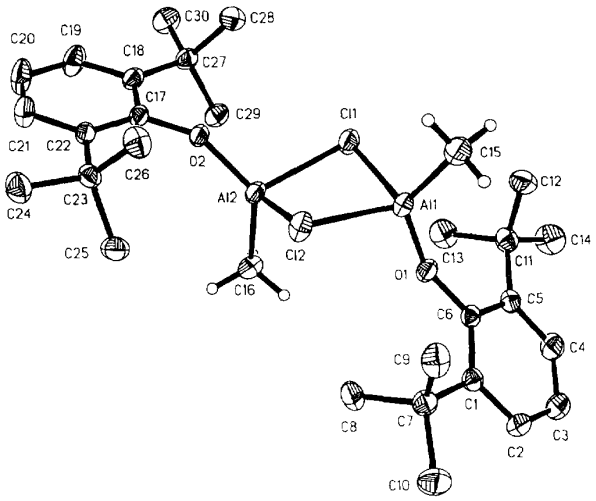


Fig 3. Molecular structure and atom numbering scheme for **5**.

Table VI. Atomic coordinates ($\times 10^5$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^4$) for $Me_2(Ph^*O)Al(NH_2{}^tBu)$ **5**.

Atom	x	y	z	U *(eq)*
Al(1)	65163(11)	19018(15)	60296	469(6)
N(1)	73333(32)	29186(38)	52877(69)	500(21)
O(1)	69871(24)	6691(32)	57448(55)	431(17)
C(1)	63232(61)	22301(64)	78700(79)	804(39)
C(2)	56234(47)	21543(56)	48462(99)	701(35)
C(3)	72409(36)	−3344(45)	60780(95)	427(23)
C(4)	67175(38)	−12011(47)	62119(85)	449(26)
C(5)	70173(44)	−21892(50)	66340(92)	582(32)
C(6)	77969(47)	−23296(53)	68697(95)	612(32)
C(7)	83074(47)	−15060(53)	66941(101)	658(33)
C(8)	80582(38)	−4849(48)	62762(84)	492(28)
C(9)	58441(42)	−11327(55)	58784(95)	541(27)
C(10)	54262(44)	−22374(53)	59845(115)	827(35)
C(11)	54151(47)	−3906(64)	68177(97)	698(33)
C(12)	57358(53)	−7540(72)	44742(91)	705(36)
C(13)	86632(42)	4050(55)	60445(128)	661(30)
C(14)	85995(51)	8066(72)	46483(104)	800(42)
C(15)	85666(55)	13084(59)	70422(102)	755(37)
C(16)	95113(40)	15(63)	61646(162)	1165(59)
C(17)	74433(47)	41183(55)	56337(90)	558(31)
C(18)	66708(49)	46486(57)	55362(122)	920(47)
C(19)	77785(59)	41771(66)	69634(109)	841(44)
C(20)	80312(62)	45947(70)	47229(110)	988(48)

Conclusion

The compounds reported in this manuscript were prepared in order to examine the possibility of preparing cationic aluminum aryloxides. This goal was not realized. However, these compounds did allow further examination of, and support for, π-bonding within aluminum aryloxide complexes.

Experimental section

General considerations

All manipulations were conducted using Schlenk techniques in conjunction with an inert atmosphere glove box. All solvents were rigorously dried prior to use. NMR data were obtained on Jeol-GSX-400 and -270 instruments at 270.17 (^{1}H). Chemical shifts are reported relative to $SiMe_4$ and are in ppm. Elemental analyses were obtained on a Perkin-Elmer 2400 Analyzer. Infrared data were recorded as KBr pellets on a Matheson Instruments 2020 Galaxy Series spectrometer and are reported in cm^{-1}. The Me_2AlI used in the reaction to form **5** was prepared according to the literature [20].

*[Me(Ph*O)AlCl]$_2$* **1**

To a solution of dimethylaluminum chloride (10.81 mmol, 1.00 g) in toluene (50 mL) was added 2,6-di-*tert*-butylphenol (10.81 mmol, 2.230 g). The colorless solution was stirred at 25 °C for 3 h and the volatiles removed under reduced pressure yielding **1** as a white, crystalline powder in essentially quantitative yield. The solid was recrystallized from toluene at −30 °C yielding **1** as colorless blocks (2.415 g, 79%) which were suitable for X- ray diffraction. Mp 146–148 °C.

^{1}H NMR (C_6D_6); δ −0.07 (s, 6H, $AlCH_3$), 1.46 (s, 36H, $C(CH_3)_3$), 6.91 (t, 2H, Ph*H*), 7.28 (d, 4H, Ph*H*).

IR: ν 3013 w, 2982 s, 2926 m, 2877 w, 1458 w, 1419 s, 1285 s, 1128 m, 1097 m, 941 s, 806 m, 748 s, 682 m.

Anal calc: C, 63.71; H, 8.55. Found: C, 64.01; H, 8.52.

*[Me(Ph*O)AlBr]$_2$* **2**

Dimethylaluminum bromide was prepared in situ using trimethlyaluminum (7.50 mmol, 0.541 g), aluminum bromide (3.75 mmol, 1.00 g), and toluene (40 mL). To this solution was added 2,6-di-*tert*-butylphenol (11.25 mmol, 2.323 g). The colorless solution was stirred for 3 h at 25 °C, concentrated to approximately 25 mL and stored at −30 °C for 5 days affording **2** as colorless blocks (2.765 g, 75%). Mp 135–138 °C.

^{1}H NMR (C_6D_6): δ 0.07 (s, 6H, $AlCH_3$), 1.47 (s, 36H, $C(CH_3)_3$), 6.91 (t, 2H, Ph*H*), 7.28 (d, 4H, Ph*H*).

IR: ν 3014 w, 2962 s, 2914 m, 2872 w, 1460 w, 1402 s, 1259 s, 1199 m, 1141 m, 1095 m, 927 m, 746 s, 678 m.

Anal calc: C, 55.06; H, 7.39. Found: C, 55.08; H, 7.27.

*[Me(Ph*O)Al(H$_2$N^{t}Bu)Cl* **3**

To a solution of **1** (1.33 mmol, 0.750 g) in toluene (30 mL) was added *tert*-butylamine (19.03 mmol, 2.00 mL) at 25 °C. The solution was stirred for 2 h and the volatiles removed under reduced pressure resulting in a nearly quantitative yield of **3** as a white powder. Dissolution in toluene (10 mL) and storage at −30 °C for 1 week yielded colorless diamonds (0.699 g, 74%) which were suitable for X-ray diffraction. Mp 125–129 °C (dec).

^{1}H NMR (C_6D_6): δ −0.09 (s, 3H, $AlCH_3$), 0.75 (s, 9H, $NC(CH_3)_3$), 1.56 (s, 18H, $PhC(CH_3)_3$), 2.74 (s(br), 2H, NH_2), 6.96 (t, 1H, Ph*H*), 7.37 (d, 2H, Ph*H*).

IR: ν 3302 m, 3196 m, 3111 m, 2962 m, 1570 w, 1460 m, 1402 s, 1263 s, 1199 w, 1167 m, 1103 m, 1022 m, 902 m, 802 m, 709 m.

Anal calc: C, 64.12; H, 9.91. Found: C, 63.76; H, 9.77.

*Me(Ph*O)Al(H$_2$N^{t}Bu)Br* **4**

The procedure was as for **3** using **2** (2.29 mmol, 1.500 g), toluene (25 mL), and *tert*-butylamine (19.03 mmol, 2.00 mL) resulting in a nearly quantitative yield of **4** as a white solid. Dissolution in toluene (15 mL) and storage at −30 °C for several days yielded colorless needles (1.138 g, 62%). Mp 140–144 °C (dec).

^{1}H NMR (C_6D_6): δ 0.03 (s, 3H, $AlCH_3$), 0.80 (s, 9H, $NC(CH_3)_3$), 1.55 (s, 18H, $PhC(CH_3)_3$), 3.04 (s (br), 2H, NH_2), 6.95 (t, 1H, Ph*H*), 7.36 (d, 2H, Ph*H*).

IR: ν 3296 s, 3196 s, 3117 w, 2964 s, 1569 s, 1462 s, 1413 s, 1263 s, 1167 m, 1134 m, 1059 m, 902 s, 758 s, 696 s.

Anal calc: C, 57.00; H, 8.81. Found: C, 56.70; H, 8.64.

*Me$_2$(Ph*O)Al(H$_2$N^{t}Bu)* **5**

To a stirred solution of dimethylaluminum iodide (13.59 mmol, 2.500 g) in toluene (50 mL) at −78 °C was added a solution of 2,6-di-*tert*-butylphenol (13.59 mmol, 2.804 g) in toluene (30 mL). The resulting pale yellow solution was stirred at −78 °C for 3 h. To this solution was added *tert*-butylamine (54.36 mmol, 5.71 mL). The solution was kept at −78 °C for an additional 2 h. After 1 h a solid began to form. The mixture was warmed to 25 °C and allowed to stir for an additional hour during which time a semi-crystalline solid appeared. The volatiles were removed under reduced pressure and the solid taken up in THF (50 mL). The pale yellow solution was filtered and cooled to −30 °C resulting in colorless needles (1.390 g) which were identified by ^{1}H NMR (d_8-THF) as [H_3N^tBu]I. The volatiles were removed from the filtrate under reduced pressure and the white residue extracted with toluene/hexanes (40 mL/50 mL) and filtered resulting in a white solid (1.151 g, 93% of [H_3N^tBu]I recovered) and a nearly colorless solution. The solution was concentrated to about 50 mL and stored at −30 °C for 2 days yielding **5** as colorless diamond-shaped crystals which were suitable for X-ray analysis (2.411 g, 53%). Mp 138–140 °C.

^{1}H NMR (C_6D_6): δ −0.26 (s, 6H, $AlCH_3$), 0.73 (s, 9H, $NC(CH_3)_3$), 1.56 (s, 18H, $PhC(CH_3)_3$), 2.52 (s (br), 2H, NH_2), 6.92 (t, 1H, Ph*H*), 7.39 (d, 2H, Ph*H*).

IR: ν 3313 s, 3216 s, 2960 s (br), 1575 m, 1460 m, 1413 s, 1282 s, 1197 m, 1157 m, 1130 m, 1028 w, 887 s, 754 m, 713 s (br).

Anal calc: C, 71.60; H, 11.42. Found: C, 71.08; H, 11.13.

*Me$_2$(Ph*O)Al(THF)* **6**

To a stirred solution of trimethylaluminum (29.08 mmol, 2.096 g) in toluene (50 mL) at −78 °C was added a solution of 2,6-di-*tert*-butylphenol (29.08 mmol, 6.000 g) in toluene (40 mL). The resulting orange solution was warmed to 25 °C where it became colorless. The solution was stirred for 12 h and then THF (10 mL) was added. The solution was stirred an additional 6 h and the volatiles removed under vacuum resulting in a nearly quantitative yield of **6** as a white powder. The solid was recrystallized from hexanes/toluene (70 mL/30 mL) at −30 °C resulting in 7.552 g (78%) of **6** as colorless cubes. Mp 124–127 °C.

^{1}H-NMR (C_6D_6): δ −0.32, (s, 6H, $AlCH_3$), 1.02 (m (br), 4H, *THF*), 1.58 (s, 18H, $C(CH_3)_3$), 3.44 (m (br), 4H, THF), 6.95 (t, 1H, Ph*H*), 7.44 (d, 2H, Ph*H*).

IR: ν 2955 s, 2877 w, 1464 m, 1421 s, 1290 s, 1192 m, 1103 w, 1008 m, 906 s, 866 s, 748 s, 675 s.

Anal calc: C, 71.82; H, 10.55. Found: C, 71.28; H, 10.01.

X-ray experimental

Details of the crystal data and a summary of data collection parameters for the complexes are given in table II. Data were collected on a Siemens P4 diffractometer using graphite monochromated Mo$K\alpha$ (0.71073 Å) radiation. The check reflections, measured every 100 reflections, indicated a less than 5% decrease in intensity over the course of data collection for each compound and hence, no correction was applied. All calculations were performed on a personal computer using the Siemens software package, SHELXTL-Plus. The structures were solved by direct methods and successive interpretation of difference Fourier maps, followed by least-squares refinement. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in the refinement in calculated positions using fixed isotropic parameters.

Supplementary material data have been deposited with the British Library, Document Supply Centre at Boston Spa, West Yorkshire, LS23 7BQ, UK, as supplementary publication No = SUP 90431 and are available on request from the Document Supply Centre.

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