# Sterically Crowded Aryloxide Compounds of Aluminium: Hydrides and Homoleptic Aryloxides†

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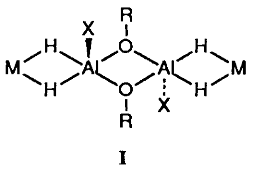
Interaction of [$AlH_3(NMe_3)$] and [$AlH_2Cl(NMe_3)$] with HOR$^1$ (R$^1$ = $C_6H_2Bu^t{}_2$-2,6-Me-4) allows for the isolation of [$AlH_2(OR^1)(NMe_3)$] **1** and [Al(H)Cl(OR$^1$)($NMe_3$)] **2** respectively. Compound **1** exists in both mono- and di-meric forms in the solid state. The reaction of **1** with $NH_2Bu^t$ results in ligand redistribution to give [$AlH(OR^1)_2(NH_2Bu^t)$] **3**. Similarly, multiple recrystallisation of **1** from $Et_2O$ allows for the isolation of [$AlH(OR^1)_2(OEt_2)$] **4**, while addition of HOR$^2$ (R$^2$ = $C_6H_3Ph_2$-2,6) to **1** yields the mixed aryloxide complex [$AlH(OR^1)(OR^2)(NMe_3)$] **5**. Interaction of compound **1** with benzophenone results in the formation of the bridged dimer [{AlH(OR$^1$)(μ-$OCHPh_2$)}$_2$] **6**. The reaction of 3 molar equivalents of HOR$^1$ with $LiAlH_4$ yields, in addition to [{Li(OR$^1$)($OEt_2$)}$_2$], compound **4**, which reacts further with $H_2O$, HOR$^1$ or $NH_2C_6H_2Cl_3$-2,4,6 to give [{Al(μ-OH)(OR$^1$)$_2$}$_2$] **7**, [$Al(OR^1)_3$] **8** or [$Al(OR^1)_2(NHC_6H_2Cl_3$-2,4,6)] **13** respectively. Compounds **8** and **13** form stable Lewis acid–base complexes [$Al(OR^1)_3L$] [L = MeCN **9**, pyridine (py) **10**, O=$PPh_3$ **11** or O=C($C_5H_9$)$Bu^t$-4 **12**] and [$Al(OR^1)_2(NHC_6H_2Cl_3$-2,4,6)L] (L = $Et_2O$ **14**, py **15** or 3,5-dimethylpyridine **16**). The presence of a slow ligand exchange for compounds **9** and **12** was investigated by $^1H$ NMR spectroscopy. The molecular structures of **1**, **3**, **4**, **8** and **12** have been confirmed by X-ray crystallography.

Although anionic alkoxy-alanes are readily prepared from the reaction of $LiAlH_4$ with alcohols ROH (R = alkyl or aryl) [equation (1)], and the benzene-soluble salts Na[$AlH(OMe)_2$(OEt)] (Red-Al) and Li[$AlH_2(OC_2H_4OMe)_2$] are commonly employed as reducing agents,[1] examples of neutral alkoxide or aryloxide–alane derivatives are rare. Those previously reported include transition-metal aluminopolyhydrides **I**.[2] However, while these may be considered as an adduct of the aluminium Lewis acid with a neutral transition-metal hydride, it is equally valid to regard them as being a transition-metal salt of an anionic alane.

$$LiAlH_4 + 3ROH \longrightarrow Li[AlH(OR)_3] + 3H_2 \quad (1)$$



**I**

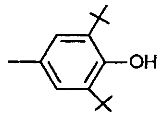
X = OR, M = Ta; X = H, M = W or Re

Two examples of undisputedly neutral alkoxyhydrides were reported by Goel *et al.*[3] to be formed as the result of the redistribution reaction between alane, $AlH_3$, and [$Al(OPr^i)_3$] in tetrahydrofuran (thf) [equations (2) and (3)], however, no structural or reactivity data were reported.

$$AlH_3 + 2[Al(OPr^i)_3] \longrightarrow 3[AlH(OPr^i)_2] \quad (2)$$

$$2AlH_3 + [Al(OPr^i)_3] \longrightarrow 3[AlH_2(OPr^i)] \quad (3)$$

Since our attempts to prepare alane derivatives of the sterically-hindered phenol $HOC_6H_2Bu^t{}_2$-2,6-Me-4 (HOR$^1$), **II**, from alkyl- or chloro-aluminium precursors have been unsuccessful, we have investigated their formation from the hydrocarbon-soluble alane complexes [$AlH_3(NMe_3)$][4] and [$AlH_2Cl(NMe_3)$].[5] We report herein the results of this study and full experimental details of our previously communicated synthesis of [$Al(OR^1)_3$] from $LiAlH_4$,[6] along with the subsequent formation of the Lewis acid–base complexes [$Al(OR^1)_3L$], and the mixed amido–aryloxide complexes [$Al(OR^1)_2(NHR)$] and [$Al(OR^1)_2(NHR)L$].



**II**

## Results and Discussion

Interaction of [$AlH_3(NMe_3)$] with 1 molar equivalent of HOR$^1$ results in the formation of [$AlH_2(OR^1)(NMe_3)$] **1** as a colourless crystalline solid. The mass spectrum of **1** shows peaks due to $M^+$ (*m*/*z* 307) and $M^+ - NMe_3$ (248) consistent with a monomeric structure. It is surprising therefore, that the IR spectrum of **1** (Nujol mull) contains broad bands between 1910 and 1800 cm$^{-1}$ due to the presence of both bridging and terminal hydrides,[7] suggesting the formation of dimer. The solution molecular weight measurements indicate an average oligomerisation of 1.1 not inconsistent with a possible monomer–dimer equilibrium [equation (4)].

$$\underset{\mathbf{1a}}{2[AlH_2(OR^1)(NMe_3)]} \rightleftharpoons \underset{\mathbf{1b}}{[\{AlH_2(OR^1)(NMe_3)\}_2]} \quad (4)$$

We have previously shown that dimeric alanes, although fluxional at room temperature, become rigid at low temperature.[7] Thus, if **1** existed as a dimer in solution then the $^1H$

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, issue 1, pp. xxiii–xxviii.

NMR spectrum at low temperature should show peaks due to both terminal and bridging hydrides.[7] However, cooling a NMR sample of **1** in [$^2H_8$]toluene only results in the sharpening of the peak at δ 4.4 due to the terminal hydrides, and no spectroscopic evidence is found for a dimer in solution. In contrast, the presence of both monomeric and dimeric forms of **1** in the solid state has been confirmed by X-ray crystallography.

The molecular structure of the dimeric and monomeric forms of **1** are shown in Figs. 1 and 2 respectively; selected bond lengths and angles are given in Table 1. Both monomer and dimer are present in the lattice as a disorder (see below). The geometry around the aluminium in the monomer **1a** is highly distorted from tetrahedral, with the angles associated with the Lewis base [*i.e.*, N(1)] being the most acute. We have observed similar distortions for other Lewis acid–base complexes of aluminium.[8] The co-ordination geometry at the aluminium atom in the dimer **1b** approximates quite well to trigonal bipyramidal, with N(1) and H(01b′) defining the axial sites [N(1)–Al(1b)–H(01b′) 169.3°], and O(1), H(01b) and H(02b) the equator (N.B. the sum of the equatorial bond angles, 358.3°, is close to that of an ideal trigonal bipyramid, 360°). Trigonal bipyramidal $AlH_xL_{3-x}$ geometries have been reliably found in a number of transition-metal aluminohydrides,[7,9,10] as well as Lewis acid–base complexes of alane.[11]

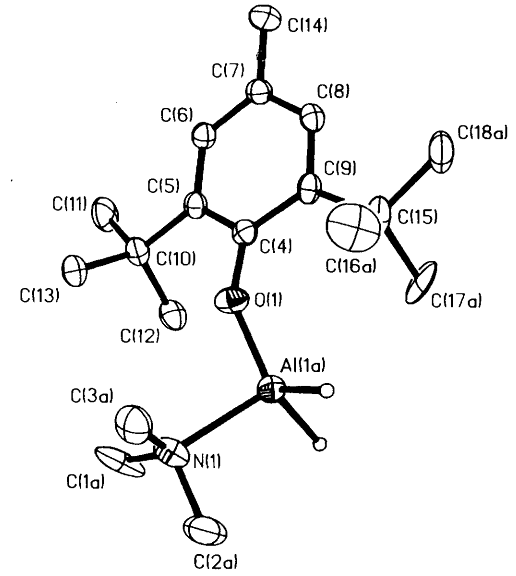


**Fig. 1** Molecular structure of [$AlH_2(OR^1)(NMe_3)$] **1a**. Thermal ellipsoids are drawn at the 40% level, and hydrogen atoms, except those attached to aluminium, are omitted for clarity

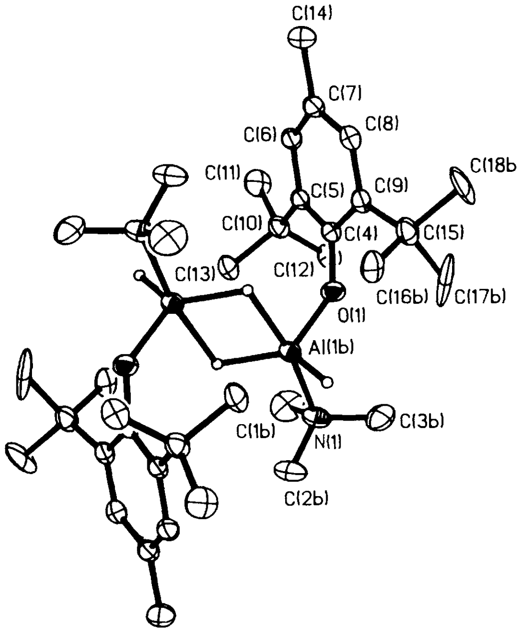


**Fig. 2** Molecular structure of [{$AlH_2(OR^1)(NMe_3)$}$_2$] **1b**. Thermal ellipsoids are drawn at the 40% level, and hydrogen atoms, except those attached to aluminium, are omitted for clarity

As has been observed for other dimeric five-co-ordinate aluminium hydrides,[7] the central $Al(\mu\text{-}H)_2Al$ unit in **1b** is highly asymmetric with the long and short distances differing by about 0.3 Å (see Table 2). Whereas the terminal Al–H bonds in **1b** (1.515 Å) are comparable not only to those in other similar dimeric hydrides (*cf.* Table 2) but also to the values obtained from *ab initio* molecular-orbital calculation (1.588–1.599 Å),[12] the terminal hydrides in **1a** are significantly longer, Al(1a)–H(01a) 1.884, Al(1a)–H(02a) 1.731 Å. We are, however, unable to rationalise this anomaly, but it is possibly an artifact of the crystallographic experiment.

The Al–N distances (Table 1) vary between the two isomers, with that to the five-co-ordinate centre in **1b** being slightly longer. This is as would be expected from a consideration of the relative Al s and p character in the respective Al–N bonds, *i.e.* five-co-ordinate axial (primarily p in character) > four-co-ordinate ($sp^3$).[13] By contrast the Al–O distances do not show the expected trend on the basis of hybridisation at aluminium. However, we have previously demonstrated[8] that there is a nearly linear relationship between the Al–O distance and the Al–O–C angles for monomeric four-co-ordinate aluminium aryloxides, $AlX_2Y(OR^1)$, and as can be clearly seen from Fig. 3, both **1a** and **1b** neatly fit this trend. This result suggests that these two parameters may, in the absence of overwhelming steric effects, correlate for non-four-co-ordinate aluminium centres.

The two isomers observed in the solid state appear as a 45:55% (**1a**:**1b**) disorder of the aluminium atom, the trimethylamine methyls, and one of the aryloxide *tert*-butyl groups (Fig. 4). The disorder can be imagined as being due to a rotation of the $AlH_2$ about the O–N vector. In this inversion, the oxygen, O(1), and nitrogen, N(1), remain fixed within the resolution of the experiment. The results of this are three-fold: the inter-aluminium distance precludes dimer formation in one isomer, isomer **1a**; the trimethylamine methyls are aligned in accordance with the N(1)–Al vector; and finally the flipping of the aluminium is accompanied by a 'rotation' of one of the aryloxide *tert*-butyl groups so as to minimise steric interactions.

Interaction of [$AlH_2Cl(NMe_3)$][5] with one equivalent of $HOR^1$ results in the formation of [$Al(H)Cl(OR^1)(NMe_3)$] **2** as a colourless crystalline solid. Unlike **1**, the IR spectrum of **2** contains a weak but sharp band at 1893 cm$^{-1}$ due to terminal hydride consistent with a purely monomeric structure in the solid state.[7]

Contrary to expectations, the reaction of **1** with $NH_2Bu^t$ does not result in ligand exchange [equation (5)], but in a ligand redistribution reaction [equation (6)].

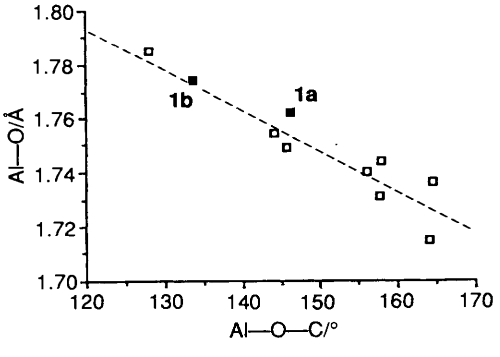


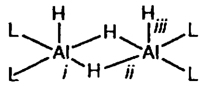
**Fig. 3** Plot of Al–O bond length (Å) *versus* Al–O–C bond angle (°) for the terminal aryloxide ligands within the compounds **1a**, **1b** and $AlX_2Y(OR^1)$ (values taken from ref. 8)

**Table 1** Selected bond lengths (Å) and angles (°) in $[AlH_2(OR^1)(NMe_3)]$ **1**

| Molecule **1a** | | Molecule **1b** | |
|---|---|---|---|
| Al(1a)-O(1) | 1.762(4) | Al(1b)-O(1) | 1.774(3) |
| Al(1a)-N(1) | 2.079(4) | Al(1b)-N(1) | 2.115(4) |
| Al(1a)-H(01a) | 1.884* | Al(1b)-H(01b) | 1.630* |
| Al(1a)-H(02a) | 1.731* | Al(1b)-H(02b) | 1.515* |
| O(1)-C(4) | 1.359(4) | Al(1b)-H(01b) | 2.006* |
| O(1)-Al(1a)-N(1) | 101.1(2) | O(1)-Al(1b)-N(1) | 99.4(1) |
| O(1)-Al(1a)-H(01a) | 121.0* | O(1)-Al(1b)-H(01b) | 125.4* |
| O(1)-Al(1a)-H(02a) | 111.3* | O(1)-Al(1b)-H(02b) | 108.5* |
| N(1)-Al(1a)-H(01a) | 106.0* | O(1)-Al(1b)-H(01b′) | 87.6* |
| N(1)-Al(1a)-H(02a) | 101.8* | N(1)-Al(1b)-H(01b) | 93.3* |
| H(01a)-Al(1a)-H(02a) | 112.8* | N(1)-Al(1b)-H(02b) | 90.5* |
| Al(1a)-O(1)-C(4) | 146.9(2) | N(1)-Al(1b)-H(01b′) | 169.3* |
| | | H(01b)-Al(1b)-H(02b) | 124.4* |
| | | H(01b)-Al(1b)-H(01b′) | 76.1* |
| | | H(02b)-Al(1b)-H(01b′) | 94.9* |
| | | Al(1b)-O(1)-C(4) | 133.6(2) |

* No standard deviations given for bond lengths and angles involving hydrogens bound to aluminium, see Experimental section.

**Table 2** Selected bond lengths for dimeric five-co-ordinate aluminium hydrides



| Compound | *i*/Å | *ii*/Å | *iii*/Å |
|---|---|---|---|
| $[\{AlH(\mu\text{-}H)(OR^1)(NMe_3)\}_2]$ **1b** | 1.630(2) | 2.006(2) | 1.515(2) |
| $[\{(dmpe)_2Mn(\mu\text{-}H)_2AlH(\mu\text{-}H)\}_2]^a$ | 1.51(3) | 1.80(3) | 1.51(3) |
| $[\{(C_5H_5)_2Ti(\mu\text{-}H)_2AlH(\mu\text{-}H)\}_2]^b$ | 1.56(1) | 1.94(1) | 1.51(1) |

[a] Ref. 9(*b*), dmpe = 1,2-bis(diphenylphosphino)ethane. [b] Ref. 10.

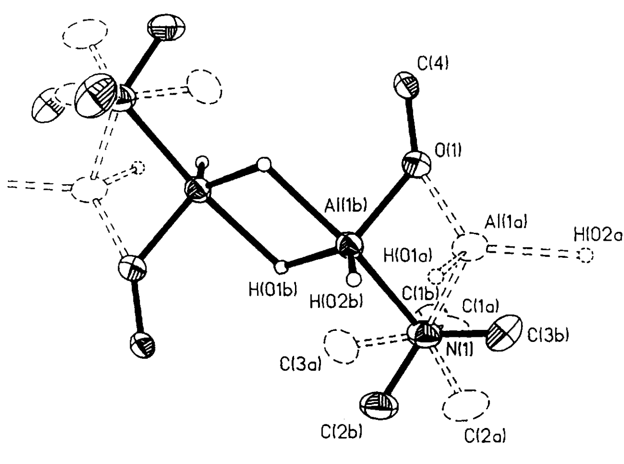


**Fig. 4** Partial co-ordination sphere of the aluminium core in $[AlH_2(OR^1)(NMe_3)]$ **1**. The monomeric isomer **1a** is indicated by dashed ellipsoids

$$[AlH_2(OR^1)(NMe_3)] + NH_2Bu^t \longrightarrow [AlH_2(OR^1)(NH_2Bu^t)] + NMe_3 \quad (5)$$

$$[AlH_2(OR^1)(NMe_3)] + NH_2Bu^t \longrightarrow \underset{\mathbf{3}}{[AlH(OR^1)_2(NH_2Bu^t)]} + \text{unidentified products} \quad (6)$$

Although not isolated, we presume that in addition, to compound **3** the amine adduct of alane, $[AlH_3(NH_2Bu^t)]$, or one of its subsequent condensation products, *e.g.*, $[\{AlH_2(NHBu^t)\}_n]$ is formed due to the redistribution [equation (7)]. Similar reactions are observed for the alkyl derivatives.[14]

$$2[AlH_2(OR^1)] \longrightarrow [AlH(OR^1)_2] + AlH_3 \quad (7)$$

Repeated recrystallisation of **1** from $Et_2O$ also results in ligand redistribution [equation (8)] and allows for the isolation

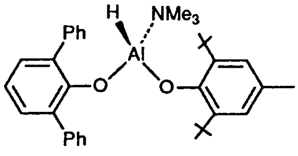
$$[AlH_2(OR^1)(NMe_3)] \xrightarrow{Et_2O} \underset{\mathbf{4}}{[AlH(OR^1)_2(OEt_2)]} + \text{unidentified products} \quad (8)$$

in low yield (< 10%) of the bis(aryloxide) solvate, $[AlH(OR^1)_2(OEt_2)]$ **4**. Compound **4** may be more conveniently prepared directly from the reaction of $HOR^1$ with $LiAlH_4$ in $Et_2O$ (see below).[6]

The room temperature $^1H$ NMR spectrum of **4** contains peaks due to aryloxide and co-ordinated $Et_2O$ only. However, at −52 °C an additional broad resonance is observed (δ 4.53) which we assign to a terminal aluminium hydride.[7] The IR spectra of **3** and **4** show sharp intense bands at 1867 and 1896 $cm^{-1}$ respectively, consistent with a terminal aluminium–hydride stretch,[7] while their mass spectra show only fragments due to a monomer. The monomeric nature of **3** and **4** has been confirmed by X-ray crystallography.

The molecular structures of **3** and **4** are shown in Figs. 5 and 6 respectively; selected bond lengths and angles are given in Tables 3 and 4. Despite difficulties in the refinement of **3** (see Experimental section) it is clear that the structures are similar. The aluminium centres are both distorted tetrahedral, with the most acute angles being associated with the Lewis base, *i.e.*, $NH_2Bu^t$ in **3** and $Et_2O$ in **4**. Those assiociated with $Et_2O$ are slightly larger than for $NH_2Bu^t$ (see Tables 3 and 4) consistent with the larger steric bulk of the former. The terminal aluminium hydrides were located [Al–H(1) 1.67(7) **3**, 1.47(3) Å **4**] and lie either side of the range calculated from *ab initio* studies (1.588–1.599 Å).

The reaction of **1** with an equivalent of $HOR^1$ results in the formation of a number of inseparable products. In contrast, the addition of 2,6-diphenylphenol ($HOR^2$) to a pentane solution of **1** allows for the isolation of the mixed aryloxide complex $[AlH(OR^1)(OR^2)(NMe_3)]$ **5** (see Experimental section). Based on the presence of an intense band at 1898 $cm^{-1}$ in the IR spectrum, the structure of **5** is most probably close to that of **3** and **4**, *i.e*, **III**.



**III**

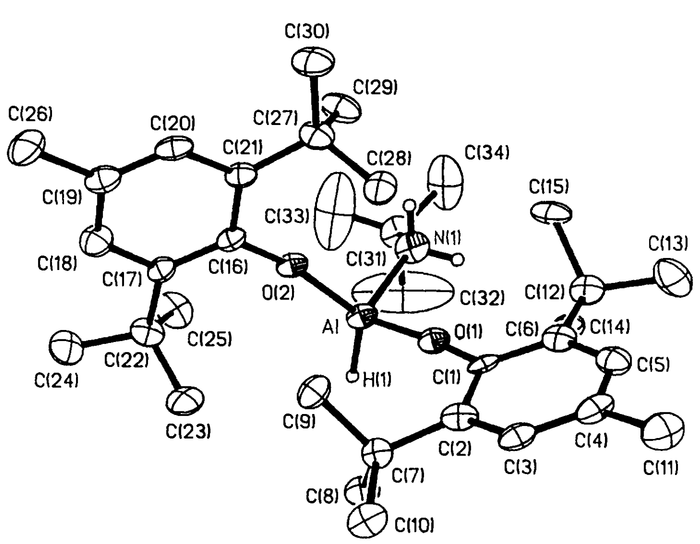


**Fig. 5** Molecular structure of [$AlH(OR^1)_2(NH_2Bu^t)$] **3**. Thermal ellipsoids are drawn at the 40% level, and hydrogen atoms, except those attached to aluminium, are omitted for clarity

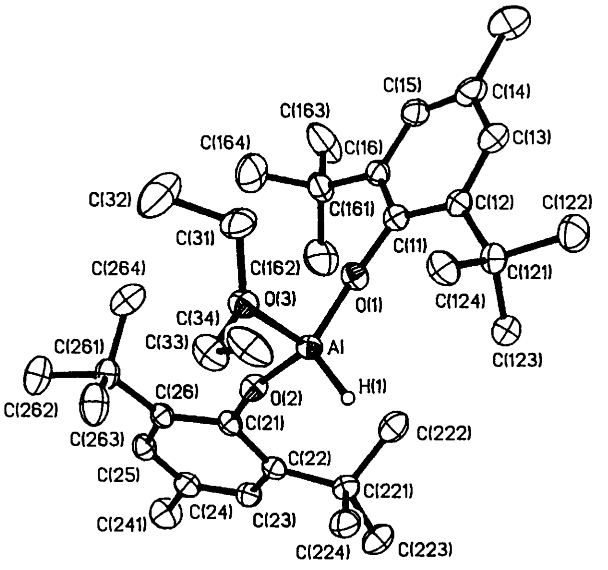


**Fig. 6** Molecular structure of [$AlH(OR^1)_2(OEt_2)$] **4**. Thermal ellipsoids are drawn at the 40% level, and hydrogen atoms, except those attached to aluminium, are omitted for clarity

Interaction of compound **1** with an excess of benzophenone in toluene results, upon hydrolysis, in the reduction of 1 molar equivalent of benzophenone per aluminium [equation (9)]. The

$$O{=}CPh_2 \xrightarrow[(ii)\,H_2O]{(i)\,[AlH_2(OR^1)(NMe_3)]} HOCHPh_2 \qquad (9)$$

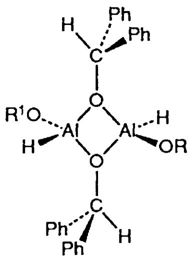
reaction of **1** with 1 equivalent of benzophenone yields the dimeric compound [$\{AlH(OR^1)(\mu\text{-}OCHPh_2)\}_2$] **6**. Based on the $^1H$ NMR spectral shifts for the $OCHPh_2$ ligand (see Experimental section) as compared to those previously reported,[15] and the value for the Al–H stretch (1913 $cm^{-1}$) which is consistent with a terminal hydride,[7] we propose that the alkoxides derived from the reduction of the benzophenone act as the bridging ligands, *i.e.* **IV**. No reactivity is observed between **6** and further equivalents of ketone, suggesting that complexation (precluded by the dimeric nature of **6**) is required prior to hydrogen transfer. A similar observation was noted for the alkyl analogues, **V**.[15]

**Table 3** Selected bond lengths (Å) and angles (°) for [$AlH(OR^1)_2(NH_2Bu^t)$] **3**

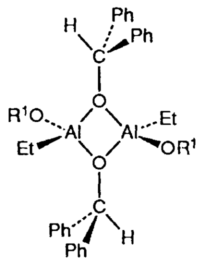
| | | | |
|---|---|---|---|
| Al–O(1) | 1.735(5) | Al–O(2) | 1.710(5) |
| Al–N(1) | 2.00(1) | Al–H(1) | 1.67(7) |
| O(1)–C(1) | 1.353(8) | O(2)–C(16) | 1.375(9) |
| N(1)–C(31) | 1.49(1) | | |
| O(1)–Al–O(2) | 118.2(3) | O(1)–Al–N(1) | 99.3(3) |
| O(1)–Al–H(1) | 109(2) | O(2)–Al–N(1) | 102.0(3) |
| O(2)–Al–H(1) | 124(2) | N(1)–Al–H(1) | 96(3) |
| Al–O(1)–C(1) | 169.1(6) | Al–O(2)–C(16) | 163.4(6) |
| Al–N(1)–C(31) | 128.8(7) | | |

**Table 4** Selected bond lengths (Å) and angles (°) for [$AlH(OR^1)_2(OEt_2)$] **4**

| | | | |
|---|---|---|---|
| Al–O(1) | 1.704(3) | Al–O(2) | 1.711(3) |
| Al–O(3) | 1.907(2) | Al–H(1) | 1.47(3) |
| O(1)–C(11) | 1.365(5) | O(2)–C(21) | 1.364(4) |
| O(3)–C(31) | 1.465(5) | O(3)–C(33) | 1.465(5) |
| O(1)–Al–O(2) | 117.2(1) | O(1)–Al–O(3) | 102.3(1) |
| O(1)–Al–H(1) | 118(1) | O(2)–Al–O(3) | 104.3(1) |
| O(2)–Al–H(1) | 113(1) | O(3)–Al–H(1) | 98(1) |
| Al–O(1)–C(11) | 165.3(3) | Al–O(2)–C(21) | 162.9(2) |
| Al–O(3)–C(31) | 124.7(3) | Al–O(3)–C(33) | 117.3(2) |
| C(31)–O(3)–C(33) | 115.3(3) | | |



**IV**



**V**

In contrast to the reactions of sterically unhindered alcohols [equation (1)], when an equimolar amount of $HOR^1$ is added to an $Et_2O$ suspension of $LiAlH_4$, no gas evolution is observed. Subsequent work-up of the reaction yields an equimolar quantity of alane, $AlH_3$, and the lithium aryloxide [equation (10)].[16]

$$\mathrm{LiAlH_4 + HOR^1 \xrightarrow{Et_2O} AlH_3 + [Li(OR^1)(OEt_2)]} \quad (10)$$

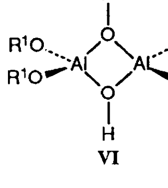
If the reaction is carried out with further equivalents of $\mathrm{HOR^1}$ gas evolution is observed, and a number of aluminium–aryloxide compounds may be observed by $^1$H NMR spectroscopy. However, no single species could be isolated until the addition of 3 equivalents of $\mathrm{HOR^1}$ per aluminium, at which point an equimolar mixture of $\mathrm{[\{Li(OR^1)(OEt_2)\}_2]}$ and $\mathrm{[AlH(OR^1)_2(OEt_2)]}$ **4** are formed in quantitative yield [equation (11)]. Compound **4** may readily be isolated, by fractional crystallisation from $\mathrm{Et_2O}$, as a moderately air-sensitive colourless crystalline solid (see above).

$$\mathrm{LiAlH_4 + 3HOR^1 \xrightarrow{Et_2O}}$$
$$\mathrm{[AlH(OR^1)_2(OEt_2)] + \tfrac{1}{2}[\{Li(OR^1)(OEt_2)\}_2] + 3H_2} \quad (11)$$

This result is in contrast to the report by Haubenstock and Yang[17] that the reaction of $\mathrm{LiAlH_4}$ with 2 equivalents of $\mathrm{HOC_6H_3Bu^t{}_2}$-2,6 gives the lithium salt in quantitative yield, *i.e.*, equation (12). However, Haubenstock *et al.*[18] reported that the reaction of $\mathrm{LiAlH_4}$ with 4 equivalents of $\mathrm{HOC_6H_3Bu^t{}_2}$-2,6 does proceed in an analogous manner to that shown in equation (11), although it should be noted that they concluded that the resulting monohydride contained a three-co-ordinate aluminium, *i.e.* $\mathrm{[AlH(OC_6H_3Bu^t{}_2\text{-}2,6)_2]}$.[18] Based on our data we suggest that it is most probably the $\mathrm{Et_2O}$ solvate, analogous to **4**.

$$\mathrm{LiAlH_4 + 2HOC_6H_3Bu^t{}_2\text{-}2,6 \longrightarrow}$$
$$\mathrm{Li[AlH_2(OC_6H_3Bu^t{}_2\text{-}2,6)_2] + H_2} \quad (12)$$

Hydrolysis of **4** in pentane solution yields hydroxide **7** with probable formulation $\mathrm{[\{Al(\mu\text{-}OH)(OR^1)_2\}_2]}$. Although we have been unable to confirm the extent of oligomerisation of **7** by X-ray crystallography the $^1$H NMR spectral shift of the hydroxide hydrogen (δ 3.93) is consistent with a bridging hydroxide,[19] the $^{27}$Al NMR peak position (δ 40.3) and width ($W_{\frac{1}{2}}$ = 6900 Hz) are consistent with a four-co-ordinate aluminium centre,[20] and finally **7** does not form Lewis acid–base adducts with $\mathrm{Et_2O}$ and thf, precluding the possibility of it being a three-co-ordinate monomeric compound. Thus, the spectroscopic data available are consistent with the formation of a hydroxide-bridged dimer **VI**.



**VI**

The interaction of **4** with a further equivalent of $\mathrm{HOR^1}$ in refluxing toluene allows for the isolation of $\mathrm{[Al(OR^1)_3]}$ **8** in quantitative yield [equation (13)], as an air-sensitive colourless crystalline solid.[6]

$$\mathrm{[AlH(OR^1)_2(OEt_2)] + HOR^1 \xrightarrow{-Et_2O} \underset{\mathbf{8}}{[Al(OR^1)_3]} + H_2} \quad (13)$$

The $^1$H and $^{13}$C NMR spectra of **8** show resonances due only to the aryloxide, while the $^{27}$Al NMR contains a single resonance (δ 3.2). Although this $^{27}$Al NMR signal is in a region normally associated with six-co-ordinate aluminium centres, it follows the general trend observed for monomeric three-co-ordinate aryloxide derivatives, *i.e.*, $\mathrm{[AlR_2(OR^1)]}$ compounds have δ($^{27}$Al) resonances around δ 190, while those for $\mathrm{[AlR(OR^1)_2]}$ are found at δ *ca.* 100.[21] The medium-resolution mass spectrum of **8** exhibits a parent ion (*m/z* 684) consistent with a monomeric structure in the gas phase. Compound **8** is also monomeric in solid state as evident from an X-ray crystallographic structure analysis, and thus represents a rare example of a monomeric three-co-ordinate aluminium compound.[22]

The molecular structure of **8** is shown in Fig. 7, with selected bond lengths and angles in Table 5, and consists of discrete molecules of $\mathrm{[Al(OR^1)_3]}$ with no unusual intermolecular distances. Two molecules of the solvent of recrystallisation, $\mathrm{CH_2Cl_2}$, are present in the asymmetric unit. The aluminium is three-co-ordinate trigonal planar [Σ O–Al–O 359.9(3)°]. The average Al–O distance and Al–O–C angle are 1.648(7) Å and 177.2(5)° respectively. The aromatic rings form a propeller-like arrangement around the aluminium, and are canted *ca.* 56° from the $\mathrm{AlO_3}$ plane. The short Al–O distances are undoubtedly a consequence of three factors. First, the sp$^2$ hybridisation at aluminium *versus* sp$^3$ in the more commonly observed four-co-ordinate complexes; secondly, the increased s character in the Al–O bond as a result of the near linear Al–O–C bond angle and thirdly, the presence of a $p_\pi$–$p_\pi$ interaction between the vacant Al 3$p_z$ orbital (*z* perpendicular to the $\mathrm{AlO_3}$ plane) and the lone pairs on the aryloxide oxygens. The latter may also account for the highly shielded aluminium centre, as evident from the upfield resonance in the $^{27}$Al NMR spectrum.

The formation of Lewis acid–base complexes of $\mathrm{[Al(OR^1)_3]}$ is not necessarily expected due to the steric congestion at the aluminium centre provided by the propeller-like arrangement of the three 2,6-disubstituted aryloxide ligands (see Fig. 8). However, previous studies on transition-metal and lanthanide analogues of **8** indicate that formation of the mono-adduct is facile. Thus, $\mathrm{[Sc(OR^1)_3]}$ reacts with thf and O=PPh$_3$ to form the appropriate complexes.[23] Similarly $\mathrm{[Ce(OC_6H_3Bu^t{}_2\text{-}2,6)_3]}$ was shown to form 1:1 adducts with thf, O=CPh$_2$, O=PEt$_3$, $\mathrm{NH_2Bu^n}$, $\mathrm{NHEt_2}$, MeCN, $\mathrm{CNBu^t}$ and tetrahydrothiophene.[24] Furthermore, with 'slender' ligands, an additional equivalent of the Lewis base may be added to the metal centre, and the crystal structure of $\mathrm{[Ce(OC_6H_3Bu^t{}_2\text{-}2,6)_3(CNBu^t)_2]}$ was reported.[24]

Compound **8** reacts with pyridine (py), acetonitrile, triphenylphosphine oxide, and 4-*tert*-butylcyclohexanone to yield the appropriate Lewis acid–base complexes $\mathrm{[Al(OR^1)_3L]}$ [equation (14), L = MeCN **9**, py **10**, O=PPh$_3$ **11** or O=C-C(C$_5$H$_9$)Bu$^t$-4 **12**]. No evidence for adduct formation was observed for benzophenone, diethyl ether or thf. Compounds **9**–**12** may be isolated as white, or pale yellow (**12**), crystalline solids, and have been fully characterised (see Experimental section).

$$\mathrm{[Al(OR^1)_3] + L \longrightarrow [Al(OR^1)_3L]} \quad (14)$$

Compound **8** was subjected to a titration with up to 5 equivalents of acetonitrile. The results of this experiment are presented in Fig. 9. The NMR data show that only 1 equivalent of MeCN is co-ordinated to each aluminium centre, *i.e.*, the formation of $\mathrm{[Al(OR^1)_3(NCMe)_2]}$ is not observed. Addition of less than one equivalent of MeCN gives two peaks in the *tert*-butyl region, δ 1.51 and 1.44, corresponding to $\mathrm{[Al(OR^1)_3]}$ and $\mathrm{[Al(OR^1)_3(NCMe)]}$ respectively. Therefore the exchange of MeCN between molecules of $\mathrm{[Al(OR^1)_3]}$ is slow on the NMR time-scale at 290 K. This is in contrast to the $\mathrm{[Ce(OC_6H_3Bu^t{}_2\text{-}2,6)_3]}$–thf system where rapid ligand exchange was observed at ambient temperatures.[24] Warming a solution in $\mathrm{C_6D_6}$ corresponding to the addition of *ca.* $\frac{2}{3}$ equivalent of MeCN per aluminium indicates that coalescence occurs at 353 K, from

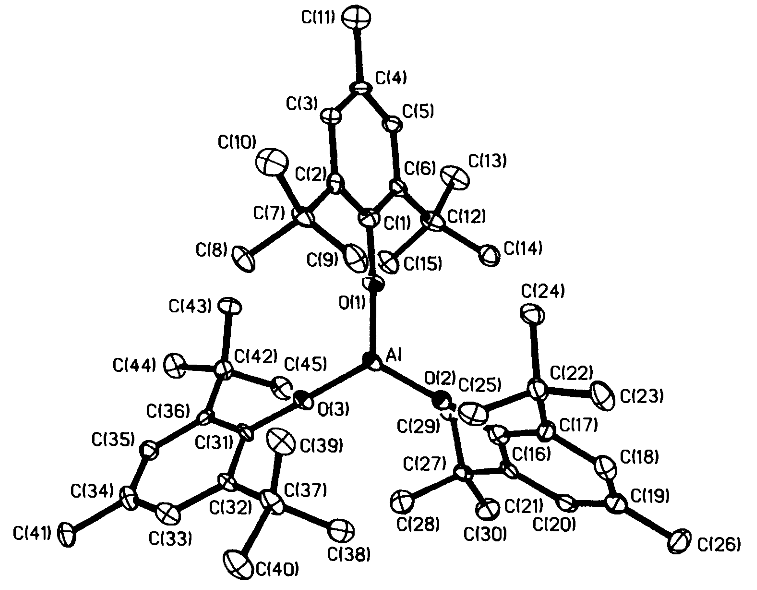


Fig. 7 Molecular structure of $[Al(OR^1)_3]$ **8**. Thermal ellipsoids are drawn at the 40% level and hydrogen atoms are omitted for clarity

**Table 5** Selected bond lengths (Å) and angles (°) for $[Al(OR^1)_3]$ **8**

| | | | |
|---|---|---|---|
| Al–O(1) | 1.657(6) | Al–O(2) | 1.640(5) |
| Al–O(3) | 1.647(7) | O(1)–C(1) | 1.37(1) |
| O(2)–C(16) | 1.380(9) | O(3)–C(31) | 1.37(1) |
| O(1)–Al–O(2) | 119.1(3) | O(1)–Al–O(3) | 120.9(3) |
| O(2)–Al–O(3) | 119.9(3) | Al–O(1)–C(1) | 175.0(6) |
| Al–O(2)–C(16) | 177.6(5) | Al–O(3)–C(31) | 179.0(3) |

which an activation energy of ($\Delta G^\ddagger$) of 18.2(3) kJ mol$^{-1}$ may be calculated[25] for the degenerate exchange given in equation (15).

$$[Al^*(OR^1)_3] + [Al(OR^1)_3(NCMe)] \rightleftharpoons [Al(OR^1)_3] + [Al^*(OR^1)_3(NCMe)] \quad (15)$$

Interestingly, this value is similar to that observed for the analogous exchanges between $[AlMe(OR^1)_2]$ and $[AlMe(OR)_2L]$, *i.e.*, 12–17 kJ mol$^{-1}$ but significantly lower than observed for the sterically less demanding bis(aryloxide) alkoxide $[Al(OR^1)_2(OCHPh_2)L]$[15] (54–59 kJ mol$^{-1}$). We may conclude therefore that while the inherent Lewis acidity of $[Al(OR^1)_3]$ is expected to be comparable to $[Al(OR^1)_2(OCHPh_2)]$, the increased steric repulsion reduces the donor–acceptor bond strength. N.B. No adduct formation is observed for **8** with sterically-demanding Lewis bases unlike $[Al(OR^1)_2(OCHPh_2)]$.[15]

In spite of the slow exchange of MeCN in solutions of compounds **8** and **9**, the $^1H$ NMR of isolated **9** shows a single set of resonances. This is in contrast to the $^1H$ NMR spectrum of $[Al(OR^1)_3\{O{=}C(C_5H_9)Bu^t\text{-}4\}]$ **12**. At room temperature (291 K) the 400 MHz $^1H$ NMR spectrum of analytically pure **12** shows a complex spectrum, consisting of a single peak associated with the Bu$^t$ protons (54 H), two peaks [$\delta$ 2.30 (6.4 H) and 2.20 (2.6 H)] associated with the methyl group on the aryloxide and two peaks [$\delta$ 0.71 (6.4 H) and 0.67 (2.6 H)] associated with the *tert*-butyl peak on the cyclohexanone. The peak at $\delta$ 2.20 is consistent with free $[Al(OR^1)_3]$, *i.e.* $\delta$ 2.19, while that at $\delta$ 2.30 may be assigned to **12**. A similar and consistent argument may be advanced for the resonances due to the *tert*-butyl on cyclohexanone. The pathological overlap of the resonances due to the 2,6-*tert*-butyl groups for **8** and **12**, is not unreasonable since we have observed that this resonance is relatively insensitive to structural changes around aluminium.[8] The $^1H$ NMR spectrum is therefore consistent with the presence of an equilibrium between 'free' and co-ordinated cyclohexanone [equation (16)].

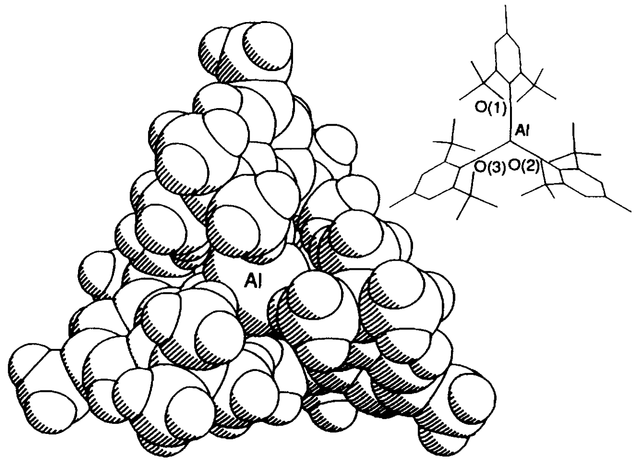


Fig. 8 Space-filling representation of $[Al(OR^1)_3]$ **8**, and its equivalent line drawing (inset), viewed perpendicular to the $AlO_3$ plane, showing the steric hindrance imposed on the aluminium centre

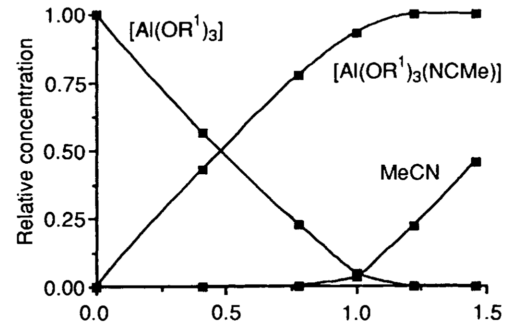


Fig. 9 Relative concentration of $[Al(OR^1)_3]$ **8**, $[Al(OR^1)_3(NCMe)]$ **9** and MeCN as a function of MeCN : $[Al(OR^1)_3]$ molar ratio

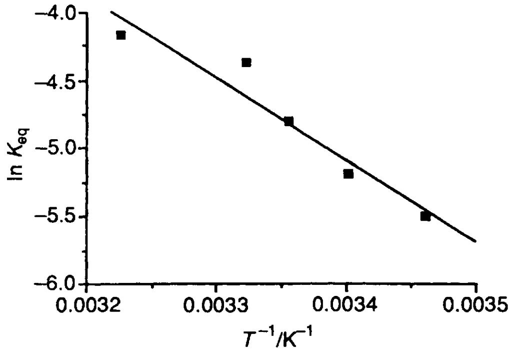


**Fig. 10** Temperature dependence of the equilibrium constant, $K_{eq}$, for the dissociation of $[Al(OR^1)_3\{O{=}C(C_5H_9)Bu^t\text{-}4\}]$ **12**

$$[Al(OR^1)_3\{O{=}C(C_5H_9)Bu^t\text{-}4\}] \underset{}{\overset{K_{eq}}{\rightleftharpoons}} [Al(OR^1)_3] + O{=}C(C_5H_9)Bu^t\text{-}4 \quad (16)$$

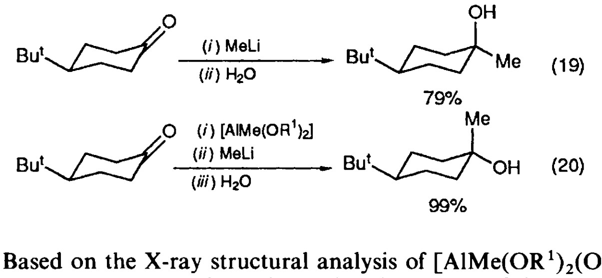
$$K_{eq} = \frac{[Al(OR^1)_3][O{=}C(C_5H_9)Bu^t\text{-}4]}{[Al(OR^1)_3\{O{=}C(C_5H_9)Bu^t\text{-}4\}]} \quad (17)$$

For the equilibrium between complex **12** and its constitutes [equation (16)], the equilibrium constant, $K_{eq}$ [equation (17)] may be derived in terms of the mole fraction of the uncomplexed 4-*tert*-butylcyclohexane present, $\chi_{free}$, and the total initial concentration, *c* [equation (18)].[15]

$$K_{eq} = \frac{c(\chi_{free})^2}{1 - \chi_{free}} \quad (18)$$

The $^1H$ NMR spectra of a $[^2H_8]$toluene solution of **12** were obtained at various temperatures (289–313 K) from which the relative concentrations of free and co-ordinated species may be calculated and subsequently the equilibrium constants, $K_{eq}$ (see Table 6). The temperature dependence of the equilibrium constant (Fig. 10) allows for the determination of $\Delta H_D$ and $\Delta S_D$, for the ligand dissociation reaction represented in equation (15), to be 47(1) kJ $mol^{-1}$ and 119(8) J $K^{-1}$ $mol^{-1}$ respectively. The value of $\Delta H_D$ may be compared to the values previously obtained for $[AlMe(OR^1)_2(O{=}CPh_2)]$ and $[Al(OR^1)_2(OCHPh_2)(O{=}CPh_2)]$ of 67.1(3) and 92.5(4) kJ $mol^{-1}$ respectively.[15] Again the difference is consistent with a large steric control over the aluminium–ligand bond strength. The value of $\Delta S_D$ is large and positive as would be expected for a dissociative process, and is reasonably comparable to those found for the Lewis acid–base adducts of $[AlMe(OR^1)_2]$ (167–237 J $K^{-1}mol^{-1}$).[15]

An important development in the area of stereoselective organic synthesis has been the use by Yamamoto and co-workers,[26] of the bulky organoaluminium compound $[AlMe(OR^1)_2]$ for the stereoselective activation of carbonyl moieties. In this system the axial alkylation of substituted cyclohexanones [equation (19)] was reversed by the addition of $[AlMe(OR^1)_2]$, *i.e.* equation (20).



Based on the X-ray structural analysis of $[AlMe(OR^1)_2(O{=}CPh_2)]$ we proposed that this Lewis acid control of the π-face selectivity was a combination of steric and electronic effects.[27]

**Table 6** Determination of $K_{eq}$* for the ligand dissociation of $[Al(OR^1)_3\{O{=}C(C_5H_9)Bu^t\text{-}4\}]$ **12**

| *T*/K | $\chi_{free}$ | $K_{eq}$/mol $dm^{-3}$ |
|---|---|---|
| 289 | 0.248 | $4.10 \times 10^{-3}$ |
| 294 | 0.283 | $5.57 \times 10^{-3}$ |
| 298 | 0.332 | $8.24 \times 10^{-3}$ |
| 301 | 0.391 | $1.25 \times 10^{-2}$ |
| 310 | 0.423 | $1.55 \times 10^{-2}$ |

* $K_{eq} = c(\chi_{free})^2/(1 - \chi_{free})$; $c$ = 0.050 mol $dm^{-3}$.

The presence of a π interaction between one set of lone pairs of one of the aryloxide ligands and the ketone Al–O σ* orbital accounted for a preferred orientation, such that one face of the ketone is hindered from external attack by the *o*-*tert*-butyl groups of this aryloxide. Since benzophenone does not have two distinct faces, and we failed to obtain crystals of suitable quality of the cyclohexanone complex, we were unable at that time to confirm that in the case of a substituted cyclohexanone the less bulky face of the ketone would be hindered by the *o*-*tert*-butyl groups, leaving the sterically more demanding equatorial face open for alkylation. However, crystals of **12** were grown suitable for X-ray crystallographic confirmation of such an effect.

The molecular structure of compound **12** is shown in Fig. 11; selected bond lengths and angles are given in Table 7. The Al–O distances for the aryloxides and the ketone are within experimental error of ranges previously observed [1.713(4)–1.754(1) and 1.851(7)–1.920(3) Å respectively],[8] while the ketone is co-ordinated such that the aluminium is in the nodal phase of the C=O π bond with an Al–O(4)–C(41) angle of 165.8(5)° towards the straight end of the range observed, 136.0(3)–171(1)°.[28]

The orientation of the aryloxide ligands with respect to the cyclohexanone may more clearly be seen in Fig. 12. One of the *o*-*tert*-butyl groups for aryloxide, O(3), C(31)... *etc.*, is situated so as to provide steric protection of the axial face of the cyclohexanone, leaving the equatorial face open for external attack, *i.e.*, alkylation. This is in perfect agreement with our previous proposal,[27] and confirms the mode of π-face selectivity of co-ordinated ketones enabled by sterically-hindered aryloxide compounds of aluminium.

In a similar manner to the formation of **8** [equation (12)], compound **4** reacts with 2,4,6-trichloroaniline ($H_2NC_6H_2Cl_3$-2,4,6) to yield the first three-co-ordinate aluminium amido–aryloxide complex, $[Al(OR^1)_2(NHC_6H_2Cl_3\text{-}2,4,6)]$ **13**, as an air-sensitive white solid. The $^1H$ and $^{13}C$ NMR spectra of **13** show resonances due only to the aryloxide and amide, while the $^{27}Al$ NMR spectrum contains a single broad resonance (δ 6.0) consistent with a monomeric three-co-ordinate aluminium complex, *cf.* **8**. The mass spectrum of **13** exhibits a parent ion (*m*/*z* 661) consistent with a monomeric structure **VII** in the gas phase. Unfortunately, we have been unable to obtain crystals of **11** suitable for X-ray diffraction to confirm this structure in the solid state.

The low congestion around the aluminium in **13**, as compared to **8**, is apparent in its ability to form complexes with $Et_2O$, in addition to py and 3,5-dimethylpyridine (3,5$Me_2$-py) [equation (21), L = $Et_2O$ **14**, py **15** or 3,5$Me_2$-py **16**]. Compounds **14**–**16** have been characterised by IR and NMR spectroscopy. Their $^1H$ NMR spectra show no evidence for the slow ligand exchange process observed for the Lewis acid–base complexes of $[Al(OR^1)_3]$.

$$[Al(OR^1)_2(NHC_6H_2Cl_3\text{-}2,4,6)] + L \longrightarrow [Al(OR^1)_2(NHC_6H_2Cl_3\text{-}2,4,6)L] \quad (12)$$

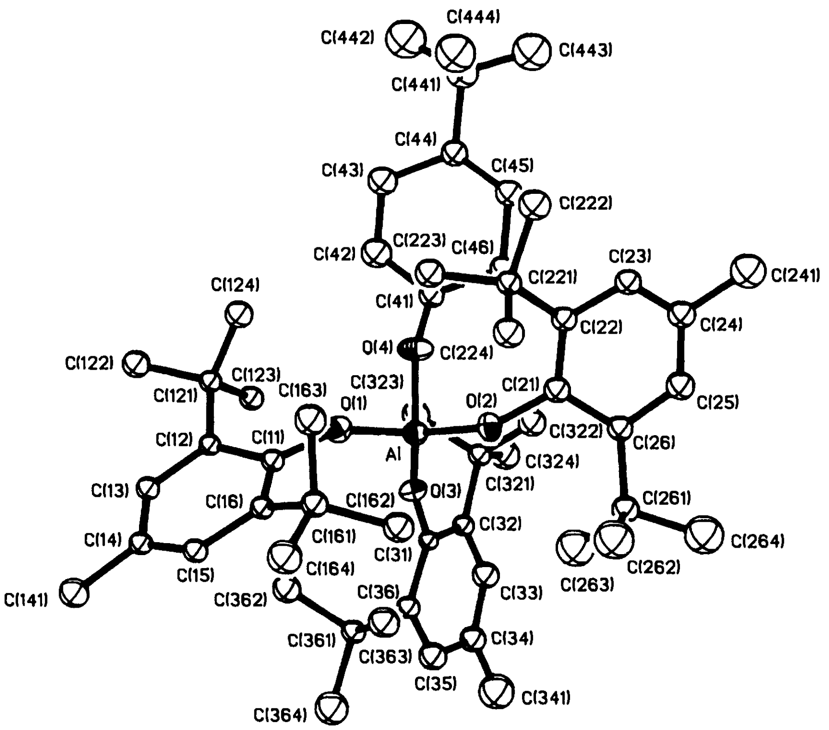


**Fig. 11** Molecular structure of $[Al(OR^1)_3\{O{=}C(C_5H_9)Bu^t\text{-}4\}]$ **12**. Thermal ellipsoids are drawn at the 30% level, and hydrogen atoms are omitted for clarity

**Table 7** Selected bond lengths (Å) and angles (°) for $[Al(OR^1)_3\text{-}\{O{=}C(C_5H_9)Bu^t\text{-}4\}]$ **12**

| | | | |
|---|---|---|---|
| Al-O(1) | 1.717(5) | Al-O(2) | 1.716(5) |
| Al-O(3) | 1.691(5) | Al-O(4) | 1.841(6) |
| O(1)-C(11) | 1.359(9) | O(2)-C(21) | 1.402(9) |
| O(3)-C(31) | 1.377(7) | O(4)-C(41) | 1.25(1) |
| O(1)-Al-O(2) | 106.3(3) | O(1)-Al-O(3) | 116.4(2) |
| O(1)-Al-O(4) | 104.1(3) | O(2)-Al-O(3) | 121.8(3) |
| O(2)-Al-O(4) | 103.6(3) | O(3)-Al-O(4) | 102.2(3) |
| Al-O(1)-C(11) | 146.7(4) | Al-O(2)-C(21) | 137.2(5) |
| Al-O(3)-C(3) | 163.9(5) | Al-O(4)-C(41) | 165.8(5) |

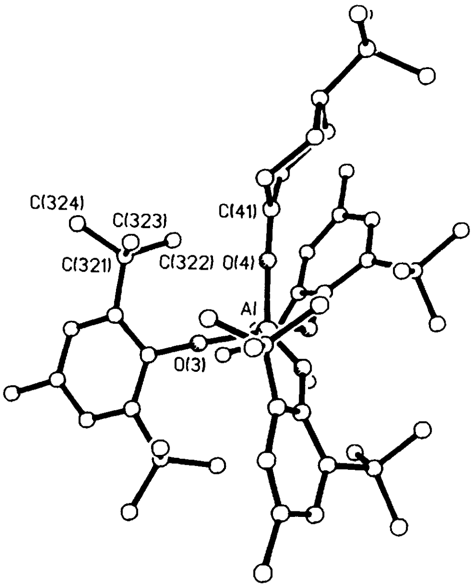
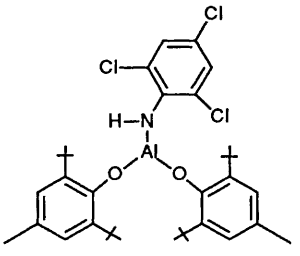


**Fig. 12** A ball and stick representation of $[Al(OR^1)_3\{O{=}C(C_5H_9)Bu^t\text{-}4\}]$ **12** viewed parallel to the cyclohexanone ring, showing the steric inhibition to the carbonyl carbon C(41) by the *o-tert*-butyl group [C(322), C(323)] of one of the aryloxide ligands



VII

## Experimental

Microanalyses were performed by Oneida Research Services, Inc., Whitesboro, NY. Melting points were determined in sealed capillaries and are uncorrected. Infrared spectra (4000–700 $cm^{-1}$) were recorded on a Nicolet 5ZDX FT-IR spectrometer as Nujol mulls (NaCl). Proton and $^{13}C$ NMR spectra, in $C_6D_6$ unless otherwise stated, were recorded on a Bruker AM-500 (δ relative to $SiMe_4$). Aluminium-27 NMR spectra were recorded on a Bruker WM-300, δ relative to $[Al(H_2O)_6]^{3+}$. Molecular weight measurements were made in benzene with the use of an instrument similar to that described by Clark.[29] Mass spectra were recorded using a JEOL AX-505 H mass spectrometer and associated data system. All manipulations were carried out under nitrogen. Solvents were dried, distilled and degassed before use. The compounds $[AlH_3(NMe_3)]$ and $[Al(H)Cl(NMe_3)]$ were prepared by literature procedures.[4,5]

*Preparations.*—*(2,6-Di-*tert*-butyl-4-methylphenoxo)dihydrido(trimethylamine)aluminium*(III) **1**. To $[AlH_3(NMe_3)]$ (18.0 g, 0.202 mol) dissolved in pentane (150 $cm^3$) was added $HOR^1$ (45.5 g, 0.207 mol) as a solid at −76 °C. The resulting suspension was slowly warmed to room temperature and subsequently stirred for 12 h, to give a clear solution. Reduction in volume *in vacuo* and cooling to −20 °C resulted in the formation of large white crystals, yield 32% (based on $HOR^1$). Similar crops of crystals may be obtained from the mother-liquor, but by $^1H$ NMR spectroscopy they were shown to be deficient in $NMe_3$, and were not used in subsequent reactions; m.p. 123–128 °C (Found: C, 70.60; H, 11.20; N, 4.25. Calc. for $C_{18}H_{34}AlNO$: C, 70.30; H, 11.15; N, 4.55%); mass spectrum (EI, %): *m*/*z* 307 ($M^+$, 10%) and 248 ($M^+ - NMe_3$, 20%); IR: 1910–1800br, m, 1378m, 1362w, 1353w, 1272 (sh), 1264s, 1247m, 1202w, 1124w, 1099w, 1033w, 1023w, 992m, 987m, 888 (sh), 877m, 863m, 835w, 787m, 778m and 751m $cm^{-1}$. NMR: $^1H$, δ 7.22 (2 H, s, $C_6H_2$), 2.33 (3 H, s, $CH_3$), 1.92 (9 H, s, $NCH_3$) and 1.62 [18 H, s, $C(CH_3)_3$]; $^{13}C$, δ 154.94 (OC), 138.84 (*o*-C), 126.28 (*m*-C), 126.08 (*p*-C), 47.38 ($NCH_3$), 35.43 [$C(CH_3)_3$], 31.66 [$C(CH_3)_3$] and 21.44 ($CH_3$). Low-temperature $^1H$ NMR (−65 °C, [$^2H_8$]toluene): δ 4.40 (s, Al–H).

(2,6-*Di*-tert-*butyl*-4-*methylphenoxo*)(*chloro*)*hydrido*(*trimethylamine*)*aluminium*(III) **2**. To [$AlH_2Cl(NMe_3)$] (0.20 g, 1.62 mmol) dissolved in pentane (40 $cm^3$) was added $HOR^1$ (0.36 g, 1.64 mmol) at room temperature. Gas evolution was noted and the slightly cloudy solution was stirred for 12 h. Significant precipitation occured after *ca*. 0.5 h. Removal of solvent *in vacuo* led to a white powder, yield *ca*. 90%; m.p. 121–126 °C (Found: C, 59.70; H, 8.85; N, 3.15. Calc. for $C_{18}H_{33}AlClNO$: C, 63.25; H, 9.75; N, 4.10%). IR: 1893w, 1293m, 1260s, 1204w, 1155w, 1123s, 1100m, 1023m, 991m, 980m, 954w, 919w, 888m, 861m, 816m, 804m, 774m, 722m, 661m, 638w and 623w $cm^{-1}$. NMR: $^1H$, δ 7.24 (2 H, s, $C_6H_2$), 2.33 (3 H, s, $CH_3$), 1.92 (9 H, s, $NCH_3$) and 1.62 [18 H, s, $C(CH_3)_3$]; $^{13}C$, δ 153.85 (OC), 138.84 (*o*-C), 127.05 (*m*-C), 126.40 (*p*-C), 47.02 ($CH_3$, $NMe_3$), 35.28 [$C(CH_3)_3$], 31.70 [$C(CH_3)_3$] and 21.33 ($CH_3$).

(tert-*Butylamine*)*bis*(2,6-*di*-tert-*butyl*-4-*methylphenoxo*)*hydridoaluminium*(III) **3**. To a pentane (30 $cm^3$) solution of [$AlH_2(OR^1)(NMe_3)$] (1.00 g, 3.26 mmol) at room temperature was added $NH_2Bu^t$ (0.5 $cm^3$, 4.76 mmol) *via* a syringe and the resulting solution refluxed overnight. Removal of volatiles *in vacuo* and crystallisation from pentane–toluene afforded colourless crystals, yield *ca*. 15%; m.p. 83–86 °C; mass spectrum (EI, %): *m*/*z* 466 ($M^+ - NH_2Bu^t$, 100). IR: 3307m, 3250w, 1867m, 1506w, 1285m, 1282 (sh), 1260 (sh), 1238s, 1216m, 1204m, 1151s, 1136 (sh), 1121m, 1025m, 927w, 873s, 859s, 776m, 741s, 724 (sh) and 690m $cm^{-1}$. NMR: $^1H$, δ 7.19 (4 H, s, $C_6H_2$), 3.24 (2 H, s, $NH_2$), 2.30 (6 H, s, $CH_3$), 1.58 [36 H, s, $C(CH_3)_3$] and 0.91 [9 H, s, $NC(CH_3)$]; $^{13}C$, δ 154.53 (OC), 138.45 (*o*-C), 126.50 (*m*-C), 126.29 (*p*-C), 53.79 [$C(CH_3)_3$, amine], 35.23 [$C(CH_3)_3$], 32.07 [$C(CH_3)_3$], 30.07 [$C(CH_3)_3$, amine] and 21.30 ($CH_3$).

*Bis*(2,6-*di*-tert-*butyl*-4-*methylphenoxo*)(*diethyl ether*)*hydridoaluminium*(III) **4**. To a suspension of $LiAlH_4$ (5.00 g, 0.125 mol) in $Et_2O$ (400 $cm^3$), at −78 °C, was added solid $HOR^1$ (82.50 g, 0.375 mol). The reaction was slowly warmed to room temperature and stirred for 12 h. Filtration, followed by fractional crystallisation allows for the isolation of colourless crystals, yield *ca*. 70%; m.p. 136–140 °C (Found: C, 74.45; H, 9.95. Calc. for $C_{34}H_{57}AlO_3$: C, 75.50; H, 10.60%). IR: 1896s, 1460vs, 1421s, 1387m, 1318w, 1258s, 1203m, 1147w, 1124w, 1088m, 1022m, 994m, 953w, 901s, 899m, 793m, 763m, 722w and 692m $cm^{-1}$. NMR: $^1H$, δ 7.22 (4 H, s, $C_6H_2$), 3.68 (4 H, m, $OCH_2$), 2.30 (6 H, s, $CH_3$), 1.59 [36 H, s, $C(CH_3)_3$], 0.64 (6 H, m, $OCH_2CH_3$); (−52 °C) δ 4.53 (br s, Al–H); $^{13}C$, δ 154.21 (OC), 138.80 (*o*-C), 126.48 (*m*-C), 126.28 (*p*-C), 66.06 ($OCH_2$), 35.39 [$C(CH_3)_3$], 31.89 [$C(CH_3)_3$], 21.36 ($CH_3$) and 11.67 ($OCH_2CH_3$); $^{27}Al$, δ 59 ($W_{\frac{1}{2}}$ 5470 Hz).

(2,6-*Di*-tert-*butyl*-4-*methylphenoxo*)(2,6-*diphenylphenoxo*)-*hydrido*(*trimethylamine*)*aluminium*(III) **5**. To a pentane solution of [$AlH_2(OR^1)(NMe_3)$] (1.0 g, 3.25 mmol), at room temperature, was added $HOR^2$ (0.80 g, 3.25 mmol). After stirring for 3 h, the solvent was removed under vacuum, and the crude product was recrystallised from toluene–pentane, yield *ca*. 1.45 g, 81%; m.p. 160.5–163.0 °C (Found: C, 78.30; H, 8.45, N, 2.45. Calc. for $C_{36}H_{46}AlNO_2$: C, 78.35; H, 8.40; N, 2.55%). IR: 1898s, 1599w, 1303w, 1281m, 1268m, 1247 (sh), 1239s, 1216w, 1200w, 1082w, 1070w, 1000m, 990m, 890s, 869s, 859 (sh), 823w, 773w, 762s, 751s, 725s, 697 (sh), 691 (sh), 658w, 611w, 591m, 574w, 536 (sh) and 531s $cm^{-1}$. NMR: $^1H$ δ 7.66 (4 H, m, *o*-CH), 7.30 (1 H, s), 7.27 (1 H, s), 7.19 (2 H, s, $C_6H_2$), 7.10 (6 H, m), 2.36 (3 H, s, $CH_3$), 1.51 [18 H, s, $C(CH_3)_3$] and 1.44 (9 H, s, $NCH_3$); $^{13}C$, δ 155.16, 153.40 (OC), 141.61, 139.18, 133.64, 131.01, 130.45, 128.71, 126.85, 126.58, 125.90, 119.57 ($C_6H_6$, $C_6H_3$, $C_6H_2$), 46.93 ($NCH_3$), 35.58 [$C(CH_3)_3$], 32.75 [$C(CH_3)_3$] and 21.23 ($CH_3$).

*Bis*[(2,6-*di*-tert-*butyl*-4-*methylphenoxo*)(*diphenylmethoxo*)-(*hydrido*)*aluminium*(III)] **6**. To a toluene solution (30 $cm^3$) of [$AlH_2(OR^1)(NMe_3)$] (1.00 g, 3.25 mmol) was added benzophenone (0.59 g, 3.24 mmol) and the resulting light red solution stirred at room temperature for 12 h, during which time the colour dissipated. All volatiles were removed *in vacuo* and the resulting white powder crystallised from toluene, yield 1.30 g, 93%; m.p. 206–209 °C (Found: C, 77.95; H, 8.10. Calc. for $C_{28}H_{35}AlO_2$: C, 78.10; H, 8.20%); mass spectrum (EI, %): *m*/*z* 429 ($M^+ - H$). IR: 1913s, 1297w, 1266s, 1220w, 1203m, 1165m, 1125w, 1086w, 1028w, 964s, 914 (sh), 907s, 893m, 876m, 861w, 773s, 748s, 730s, 699s, 685s, 669s, 657m, 628w, 590w and 561m $cm^{-1}$. NMR ($C_7H_8$): $^1H$, δ 7.47–6.79 (12 H, $C_6H_5$, $C_6H_2$), 6.55 (1 H, s, OCH), 2.30 (3 H, s, $CH_3$) and 1.38 [18 H, br s, $C(CH_3)_3$]; $^{13}C$, δ 153.62 (OC), 140.74, 139.18, 129.52, 129.00, 128.41, 126.99, 126.20 ($C_6H_5$ and $C_6H_2$), 81.75 (OCH), 35.22 [$C(CH_3)_3$], 31.80 [$C(CH_3)_3$] and 21.31 ($CH_3$).

*Bis*(2,6-*di*-tert-*butyl*-4-*methylphenoxo*)(*hydroxo*)*aluminium*-(III) **7**. Water (133 µl, 7.39 mmol) was injected into a cooled (−78 °C) suspension of [$AlH(OR^1)_2(OEt_2)$] (4.00 g, 7.39 mmol) in pentane (150 $cm^3$) and the mixture was slowly warmed to room temperature. After the resulting clear solution was stirred for an additional 2 h the solvent was reduced by half *in vacuo*. Cooling at −20 °C overnight yielded the white crystalline product. A smaller second crop was similarly obtained from the filtrate, yield 2.14 g, 60.1%; m.p. >220 °C (Found: C, 74.70; H, 9.85. Calc. for $C_{30}H_{47}AlO_3$: C, 74.65; H, 9.80%). IR: 3699m ($\nu_{OH}$), 1424s, 1295 (sh), 1266s, 1206w, 966m, 936m, 921m, 908s and 633m $cm^{-1}$. NMR: $^1H$, δ 7.11 (4 H, s, $C_6H_2$), 3.93 (1 H, s, OH), 2.20 (6 H, s, $CH_3$) and 1.45 [36 H, s, $C(CH_3)_3$]; $^{13}C$, δ 152.21 (OC), 138.07 (*o*-C), 127.89 (*m*-C), 126.62 (*p*-C), 35.11 [$C(CH_3)_3$], 31.94 [$C(CH_3)_3$] and 21.28 ($CH_3$); $^{27}Al$, δ 40.3 ($W_{\frac{1}{2}}$ 6900 Hz).

*Tris*(2,6-*di*-tert-*butyl*-4-*methylphenoxo*)*aluminium*(III) **8**. To a toluene (40 $cm^3$) solution of [$AlH(OR^1)_2(OEt_2)$] (4.00 g, 7.40 mmol) was added $HOR^1$ (1.63 g, 7.41 mmol). The reaction mixture was refluxed for 12 h. Upon cooling, the solvent was removed under vacuum, and the residue crystallised from $CH_2Cl_2$ (−20 °C) to give X-ray quality crystals, yield *ca*. 90%; m.p. 116–124 °C (Found: C, 79.30; H, 10.40. Calc. for $C_{45}H_{69}AlO_3$: C, 78.90; H, 10.15%); mass spectrum (EI, %): *m*/*z* 684.1000 ($M^+$). IR: 1422s, 1390m, 1363m, 1295m, 1265s, 1209m, 1184w, 1157w, 1125m, 1081w, 1026w, 977s, 941m, 909w, 899w, 859m, 810w, 802w, 768m, 727w, 659m and 635w $cm^{-1}$. NMR: $^1H$, δ 7.11 (2 H, s, $C_6H_2$), 2.19 (3 H, s, $CH_3$) and 1.51 [18 H, s, $C(CH_3)_3$]; $^{13}C$, δ 151.71 (OC), 138.51 (*o*-C), 128.64 (*m*-C), 126.77 (*p*-C), 35.45 [$C(CH_3)_3$], 32.49 [$C(CH_3)_3$] and 21.25 ($CH_3$); $^{27}Al$, δ 3.2 ($W_{\frac{1}{2}}$ 585 Hz).

(*Acetonitrile*)*tris*(2,6-*di*-tert-*butyl*-4-*methylphenoxo*)-*aluminium*(III) **9**. To [$Al(OR^1)_3$] (0.40 g, 0.58 mmol) was added hexane (30 $cm^3$) and MeCN (10 $cm^3$) resulting in a slightly yellowed slurry. After stirring for 12 h, the solvent was removed and the residue was recrystallised from pentane–toluene, yield *ca*. 90%, m.p. >250 °C (Found: C, 75.40; H, 10.30; N, 1.45. Calc. for $C_{47}H_{72}AlNO_3$: C, 77.75; H, 10.00; N, 1.95%), mass spectrum (EI, %): *m*/*z* 684 ($M^+ - MeCN$, 100%). NMR: $^1H$, δ 7.12 (6 H, s, $C_6H_2$) 2.32 (9 H, s, $CH_3C_6H_2$), 1.45 [54 H, s, $C(CH_3)_3$] and 0.81 (3 H, s, $CH_3CH$); $^{13}C$, δ 154.94 (OC), 138.42 (*o*-C), 126.34 (*m*-C), 125.82 (*p*-C), 118.79 (NCMe), 35.47 [$C(CH_3)$], 32.45 [$C(CH_3)_3$], 21.29 ($CH_3$) and 0.61 ($NCCH_3$).

*Tris*(2,6-*di*-tert-*butyl*-4-*methylphenoxo*)(*pyridine*)*aluminium*(III) **10**. To a sample of $[Al(OR^1)_3]$ (0.25 g, 0.37 mmol) in pentane (30 $cm^3$) was added an excess of pyridine (2 $cm^3$), and the resulting yellow solution stirred for 0.5 h. Removal of all volatiles led to the isolation of an off-white powder, which was recrystallised from pyridine, yield 90%; m.p. 135–139 °C (Found: C, 74.25; H, 9.35; N, 1.15. Calc. for $C_5H_{74}AlNO_3$: C, 78.60; H, 9.75; N, 1.85%); mass spectrum (EI, %): *m/z* 684 ($M^+$ − L, 100%). NMR: $^1H$, δ 8.30 [2 H, d, *J*(H–H) 5.5, *o*-CH], 7.08 (6 H, s, $C_6H_2$), 6.71 (2 H, m, *m*-CH), 6.39 [2 H, d, *J*(H–H) 6.9 Hz, *p*-CH], 2.28 (9 H, s, $CH_3$) and 1.43 [54 H, s, $C(CH_3)_3$].

*Tris*(2,6-*di*-tert-*butyl*-4-*methylphenoxo*)(*triphenylphosphine oxide*)*aluminium*(III) **11**. To $[Al(OR^1)_3]$ (0.50 g, 0.93 mmol) and $O{=}PPh_3$ (0.26 g, 0.93 mmol), was added pentane (20 $cm^3$) partially dissolving the reactants. Toluene (1–2 $cm^3$) was then added dropwise, while heating with a heat gun until complete dissolution was achieved. Slow cooling to room temperature, and then standing for 2 d resulted in crystals of the product, yield 85%; m.p. 192–197 °C (Found: C, 79.35; H, 8.45. Calc. for $C_{63}H_{84}AlO_4P$: C, 78.55; H, 8.80%). IR: 1591w, 1311w, 1262s, 1230s, 1223s, 1198m, 1143s, 1118s, 1089s, 1077m, 1027m, 998w, 977w, 935w, 888w, 868s, 847m, 802m, 776w, 769w, 756w, 746w, 721s, 695m, 622m, 616m, 545s and 536m $cm^{-1}$. NMR: $^1H$, δ 7.66–7.58 (6 H, m, *o*-CH), 7.14 (6 H, s, $C_6H_2$). 7.05–6.93 (9 H, m, *m*-, *p*-CH), 2.34 (9 H, s, $CH_3$) and 1.46 [54 H, s, $C(CH_3)_3$]; $^{13}C$, δ 155.89 (OC), 139.52 (*o*-C), 134.59 [d, *J*(P–C) 11, *p*-C], 133.68 [d, *J*(P–C) 10, *o*-C], 131.96 [d, *J*(P–C) 14, *m*-C], 126.85 (*m*-C), 126.79 [d, *J*(P–C) 113 Hz, PC], 125.20 (*p*-C), 36.48 [*C*($CH_3$)], 33.90 [C(*C*$H_3$)$_3$], and 21.15 ($CH_3$).

(4-tert-*Butylcyclohexanone*)*tris*(2,6-*di*-tert-*butyl*-4-*methylphenoxo*)*aluminium*(III) **12**. To $[Al(OR^1)_3]$ (0.30 g, 0.44 mmol) and 4-*tert*-butylcyclohexanone (0.068 g, 0.44 mmol) was added pentane (10 $cm^3$). The resulting yellow solution was stirred for 10 min, and then the solvent was removed under vacuum. Recrystallisation from pentane (20 $cm^3$) at −20 °C resulted in pale green crystals, yield *ca.* 80%; m.p. 113–114 °C (Found: C, 77.75; H, 10.05. Calc. for $C_{55}H_{87}AlO_4$: C, 78.70; H, 10.45%); mass spectrum (EI, %): *m/z* 684 ($M^+$ − $O{=}CC_5H_9Bu^t$-4, 100%). IR: 1678m, 1313w, 1266m, 1241s, 1224m, 1199w, 1181w, 1167w, 1156w, 1122w, 1077w, 1025w, 900m, 881m, 859m, 773w, 722m, 646w and 635w $cm^{-1}$. NMR: $^1H$, δ 7.12 (6 H, s, $C_6H_2$), 2.30 (9 H, s, $CH_3$), 1.51 [18 H, s, $C(CH_3)_3$] and 0.71 and 0.67 [9 H, s, $C(CH_3)_3$, ketone] $^{13}C$, δ 235.92 (OC, ketone), 155.98 (OC), 139.17 (*o*-C), 126.04 (*m*-C), 125.82 (*p*-C), 44.74 ($C^2$, ketone), 43.74 ($C^3$, ketone), 35.94 [*C*$(CH_3)_3$], 34.29 [*C*$(CH_3)_3$, ketone], 32.46 [C,(*C*$H_3$)$_3$], 32.28 [C(*C*$H_3$)$_3$, ketone], 27.28 ($C^4$, ketone) and 21.17 (*C*$H_3$).

*Bis*(2,6-*di*-tert-*butyl*-4-*methylphenoxo*)(2,4,6-*trichlorophenylamido*)*aluminium*(III) **13**. To $[AlH(OR^1)_2(OEt_2)]$ (1.00 g, 1.85 mmol) and $NH_2C_6H_2Cl_3$-2,4,6 (0.36 g, 1.83 mmol) was added pentane (40 $cm^3$) and the resulting light brown–red solution stirred for 4 h. After this time the volatiles were removed under vacuum. The residue was crystallised from pentane–toluene to give a white powder, yield >90%; m.p. 83–86 °C (Found: C, 63.20; H, 7.20; N, 2.50. Calc. for $C_{36}H_{49}AlCl_3NO_2$: C, 65.40; H, 7.45; N, 2.10%); mass spectrum (EI, %): *m/z* 661 ($M^+$). IR: 3339w, 1612w, 1586w, 1569w, 1559w, 1424s, 1365 (sh), 1294 (sh), 1266s, 1209w, 1170w, 1157w, 1125m, 1085w, 1053w, 1025w, 967m, 937m, 910m, 892w, 860m, 792m, 772w, 772m, 658w, 635w and 605w $cm^{-1}$. NMR: $^1H$, δ 7.15 (4 H, s, $C_6H_2$), 6.69 (2 H, s, $C_6H_2Cl_3$), 4.59 (1 H, s, NH), 2.24 (6 H, s, $CH_3$) and 1.48 [36 H, s, $C(CH_3)_3$]; $^{13}C$, δ 152.00 (OC), 142.91 (NC), 138.44 (*o*-C), 127.36 (*o*-C), 126.49 (*m*-C), 125.82 (*p*-C), 120.11 (*m*-C), 119.73 (*p*-C), 35.18 [*C*$(CH_3)_3$], 31.82 [C(*C*$H_3$)$_3$] and 21.33 ($CH_3$).

*Bis*(2,6-*di*-tert-*butyl*-4-*methylphenoxo*)(*diethyl ether*)(2,4,6-*trichlorophenylamido*)*aluminium*(III) **14**. The compound $[Al(OR^1)_2(NHC_6H_2Cl_3\text{-}2,4,6)]$ was recrystallised from a minimal amount of $Et_2O$ to afford white crystals of the diethyl ether adduct, yield (double crystallisation) *ca.* 29%; m.p. 69–72 °C (Found: C, 65.15; H, 8.35; N, 1.50. Calc. for $C_{40}H_{59}AlCl_3NO_3$: C, 65.35; H, 8.10. N, 1.90%); mass spectrum (EI, %): *m/z* 661 ($M^+$ − $Et_2O$). IR: 3690w, 3650m, 3502w, 3398m, 3340w, 1614w, 1569w, 1559w, 1424s, 1295m, 1265s, 1233s, 1215m, 1169m, 1157m, 1123m, 1087w, 1074w, 1069w, 1025w, 967m, 937m, 922w, 910m, 889m, 859m, 787m, 771m, 721m, 669w, 658w, 634m, 620w, 605w, 576w, 560w, 503w and 485w $cm^{-1}$. NMR: $^1H$, δ 7.14 (4 H, s, $C_6H_2$), 6.69 (2 H, s, $C_6H_2Cl_3$), 4.58 (1 H, s, NH), 3.25 [4 H, q, *J*(H–H) 7.0, $OCH_2$], 2.23 (6 H, s, $CH_3$), 1.47 [36 H, s, $C(CH_3)_3$] and 1.09 [6 H, t, *J*(H–H) 6.9 Hz, $OCH_2CH_3$]; $^{13}C$, δ 152.20 (OC), 143.01 (NC), 138.33 (*o*-C), 127.27 (*o*-C), 126.56 (*m*-C), 125.84 (*p*-C), 120.26 (*m*-C), 119.77 (*p*-C), 65.90 ($OCH_2$), 35.15 [*C*$(CH_3)_3$], 31.77 [C(*C*$H_3$)$_3$], 21.31 ($CH_3$) and 15.35 ($OCH_2$*C*$H_3$).

*Bis*(2,6-*di*-tert-*butyl*-4-*methylphenoxo*)(*pyridine*)(2,4,6-*trichlorophenylamido*)*aluminium*(III) **15**. To a pentane (30 $cm^3$) solution of $[Al(OR^1)_2(NHC_6H_2Cl_3\text{-}2,4,6)]$ (0.50 g, 0.68 mmol) was added pyridine (excess) *via* a syringe. After stirring for 1 h, the solvent and excess pyridine was removed *in vacuo*. Crystals suitable for X-ray diffraction could not be grown from a variety of solvents, yield *ca.* 90%. $^1H$ NMR: δ, 8.46 [2 H, d, *J*(H–H) 7.0 *o*-H, py], 7.21 (4 H, s, $C_6H_2$), 6.90 (2 H, s, *m*-H, amine), 6.63 (2 H, m, *m*-H, py), 6.25 [1 H, t, *J*(H–H) 7.0 Hz, *p*-H, py], 3.95 (1 H, s, NH), 2.31 (6 H, s, $CH_3$) and 1.54 [36 H, s, $C(CH_3)_3$].

*Bis*(2,6-*di*-tert-*butyl*-4-*methylphenoxo*)(3,5-*dimethylpyridine*)-(2,4,6-*trichlorophenylamido*)*aluminium*(III) **16**. To a pentane (30 $cm^3$) solution of $[Al(OR^1)_2(NHC_6H_2Cl_3\text{-}2,4,6)]$ (0.50 g, 0.68 mmol) was added 3,5$Me_2$-py (excess) *via* a syringe. After stirring for 1 h, the solvent and excess pyridine were removed *in vacuo*. Crystals suitable for X-ray diffraction could not be grown from a variety of solvents, yield *ca.* 90%. $^1H$ NMR: δ, 8.15 (2 H, s, *o*-H, py), 7.07 (4 H, s, $C_6H_2$), 6.45 (1 H, s, *p*-H, py), 5.07 (1 H, s, NH), 2.29 (6 H, s, $CH_3$), 1.53 (6 H, s, $CH_3$, py), 1.46 [36 H, s, $C(CH_3)_3$].

*Crystallography*.—Crystals of **1**, **3** and **8** were mounted directly onto the goniometer with silicon grease. X-Ray data were collected on a Nicolet R3m/V four-circle diffractometer equipped with an LT-1 low-temperature device. Data collection was controlled using the Nicolet P3 program, in a manner previously described.[8] A semi-empirical absorption correction and Lorentz and polarisation corrections were applied to all data. Use of the direct methods program XS[30] readily revealed the positions of the Al, O, N and the majority of the C atoms. Subsequent Fourier difference maps eventually revealed the position of all of the non-hydrogen atoms for all structures.

The solution for **1** revealed alternative positions shown for the Al, $NMe_3$ carbons and one of the aryloxide *tert*-butyl groups. These were initially included in the refinement such that equivalent atoms were treated with linked thermal parameters and the group occupancies were constrained to total 1. The latter converged at values of 0.55 and 0.45, and were subsequently fixed as such in subsequent refinements. The thermal parameters of the disordered atoms were then allowed to refine freely. After all of the non-hydrogen atoms were located and refined anisotropically, a difference map revealed some but not all of the hydrogen atom positions. It was possible to identify and successfully refine (*i.e.* with sensible $U_{iso}$ parameters and reasonable bond distances) four hydrogens, two attached to each aluminium. All 'organic' hydrogen atoms were placed in calculated positions $\{U_{iso}(H) = 1.2[U_{iso}(C)]$; $d$(C–H) 0.96 Å$\}$ for refinement. The methyl groups were refined as rigid bodies with free rotation about the N–C(methyl) and the C–C(methyl) bonds. All hydrogen atoms were fixed in the final refinement. Since standard deviations are meaningless for Al–H distances and X–Al–H angles when the H atoms are included as invariants and also when the Al centres are disordered, they have been omitted from the text and Table 1.

Despite the anisotropic refinement of all non-hydrogen atoms and the aluminium hydride (isotropic) the *R* factor for **3** remained high $R = 0.113$, $R' = 0.159$. In addition, the

**Table 8** Summary of X-ray diffraction data *

| Compound | [{AlH$_2$(OR$^1$)(NMe$_3$)}$_n$] **1** | [AlH(OR$^1$)$_2$(NH$_2$Bu$^t$)] **3** | [AlH(OR$^1$)$_2$(OEt$_2$)] **4** | [Al(OR$^1$)$_3$]·2CH$_2$Cl$_2$ **8** | [Al(OR$^1$)$_3${O=C(C$_5$H$_9$)-Bu$^t$-4}]·C$_5$H$_{12}$ **12** |
|---|---|---|---|---|---|
| Formula | $C_{18}H_{34}AlNO$ | $C_{34}H_{58}AlNO_2$ | $C_{34}H_{57}AlO_3$ | $C_{47}H_{73}AlCl_4O_3$ | $C_{60}H_{99}AlO_4$ |
| *M* | 307.4 | 539.8 | 540.8 | 912.8 | 911.44 |
| Crystal system | Monoclinic | Triclinic | Monoclinic | Triclinic | Monoclinic |
| Space group | $P2_1/n$ | $P\bar{1}$ | $P2_1/n$ | $P\bar{1}$ | $P2_1/c$ |
| $a$/Å | 9.423(5) | 9.946(5) | 12.427(5) | 12.903(9) | 11.738(1) |
| $b$/Å | 14.612(4) | 14.359(8) | 11.201(8) | 13.911(8) | 18.618(4) |
| $c$/Å | 15.033(4) | 14.921(9) | 24.866(9) | 16.201(9) | 26.953(5) |
| $\alpha$/° | | 118.38(6) | | 99.71(5) | |
| $\beta$/° | 107.79(3) | 100.52(6) | 102.64(3) | 103.16(5) | 97.29(1) |
| $\gamma$/° | | 92.91(4) | | 114.63(6) | |
| $U$/Å$^3$ | 1970.9(13) | 1819.89(10) | 3373(3) | 2457(3) | 5842(2) |
| $Z$ | 4 | 2 | 4 | 2 | 4 |
| $D_c$/g cm$^{-3}$ | 1.662 | 0.985 | 1.064 | 1.155 | 1.036 |
| $F$(000) | 3060 | 596 | 1182 | 1605 | 2016 |
| Crystal dimensions/mm | 0.09 × 0.08 × 0.11 | 0.1 × 0.3 × 0.5 | 0.25 × 0.32 × 0.62 | 0.41 × 0.42 × 0.38 | 0.40 × 0.42 × 0.38 |
| $T$/°C | −78 | −78 | 25 | −78 | 25 |
| 2θ limit/° | 4–55 | 4.0–35.0 | 4.0–22.0 | 4.0–40.0 | 2.0–40.0 |
| No. of collected data | 6678 | 5430 | 4600 | 6836 | 6016 |
| No. of unique data | 5721 | 4769 | 4382 | 6348 | 5677 |
| Observed data | 3586 ($\lvert F_o\rvert > 5.0\sigma\lvert F_o\rvert$) | 3256 ($\lvert F_o\rvert > 6.0\sigma\lvert F_o\rvert$) | 2539 ($\lvert F_o\rvert > 6.0\sigma\lvert F_o\rvert$) | 3758 ($\lvert F_o\rvert > 6.0\sigma\lvert F_o\rvert$) | 2171 ($\lvert F_o\rvert > 5.0\sigma\lvert F_o\rvert$) |
| $R$ | 0.089 | 0.113 | 0.045 | 0.083 | 0.0542 |
| $R'$ | 0.10 | 0.152 | 0.045 | 0.085 | 0.0681 |
| Largest difference peak/e Å$^{-3}$ | 1.57 | 2.04 | 0.184 | 1.11 | 0.43 |

* Details in common: Mo-Kα radiation (λ = 0.710 73 Å), graphite monochromator; weighting scheme $w^{-1} = \sigma^2(|F_o|) + x(|F_o|)^2$, $x$ = 0.0044 **1**, 0.0373 **3**, 0.0044, **4**, 0.001 **8** and 0.14 **12**; $R = \Sigma||F_o| - |F_c|/\Sigma|F_o|$, $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$.

**Table 9** Atomic coordinates ( × 10$^4$) for [AlH$_2$(OR$^1$)(NMe$_3$)] **1**

| Atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| Al(1a) | 7 213(3) | 848(2) | 8 752(2) |
| Al(1b) | 6 072(2) | 185(1) | 9 518(1) |
| O(1) | 5 409(3) | 1 140(2) | 8 776(2) |
| N(1) | 7 059(3) | −566(2) | 8 660(2) |
| C(1a) | 6 078(29) | −887(21) | 7 753(9) |
| C(1b) | 5 900(27) | −1 040(18) | 7 922(8) |
| C(2a) | 8 613(7) | −800(8) | 8 682(8) |
| C(2b) | 7 836(9) | −1 318(4) | 9 273(5) |
| C(3a) | 6 848(12) | −945(6) | 9 505(5) |
| C(3b) | 7 985(8) | 10(5) | 8 285(6) |
| C(4) | 4 428(3) | 1 821(2) | 8 769(2) |
| C(5) | 2 942(3) | 1 743(2) | 8 171(2) |
| C(6) | 1 895(3) | 2 382(2) | 8 259(2) |
| C(7) | 2 263(3) | 3 108(2) | 8 881(2) |
| C(8) | 3 742(4) | 3 212(2) | 9 392(2) |
| C(9) | 4 854(3) | 2 607(2) | 9 346(2) |
| C(10) | 2 464(4) | 1 000(2) | 7 406(2) |
| C(11) | 875(5) | 1 146(3) | 6 756(3) |
| C(12) | 3 489(4) | 1 038(2) | 6 788(2) |
| C(13) | 2 482(5) | 48(2) | 7 841(3) |
| C(14) | 1 097(5) | 3 775(3) | 8 971(3) |
| C(15) | 6 458(4) | 2 838(2) | 9 916(2) |
| C(16a) | 6 976(26) | 2 143(13) | 10 721(12) |
| C(16b) | 6 986(11) | 2 311(8) | 10 840(6) |
| C(17a) | 7 563(13) | 2 989(8) | 9 368(10) |
| C(17b) | 7 510(10) | 2 546(7) | 9 353(7) |
| C(18a) | 6 542(11) | 3 730(6) | 10 504(9) |
| C(18b) | 6 725(11) | 3 875(3) | 9 951(9) |

difference map for **3** showed a number of large peaks, with 1 < e Å$^{-3}$ < 6. Inclusion of these as carbon atoms resulted in a drastic decrease in the $R$ factor (to 0.075), however, they did not correlate to any chemically reasonable solution, and were therefore omitted in the final refinement. We propose that this electron density may be due to the presence of a non stoichiometric amount of uncomplexed NH$_2$Bu$^t$ in the crystal

**Table 10** Atomic coordinates ( × 10$^4$) for [AlH(OR$^1$)$_2$(NH$_2$Bu$^t$)] **3**

| Atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| Al | 2446(2) | 2 879(2) | 6 836(2) |
| O(1) | 745(5) | 2 393(4) | 6 112(4) |
| C(1) | −542(7) | 2 156(5) | 5 494(5) |
| C(2) | −796(8) | 2 427(6) | 4 682(6) |
| C(3) | −2162(8) | 2 227(6) | 4 144(6) |
| C(4) | −3247(8) | 1 780(6) | 4 319(6) |
| C(5) | −2959(9) | 1 463(6) | 5 054(6) |
| C(6) | −1622(8) | 1 641(6) | 5 667(6) |
| C(7) | 342(8) | 2 917(6) | 4 389(6) |
| C(8) | 1478(8) | 2 203(6) | 4 116(7) |
| C(9) | 950(8) | 4 052(6) | 5 272(6) |
| C(10) | −206(9) | 3 009(7) | 3 404(7) |
| C(11) | −4736(9) | 1 610(7) | 3 729(7) |
| C(12) | −1425(9) | 1 251(6) | 6 476(6) |
| C(13) | −2751(10) | 593(9) | 6 411(9) |
| C(14) | −293(9) | 500(6) | 6 279(6) |
| C(15) | −1022(10) | 2 222(7) | 7 594(6) |
| O(2) | 2949(5) | 4 238(4) | 7 563(4) |
| C(16) | 3247(8) | 5 307(5) | 7 866(6) |
| C(17) | 4353(8) | 5 709(6) | 7 648(6) |
| C(18) | 4609(9) | 6 815(6) | 7 969(7) |
| C(19) | 3733(8) | 7 496(6) | 8 505(6) |
| C(20) | 2679(8) | 7 102(6) | 8 741(6) |
| C(21) | 2367(8) | 6 024(6) | 8 456(6) |
| C(22) | 5400(8) | 5 005(7) | 7 052(7) |
| C(23) | 4656(9) | 4 200(7) | 5 929(7) |
| C(24) | 6602(9) | 5 689(7) | 7 023(8) |
| C(25) | 6051(8) | 4 425(8) | 7 621(8) |
| C(26) | 4008(11) | 8 684(6) | 8 821(8) |
| C(27) | 1189(8) | 5 664(6) | 8 785(6) |
| C(28) | 59(8) | 4 847(6) | 7 815(7) |
| C(29) | 1727(10) | 5 193(7) | 9 486(7) |
| C(30) | 446(10) | 6 601(7) | 9 428(7) |
| N(1) | 2370(7) | 2 481(6) | 7 948(6) |
| C(31) | 3504(10) | 2 207(7) | 8 548(7) |
| C(32) | 4009(23) | 1 317(16) | 7 805(13) |
| C(33) | 4599(17) | 3 014(15) | 9 074(16) |
| C(34) | 2956(13) | 1 974(12) | 9 287(11) |

**Table 11** Atomic coordinates for $[AlH(OR^1)_2(Et_2O)]$ **4**

| Atom | *x* | *y* | *z* | Atom | *x* | *y* | *z* |
|---|---|---|---|---|---|---|---|
| Al | 0.569 12(9) | 0.194 5(1) | 0.334 55(5) | C(34) | 0.556 4(4) | 0.006 3(5) | 0.207 7(2) |
| O(1) | 0.467 7(2) | 0.174 6(2) | 0.370 0(1) | C(121) | 0.471 2(3) | −0.082 7(4) | 0.400 1(2) |
| O(2) | 0.623 3(2) | 0.335 0(2) | 0.334 4(1) | C(122) | 0.450 7(4) | −0.206 6(4) | 0.423 5(2) |
| O(3) | 0.492 4(2) | 0.169 4(2) | 0.260 2(1) | C(123) | 0.580 8(3) | −0.039 6(4) | 0.435 9(2) |
| C(11) | 0.384 8(3) | 0.130 4(4) | 0.392 3(1) | C(124) | 0.478 5(4) | −0.102 8(4) | 0.340 6(2) |
| C(12) | 0.379 2(3) | 0.006 6(4) | 0.403 6(1) | C(141) | 0.102 1(4) | −0.008 2(5) | 0.446 1(2) |
| C(13) | 0.285 1(3) | −0.033 5(4) | 0.419 7(2) | C(161) | 0.310 5(3) | 0.345 7(4) | 0.398 6(2) |
| C(14) | 0.202 5(3) | 0.040 1(4) | 0.428 3(2) | C(162) | 0.423 6(5) | 0.397 4(5) | 0.422 8(2) |
| C(15) | 0.216 1(3) | 0.160 2(4) | 0.421 9(2) | C(163) | 0.228 8(5) | 0.410 8(5) | 0.426 2(2) |
| C(16) | 0.305 7(3) | 0.210 2(4) | 0.404 7(2) | C(164) | 0.277 4(4) | 0.376 4(5) | 0.337 5(2) |
| C(21) | 0.677 2(3) | 0.439 4(3) | 0.350 5(1) | C(221) | 0.805 5(3) | 0.333 0(4) | 0.433 8(2) |
| C(22) | 0.761 6(3) | 0.443 8(4) | 0.399 9(1) | C(222) | 0.717 4(4) | 0.276 2(4) | 0.459 7(2) |
| C(23) | 0.807 6(3) | 0.554 7(4) | 0.415 8(2) | C(223) | 0.903 1(4) | 0.361 5(4) | 0.482 5(2) |
| C(24) | 0.780 6(3) | 0.657 5(4) | 0.386 4(2) | C(224) | 0.851 9(4) | 0.244 4(4) | 0.397 7(2) |
| C(25) | 0.704 1(3) | 0.648 7(4) | 0.336 6(2) | C(241) | 0.833 0(4) | 0.776 3(4) | 0.405 7(2) |
| C(26) | 0.652 5(3) | 0.541 3(4) | 0.317 2(1) | C(261) | 0.573 5(3) | 0.539 5(4) | 0.260 4(2) |
| C(31) | 0.374 1(4) | 0.145 0(4) | 0.242 9(2) | C(262) | 0.562 6(4) | 0.661 7(4) | 0.231 8(2) |
| C(32) | 0.319 2(5) | 0.216 3(6) | 0.194 4(3) | C(263) | 0.617 1(4) | 0.452 7(5) | 0.222 5(2) |
| C(33) | 0.558 3(4) | 0.136 6(4) | 0.220 3(2) | C(264) | 0.458 1(4) | 0.504 3(5) | 0.265 2(2) |

**Table 12** Atomic coordinates ( × $10^4$) for $[Al(OR^1)_3]$ **8**

| Atom | *x* | *y* | *z* | Atom | *x* | *y* | *z* |
|---|---|---|---|---|---|---|---|
| Al | 476(2) | 3014(2) | −2487(1) | C(26) | 5629(9) | 7989(7) | −2493(6) |
| O(1) | −916(5) | 2667(4) | −3097(3) | C(27) | 3483(7) | 3831(7) | −3124(6) |
| C(1) | −2099(7) | 2286(6) | −3605(5) | C(28) | 3527(8) | 3273(8) | −2390(6) |
| C(2) | −2962(7) | 2189(6) | −3167(5) | C(29) | 2329(8) | 3060(7) | −3924(6) |
| C(3) | −4165(7) | 1774(6) | −3713(6) | C(30) | 4551(8) | 3961(8) | −3421(7) |
| C(4) | −4491(7) | 1522(6) | −4636(6) | O(3) | 727(5) | 2273(4) | −1851(3) |
| C(5) | −3629(7) | 1668(6) | −5007(5) | C(31) | 918(7) | 1639(6) | −1332(5) |
| C(6) | −2412(7) | 2048(6) | −4529(5) | C(32) | 1536(7) | 2136(6) | −402(5) |
| C(7) | −2628(8) | 2523(7) | −2148(5) | C(33) | 1712(8) | 1462(7) | 83(5) |
| C(8) | −2261(9) | 1739(7) | −1781(5) | C(34) | 1343(8) | 363(7) | −280(5) |
| C(9) | −1662(9) | 3707(7) | −1708(6) | C(35) | 745(7) | −103(6) | −1188(5) |
| C(10) | −3738(9) | 2417(9) | −1877(6) | C(36) | 516(6) | 500(6) | −1738(5) |
| C(11) | −5800(8) | 1104(8) | −5194(6) | C(37) | 1957(8) | 3349(7) | 56(5) |
| C(12) | −1498(8) | 2171(7) | −5032(5) | C(38) | 2934(8) | 4129(7) | −255(6) |
| C(13) | −2127(9) | 1815(9) | −6055(6) | C(39) | 878(8) | 3583(7) | −58(5) |
| C(14) | −495(8) | 3375(7) | −4750(6) | C(40) | 2579(10) | 3665(8) | 1080(5) |
| C(15) | −968(8) | 1395(7) | −4855(5) | C(41) | 1582(8) | −339(7) | 277(6) |
| O(2) | 1613(5) | 4125(4) | −2509(3) | C(42) | −114(8) | −64(6) | −2743(5) |
| C(16) | 2593(7) | 5065(6) | −2491(5) | C(43) | −1304(7) | −38(7) | −3065(5) |
| C(17) | 2643(7) | 6093(6) | −2209(5) | C(44) | −444(9) | −1293(6) | −2983(6) |
| C(18) | 3646(8) | 7017(7) | −2216(5) | C(45) | 721(8) | 482(7) | −3251(6) |
| C(19) | 4557(8) | 6965(7) | −2485(5) | Cl(1) | 7558(3) | 5818(2) | 6508(2) |
| C(20) | 4474(8) | 5913(7) | −2770(5) | Cl(2) | 6809(3) | 4307(3) | 4766(2) |
| C(21) | 3497(7) | 4946(6) | −2788(5) | C(46) | 7261(9) | 4507(7) | 5902(5) |
| C(22) | 1675(8) | 6261(7) | −1884(5) | Cl(3) | 6212(6) | 9708(3) | 1342(5) |
| C(23) | 1986(9) | 7477(7) | −1587(6) | Cl(4) | 5161(3) | 7696(4) | −92(2) |
| C(24) | 443(8) | 5675(7) | −2657(6) | C(47) | 6102(9) | 8453(8) | 941(7) |
| C(25) | 1567(8) | 5842(7) | −1081(5) | | | | |

lattice. Supporting evidence comes from the elemental analysis of this material which was consistently high in C, H and N. Although the structure refined to a chemically reasonable solution the *R* and weighted *R* factors remained high. However, since the bond lengths and angles and atom connectivity are entirely consistent with analogous structures, *i.e.*, **4**, and analytical, IR and NMR spectral characterisation, the solution is undoubtedly correct.

Compound **8** was successfully refined without difficulty. Neutral-atom scattering factors were taken from the usual source.[31] Refinement of positional and anisotropic thermal parameters led to convergence (see Table 8). Final atomic positional parameters for compounds **1**, **3** and **8** are given in Tables 9, 10 and 12 respectively.

Crystals of compounds **4** and **12** were sealed in glass capillaries under argon and mounted on the goniometer of an Enraf-Nonius CAD-4 automated diffractometer. Final lattice parameters, as determined from a least-squares fit of the setting angles of 25 accurately centred reflections are given in Table 8. Examination of the data, which were corrected for Lorentz and polarisation effects, but not for absorption, revealed the space group to be $P2_1/n$ for **4** and $P2_1/c$ **12**. Structure solution was accomplished readily by using the direct methods option of SHELX,[32] through which the bulk of the molecules were located. The remaining atomic coordinates were determined through the generation of Fourier difference maps using SHELX-76.[32]

Treatment of all non-hydrogen atoms in **4** with anisotropic thermal parameters permitted the location of the hydrogen attached to aluminium and some but not all the organic hydrogens. The latter were included in the final model with fixed thermal parameters and constrained to 'ride' upon the

**Table 13** Atomic coordinates of $[\mathrm{Al(OR^1)_3\{O{=}C(C_5H_9)Bu^t\text{-}4\}}]$ **12**

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Al | 0.613 2(2) | 0.052 2(1) | 0.182 70(8) |
| O(1) | 0.635 7(4) | −0.000 7(3) | 0.132 7(2) |
| O(2) | 0.487 5(4) | 0.022 8(3) | 0.202 1(2) |
| O(3) | 0.730 3(4) | 0.071 7(3) | 0.223 8(2) |
| O(4) | 0.575 1(4) | 0.140 5(3) | 0.154 7(2) |
| C(11) | 0.710 2(6) | −0.043 5(4) | 0.111 6(3) |
| C(12) | 0.794 2(6) | −0.013 7(4) | 0.082 5(3) |
| C(13) | 0.880 4(6) | −0.059 2(4) | 0.070 7(3) |
| C(14) | 0.887 6(6) | −0.128 4(4) | 0.082 0(3) |
| C(15) | 0.795 1(6) | −0.159 8(4) | 0.100 9(3) |
| C(16) | 0.702 5(6) | −0.119 6(4) | 0.114 3(3) |
| C(21) | 0.388 8(6) | 0.053 7(5) | 0.217 4(3) |
| C(22) | 0.295 9(6) | 0.073 3(4) | 0.182 7(3) |
| C(23) | 0.213 1(6) | 0.117 4(5) | 0.199 7(3) |
| C(24) | 0.217 8(7) | 0.136 6(5) | 0.248 2(3) |
| C(25) | 0.294 3(7) | 0.104 0(5) | 0.282 9(3) |
| C(26) | 0.380 9(6) | 0.059 3(5) | 0.269 7(3) |
| C(31) | 0.806 0(6) | 0.080 9(4) | 0.266 7(2) |
| C(32) | 0.811 3(6) | 0.144 8(4) | 0.293 1(3) |
| C(33) | 0.875 6(7) | 0.148 5(5) | 0.339 8(3) |
| C(34) | 0.939 6(7) | 0.092 0(5) | 0.360 0(3) |
| C(35) | 0.942 2(7) | 0.029 5(5) | 0.331 1(3) |
| C(36) | 0.878 5(6) | 0.023 9(4) | 0.284 3(3) |
| C(41) | 0.530 6(6) | 0.200 3(5) | 0.142 8(3) |
| C(42) | 0.571 7(8) | 0.243 7(5) | 0.101 2(3) |
| C(43) | 0.470 6(7) | 0.266 6(5) | 0.064 1(3) |
| C(44) | 0.379 8(7) | 0.307 6(5) | 0.089 2(3) |
| C(45) | 0.338 3(7) | 0.261 8(5) | 0.129 1(3) |
| C(46) | 0.437 7(6) | 0.233 6(5) | 0.167 0(3) |
| C(121) | 0.785 7(6) | 0.065 2(4) | 0.063 9(3) |
| C(122) | 0.861 3(7) | 0.078 2(5) | 0.022 6(3) |
| C(123) | 0.825 4(6) | 0.117 5(5) | 0.104 6(3) |
| C(124) | 0.661 4(7) | 0.081 0(5) | 0.040 5(3) |
| C(141) | 0.988 2(7) | −0.172 4(5) | 0.071 5(3) |
| C(161) | 0.590 8(6) | −0.158 6(5) | 0.122 7(3) |
| C(162) | 0.550 1(7) | −0.146 1(5) | 0.173 5(3) |
| C(163) | 0.500 7(7) | −0.133 3(5) | 0.080 6(3) |
| C(164) | 0.602 1(7) | −0.239 8(5) | 0.117 6(3) |
| C(221) | 0.273 9(6) | 0.041 4(4) | 0.129 5(3) |
| C(222) | 0.158 9(7) | 0.065 7(5) | 0.100 9(3) |
| C(223) | 0.360 1(7) | 0.057 4(5) | 0.094 2(3) |
| C(224) | 0.266 7(7) | −0.040 7(5) | 0.136 2(3) |
| C(241) | 0.124 4(8) | 0.186 6(6) | 0.264 3(4) |
| C(261) | 0.448 1(7) | 0.011 5(5) | 0.307 6(3) |
| C(262) | 0.424 9(9) | −0.066 3(7) | 0.294 6(4) |
| C(263) | 0.577 1(9) | 0.021 8(7) | 0.315 9(4) |
| C(264) | 0.409(1) | 0.021 3(7) | 0.360 8(4) |
| C(321) | 0.748 3(6) | 0.214 4(4) | 0.273 9(3) |
| C(322) | 0.620 9(7) | 0.205 5(5) | 0.273 7(3) |
| C(323) | 0.779 8(7) | 0.232 7(5) | 0.221 8(3) |
| C(324) | 0.786 2(8) | 0.279 7(6) | 0.306 4(4) |
| C(341) | 1.008 3(9) | 0.095 2(7) | 0.410 8(4) |
| C(361) | 0.897 9(6) | −0.045 7(4) | 0.252 9(3) |
| C(362) | 0.938 9(7) | −0.019 8(5) | 0.204 0(3) |
| C(363) | 0.790 0(7) | −0.089 5(5) | 0.244 9(3) |
| C(364) | 0.994 1(8) | −0.093 9(6) | 0.278 0(4) |
| C(441) | 0.278 2(8) | 0.341 7(6) | 0.051 0(4) |
| C(442) | 0.329(1) | 0.385 8(8) | 0.012 1(5) |
| C(443) | 0.201(1) | 0.384 2(7) | 0.079 2(4) |
| C(444) | 0.208(1) | 0.280 0(7) | 0.025 0(4) |
| C(501) | 0.858(1) | 0.148 6(8) | 0.589 8(5) |
| C(502) | 0.794(1) | 0.141(1) | 0.548 9(7) |
| C(503) | 0.823(1) | 0.196 6(8) | 0.513 6(5) |
| C(504) | 0.718(1) | 0.096 9(8) | 0.530 0(5) |
| C(505) | 0.755(1) | 0.195 8(9) | 0.468 2(6) |
| C(506) | 0.675(2) | 0.111(1) | 0.485 1(9) |
| C(507) | 0.666(2) | 0.142(1) | 0.449 7(9) |

appropriate atoms [*d*(C–H) 0.95 Å], while the hydrogen on aluminium was freely refined. Final residuals are *also* listed in Table 8 and final atomic positional parameters are given in Table 11.

In the case of **12** the refinement of aluminium and oxygen atoms with anisotropic thermal parameters, and all carbon atoms with isotropic thermal parameters, with hydrogen atoms included in the model in calculated positions, led to a chemically reasonable solution. However the difference map showed a number of large peaks. Inclusion of these as carbon atoms of pentane (the solvent of crystallisation) resulted in further reduction of the *R* and weighted *R* factors. Supporting evidence for the presence of a volatile solvent of crystallisation comes from the solvent dependent nature of the crystals; the crystals readily 'powder' under an inert atmosphere when removed from the supernatant thus requiring them to be handled in paraffin oil. However, as with the solution for **3**, the bond lengths and angles, and atom connectivity are self consistent with the spectroscopy and that of related structures.

Scattering factors were taken from ref. 31 Final atomic positional parameters are given in Table 13.

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

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