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FULL PAPER

A crowded lithium diaryloxo{tris(trimethylsilyl)methyl}aluminate and a bis(triarylsiloxo){tris(trimethylsilyl)methyl}alane

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The reaction of [Li(thf)$_2$AlH$_3${C(SiMe$_3$)$_3$}]$_2$ (**1**) with four equivalents of ArOH (Ar = C$_6$H$_3$Pr$^i_2$-2,6) yielded [Li(thf)(μ-OAr)$_2$AlH{C(SiMe$_3$)$_3$}] (**2**) (thf = tetrahydrofuran), which has a structure containing a four-membered LiO$_2$Al ring both in the crystal and in toluene solution. The corresponding reaction with ArOH (Ar = C$_6$H$_3$Bu$^t_2$-2,6) gave a mixture that could not be separated by fractional crystallisation. The reaction of **1** with Ph$_3$SiOH gave [Al(OSiPh$_3$)$_2${C(SiMe$_3$)$_3$}(thf)] (**3**), which was shown by an X-ray structure determination to be monomeric.

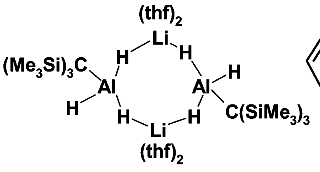
There is considerable interest in the chemistry of alkoxo- and alkoxo(alkyl)-alanes and aluminates bearing bulky groups because their structures provide insight into intermediates involved in the reduction of carbonyl compounds by aluminium hydrides,[1–4] the stereochemistry of the addition of organolithium reagents to carbonyl compounds,[2,5,6] and Ziegler–Natta catalysis.[7] The presence of the alkoxo groups has been shown to modify both the reactivity and selectivity of aluminium hydride reagents and a range of alkoxohydrido species has been detected in solution.[1,8] A number of lithium alkoxo- or aryloxo-aluminates containing four-membered LiO$_2$Al rings have been characterized in the solid state.[3,5,9–11]

However, it is not clear what factors determine whether species containing both lithium and aluminium are stable in solution or whether they separate to give a mixture of species, some of which contain only lithium and others only aluminium.

We have studied the reactions of the alkyltrihydroaluminate [Li(thf)$_2$AlH$_3${C(SiMe$_3$)$_3$}]$_2$ (**1**)[12] with alcohols,[9,10] aldehydes and ketones,[10] thiols and disulfides,[13] and aniline,[14] and have isolated a series of crowded functionalised tris(trimethylsilyl)methylaluminates. In most cases, all three Al–H bonds in the parent **1** are replaced by bonds between aluminium and a group X containing donor atoms such as oxygen, sulfur, or nitrogen, but in two cases only two Al–H bonds are replaced and alkylhydroaluminates containing larger groups X (X = NHPh or SBu^t) have been isolated.[13,14] In this article we describe the extension of this work to reactions of compound **1** with the bulky phenols ArOH (Ar = C$_6$H$_3$Pr$^i_2$-2,6 and C$_6$H$_3$Bu$^t_2$-2,6) and the silanol Ph$_3$SiOH, and bring together results from several of our previous papers. There are few structural data on (triorganosiloxo)organoalanes, even though these compounds have a number of applications as catalysts.[15]

Experimental

Air and moisture were excluded as far as possible from all manipulations by the use of flame-dried glassware, Schlenk techniques and Ar as blanket gas. NMR spectra from samples dissolved in benzene-d_6 or toluene-d_8 were recorded at 300.1 (^{1}H), 75.4 (^{13}C), 194.5 (^{7}Li), 130.4 (^{27}Al) and 99.4 MHz (^{29}Si). Chemical shifts are relative to SiMe$_4$ (H, C, and Si), aqueous LiCl or Al(NO$_3$)$_3$. IR spectra were recorded from Nujol mulls.



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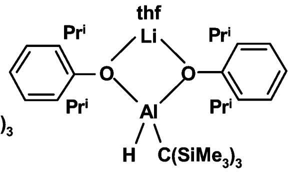

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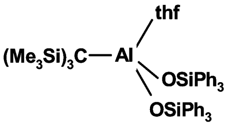

3

[Li(thf)Al(OC$_6$H$_3$Pr$^i_2$)$_2$H{C(SiMe$_3$)$_3$}] (2)

A solution of 2,6-diisopropylphenol (0.20 cm^3, 1.08 mmol) in toluene (20 cm^3) was added to a stirred solution of **1** (0.22 g, 0.27 mmol) in toluene (10 cm^3). Gas was evolved and the mixture was stirred at room temperature for 16 h then heated to 70 °C for 2 h and allowed to cool to room temperature. The solvent was removed under vacuum and the residue extracted into heptane. The extract was cooled to −30 °C to give colourless very air-sensitive crystals of **2** (0.28 g, 75%), mp 172 °C (found: C, 64.00, H, 10.28; C$_{38}$H$_{70}$AlLiO$_3$Si$_3$ requires C, 65.85, H, 10.18%). ν_{max}/cm^{-1} 1915w, 1814m (Al–H), 1591m, 1260s, 1196m, 1113m, 1044s, 1028s, 859s, 798s; δ_H (298 K) 0.43 (27 H, s, SiMe$_3$), 0.76 and 2.52 (4 H, thf), 1.1 and 1.4 (12 H, vb, Pr^i) [0.97, 1.07, 1.41 and 1.49 (6 H, d, $^3J_{HH}$ = 6.7 Hz) at 248 K], 3.9 and 4.5 (4 H, vb, Pr^i) [3.91 and 4.53 (2 H, sept, $^3J_{HH}$ = 6.7 Hz) at 248 K], 5.3 (1 H, vb, AlH), 6.94 (2 H, t, $^3J_{HH}$ = 7.6 Hz, *p*-H), 7,14 (4 H, s, *m*-H) [7.04 and 7.09 (2 H, dd, $^3J_{HH}$ = 7.6, $^4J_{HH}$ = 1.6 Hz) at 248 K]; δ_C (248 K) 5.8 ($^1J_{SiC}$ = 44.5 Hz, SiMe$_3$), 22.2, 22.7 and 26.0 (×2) (CH*Me*$_2$), 23.7 and 67.8 (thf), 25.8 and 26.7 ($^1J_{CH}$ = 123 Hz, *C*HMe$_2$), 121.4 (*p*-C), 123.6 and 124.7 (*m*-C), 137.4 and 138.8 (*o*-C), 151.5 (*i*-C); δ_{Li} (258 K) 0.24; δ_{Al} (298 K) 108 ($\Delta\nu_{1/2}$ *ca.* 5 kHz); δ_{Si} (298 K) −4.2. The spectra showed that **2** was essentially free from impurities, despite the low C analysis.

Reactions of **1** with two equivalents of ArOH gave a complex mixture showing eight signals in the SiMe$_3$ region of the NMR

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spectrum, including one from **2**. The product from the reaction with six equivalents of ArOH gave a mixture showing five $SiMe_3$ signals; a few crystals that appeared to be of LiOAr were obtained but no attempt was made to isolate other products.

Reaction of 1 with 2,6-$Bu^t_2C_6H_3OH$

A solution of 2,6-di-t-butylphenol (0.16 g, 0.77 mmol) in toluene (5 cm^3) was slowly added to a stirred solution of **1** (0.32 g, 0.39 mmol) in toluene (20 cm^3) at −70 °C. The mixture was stirred at −70 °C for 1 h, then the solvent was removed under vacuum to give a sticky white solid. This was stirred with heptane (10 cm^3) and the mixture filtered. The filtrate was cooled to −30 °C to give as major product a colourless crystalline solid with a ^1H NMR spectrum[3] and unit cell dimensions[16] identical with those of $[LiOC_6H_3Bu^t_2{\cdot}thf]$ made independently from ArOH and $LiBu^n$. A second crop of crystals was identical. The third crop, consisting of only a few crystals, was an unidentified product with δ_H 0.40 ($SiMe_3$), 1.51 (Bu^t), 6.85 (m) and 7.25 (d, Ar). $[LiOC_6H_3Bu^t_2{\cdot}thf]$ was similarly identified as a product from the reaction between **1** and four equivalents of ArOH.

$[Al(OSiPh_3)_2\{C(SiMe_3)_3\}(thf)]$ (3)

A solution of Ph_3SiOH (0.48 g, 1.74 mmol) in toluene (10 cm^3) was added dropwise to a stirred solution of **1** (0.24 g, 0.29 mmol) in toluene (20 cm^3) at 0 °C. Gas was evolved. The mixture was allowed to warm to room temperature and stirred for 18 h, and the suspended white solid was filtered off. The solvent was removed from the filtrate and the white solid residue recrystallised from a 1 : 1 heptane–toluene mixture to give colourless crystals of **2** (0.50 g, 98%), mp 202 °C (Found: C, 67.63; H, 7.54. $C_{50}H_{65}AlO_3Si_5$ requires C, 68.13; H, 7.43%). ν_{max}/cm^{-1} 1962m, 1901m, 1828m, 1663w, 1588m, 1567w, 1428m, 1298m, 1250s, 1187m, 1157w, 1111s, 1056s, 1033s, 1016s, 938w, 917w, 850s bd, 741m, 704m, 664m, 614w; δ_H (298 K) 0.27 (27 H, s, $SiMe_3$), 0.88 and 3.97 (4 H, thf), 7.11 (18 H, *m*- and *p*-C), 7.87 (12 H, *o*-H); δ_C 6.8 ($SiMe_3$), 24.2 and 73.9 (thf), 127.7 (*m*-C), 129.5 (*p*-C), 136.8 (*o*-C), 138.4 (*i*-C); δ_{Si} −25.1 ($SiPh_3$), −3.9 ($SiMe_3$); the ^{27}Al signal was not observed and therefore assumed to be very broad; *m*/*z* 793 (6, M–Me–thf), 607 (15), 217 (90), 129 (50), 92 (70), 71 (80), 42 (100).

Crystallography

Crystal data: for **2**: $M = 693.1$; orthorhombic, space group *Pbca* (no. 61), $a = 19.071(4)$, $b = 20.379(8)$, $c = 22.142(6)$ Å; $U = 8605(4)$ Å^3; $Z = 8$; $\mu = 0.16$ mm^{-1}; 5963 unique reflections, 3586 with $I > 2\sigma(I)$, R_1, $wR_2 = 0.081$, 0.207 [$I > 2\sigma(I)$] and 0.138, 0.244 (all data). For **3**: $M = 881.5$; monoclinic, space group $P2_1/c$ (no. 14), $a = 9.596(2)$, $b = 21.418(5)$, $c = 24.212(9)$ Å, $\beta = 101.16(2)°$; $U = 4882(2)$ Å^3; $Z = 4$; $\mu = 0.20$ mm^{-1}; 9111 reflections, 8576 unique [$R_{int} = 0.046$], 5354 with $I > 2\sigma(I)$, R_1, $wR_2 = 0.061$, 0.112 [$I > 2\sigma(I)$] and 0.117, 0.133 (all data).

Data were collected from a CAD4 diffractometer and structures were refined by full matrix least squares refinement (SHELXL-97)[17] with most (**2**) or all (**3**) non-H atoms anisotropic and H atoms included in riding mode. For **2**, the molecule was disordered, with an alternative low occupancy Al site on the opposite side of the LiO_2 plane, associated with a different orientation of the $C(SiMe_3)_3$ group sharing a common C1 position. The alternative orientation was further disordered with two sets of Si positions. The C atoms were located only for the major occupancy $C(SiMe_3)_3$ group, and the hydrogen attached to Al was fixed at a position obtained from a difference map. The lower occupancy Al and Si sites were left isotropic.

CCDC reference numbers 189680 and 189681.

See http://www.rsc.org/suppdata/dt/b2/b206770f/ for crystallographic data in CIF or other electronic format.

Results and discussion

The reaction between the compound **1** and four equivalents of 2,6-$Pr^i_2C_6H_3OH$ (ArOH) gave in good yield the novel alkylbis(aryloxy)hydridoaluminate $[Li(thf)Al(OAr)_2H\{C(SiMe_3)_3\}]$ **2**, analogous to the alkanethiolato compound $[Li(thf)Al(SBu^t)_2H\{C(SiMe_3)_3\}]$ previously described.[13] The molecular structure is shown in Fig. 1. The LiO_2Al ring has a fold angle of 15° across the O1 ··· O2 vector with the $C(SiMe_3)_3$ group on the less crowded convex side and the thf and the hydrogen attached to aluminium on the concave side of the ring. In the crystal there is a small amount of another conformer with the hydrogen and $C(SiMe_3)_3$ group attached to aluminium interchanged, but the conformers pack in a disordered fashion leaving the aryloxo groups well-defined. The bond lengths and angles for the major conformation are given in Table 1. The corresponding bond lengths on either side of a plane through Al and Li and perpendicular to the OLiO and OAlO planes are not significantly different but the molecule as a whole has no symmetry since the two aryl groups are not quite equally twisted about the C–O bonds. The Li–O(Ar) distances (mean 1.885 Å) are only just outside and the Al–O distances (mean 1.804 Å) are within the range of values previously found in compounds with LiO_2Al rings having three-coordinate Li and four-coordinate Al [Li–O 1.910(8) to 1.97(2) Å; Al–O 1.786(1) to 1.808(2) Å].[3,9,18] The differences between the Li–O and Al–O

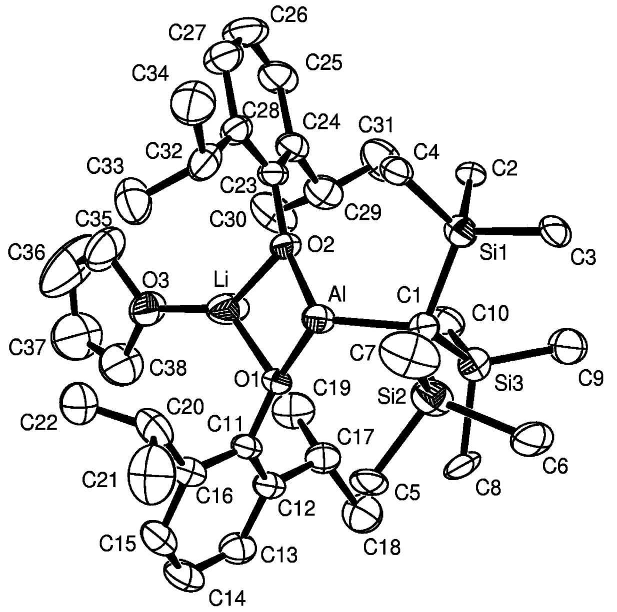


Fig. 1 Molecular structure of the predominant conformer of $[Li(thf)(\mu\text{-}OC_6H_3Pr^i_2\text{-}2,6)_2AlH\{C(SiMe_3)_3\}]$ (**2**).

Table 1 Bond lengths (Å) and angles (°) for $[Li(thf)(\mu\text{-}OC_6H_3Pr^i_2\text{-}2,6)_2AlH\{C(SiMe_3)_3\}]$ (**2**)

Al–O1,2	1.804(4)[a]	O1–Al–O2	88.24(17)
Al–C1	2.005(6)	O1–Al–C	120.9(2)
Li–O1,2	1.885(11)[a]	O2–Al–C	121.0(2)
Li–O3	1.832(11)	O1–Li–O2	83.6(4)
O–C(Ar)	1.375(6)[a]	O1–Li–O3	132.4(4)
Al ··· Li	2.677(11)	O2–Li–O3	140.1(6)
Li ··· C29[b]	3.36	Si–C1–Si	108.9(3)–112.7(3)
Si–C1	1.885(6)[a]	Me–Si–Me	102.5(3)–107.7(3)
Si–Me	1.875(6)[a]	Li–O–Al	93.0(3)[a]
C–O–Al	148.4(3), 150.2(3)		
C–O–Li	110.6(4), 114.6(4)		

[a] Mean; no individual value (standard deviation in parentheses) differs significantly. [b] Others are Li ··· C20, 3.61; Li ··· C17, 3.71; Li ··· C32, 3.96 Å.

bond distances in such compounds vary from 0.11 to 0.17 Å, and probably reflect differences in the crowding around the metal centres; the difference between the Li–O and Al–O bond distances in **2** (0.08 Å) is smaller but it is intermediate between the difference in the widely used ionic radii (0.2 Å) and the difference in the covalent radii (0.04 Å).[19] The short Li–O(thf) distance [1.832(11) Å] in **2** (*cf.* 1.897(4) to 1.976(8) Å in the previously described compounds) may be attributed to strong electron-withdrawal by the aryl groups, as there is also a short bond [1.822(7) Å] in [Li(thf)V($OC_6H_3Pr^i_2$-2,6)$_4$].[20] The Li–OEt_2 bond in [Li(OEt_2)AlH($OC_6H_3Pr^i_2$-2,6)$_3$] is longer [1.892(4) Å], but this may reflect the larger size of Et_2O than of thf. The aryloxo groups lean away from the bulky alkyl group as do the alkoxo groups in [Li(thf)$_n$Al(OR)$_3${C($SiMe_3$)$_3$}] (n = 1, R = Bu^t and n = 2, R = Et).[10] The Al–C, Si–C1 and Si–Me bond lengths are all normal.

In order to determine whether the structure found in the crystal is also present in solution we recorded a range of NMR spectra. In the ^1H and ^{13}C spectra of samples at room temperature the peaks in the aromatic (*meta*-proton) and isopropyl regions were broad, suggesting that within each set protons were undergoing chemical exchange on the NMR timescale between alternative sites. It was clear from spectra of samples at 248 K that (i) within the isopropyl groups there were four distinct methyl as well as two distinct methine environments and (ii) there were two distinct *meta*-proton environments but only one *para*-. Selective decoupling experiments show that the CH resonance at δ 4.53 is associated with the CH_3 resonances at δ 1.07 and 1.49, so that these three resonances are from one isopropyl group, and saturation transfer measurements show that the signal at δ 1.49 is from protons that are exchanging with those giving the signal at δ 0.97, *i.e.* protons from a different isopropyl group. These NMR data indicate that at 248 K the two aryloxo groups are equivalent but that rotation about the O–C bond is restricted so that the isopropyl groups on the convex and concave sides of the LiO_2Al ring are different. The $^6Li\{^1H\}$ nuclear Overhauser spectra[21] for **2** show that the low frequency septet at δ 3.91 is associated with protons, attached to C17 and C29 (Fig. 1), that are slightly nearer to the lithium and thf (mean Li ··· C 3.53 Å). than those, attached to C20 and C32, giving the high frequency septet (mean Li ··· C 3.78 Å). An alternative explanation is that the exchange between isopropyl groups on opposite sides of the shallow LiO_2Al ring involves Al–O bond opening and recombination to give the minor conformer detected by crystallography, followed by ring inversion. Both rotation about O–C bonds and ring opening (the latter having the higher activation energy) have been postulated to account for exchange processes in solutions of [Al(OPr^i)(acac)$_2$]$_2$.[22] The value of $\Delta G^\ddagger$ calculated from the coalescence temperature (315 K) of the methine signal of the isopropyl group in **2** is 60.4 kJ mol^{-1}.

An attempt to prepare the analogue of **2** with Ar = $C_6H_3Bu^t_2$-2,6 at room temperature gave a mixture that could not be separated by fractional crystallisation. One of the components appeared to be [LiOAr(thf)], identified by comparison of its NMR spectrum[3] and unit cell dimensions[16] with those of an authentic sample, but a pure sample of the aluminium-containing product could not be obtained. Even with a **1** : ArOH mole ratio of 1 : 2, [LiOAr(thf)] was the only isolable product. [The lithium aryloxides LiOAr or LiOAr′ (Ar′ = $C_6H_2Bu^t_2$-2,6-Me-4) have been reported as the major products from the reaction between bulky phenols and $LiAlH_4$.[2,3]] The results with ArOH suggested, however, that the reaction of **1** with bulky phenols could, under certain circumstances, give mixtures from which two products could be separated, one containing the lithium and the other the aluminium.

Such separation was realised when **1** was treated with triphenylsilanol (6 equiv.) to give an almost quantitative yield of crystalline [Al($OSiPh_3$)$_2${C($SiMe_3$)$_3$}(thf)] (**3**) in a form suitable for structural characterization. The molecule is shown in Fig. 2.

Table 2 Bond lengths (Å) and angles (°) for Al($OSiPh_3$)$_2$C($SiMe_3$)$_3$·thf (**3**)

Al–O1,2	1.726(3)[a]	C–Al–O2	115.52(15)
Al–O3	1.927(3)	C–Al–O3	110.00(14)
Al–C	1.998(4)	O1–Al–O2	112.37(13)
Si–C1	1.894(4)[a]	O2–Al–O3	99.13(13)
Si–Me	1.880(4)[a]	O1–Al–O3	100.27(13)
Si–O	1.616(3)[a]	Al–O1–Si4	163.71(18)
Si–Ph	1.877(4)[a]	Al–O2–Si5	170.42(18)
		O–Si–Ph	111.0[b]
C–Al–O1	116.78(15)	Si–C–Si	109.61(19)[a]
		Me–Si–Me	105.0(2)[a]

[a] Mean; no individual value (standard deviation in parentheses) differs significantly. [b] Mean; range from 109.51 (17) to 112.64(16)°.

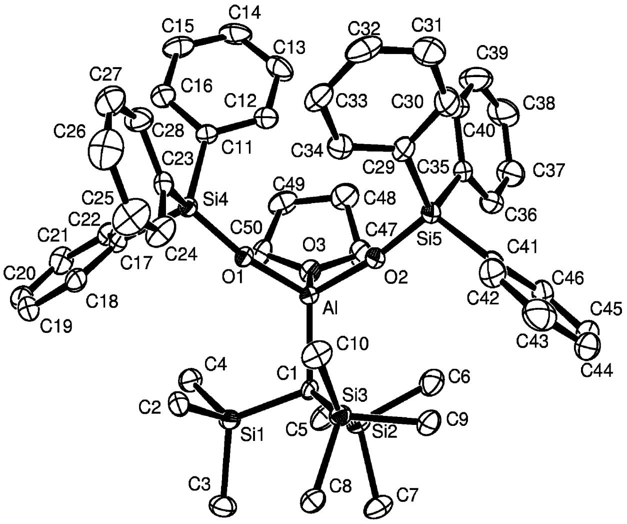


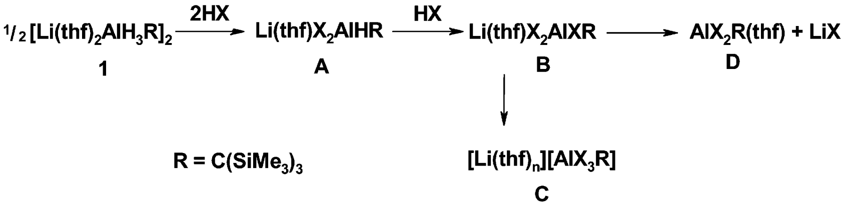
Fig. 2 Molecular structure of [Al($OSiPh_3$)$_2$C($SiMe_3$)$_3$(thf)] (**3**).

The coordination at aluminium is that of a distorted tetrahedron with Al–OSi distances [mean 1.726(3) Å, Table 2] somewhat greater than those found for similar compounds, *e.g.* [Al($OSiPh_3$)$_2$(acac)] [1.680(4) and 1.700(4) Å],[22] [Al($OSiPh_3$)$_3$(thf)] (**4**) [1.696(4) to 1.709(4) Å] or Al($OSiPh_3$)$_3$(H_2O)(thf)$_2$ (**5**) [1.708(5) Å],[23] and much longer than that in the solvent-free compound Al($OC_6H_2Bu^t_2$-2,6-Me-4)$_3$ [1.648(7) Å].[24] The Al–O(thf) distance in **3** [1.927(3) Å] is significantly longer than the corresponding distances in **4** [1.861(5) Å], **5** [1.83(1) Å to H_2O], and the dihalides [AlX_2{C($SiMe_3$)$_3$}(thf)] [X = Cl, 1.883(2),[25] Br 1.881(6) or I 1.886(4) Å [14,25]], indicating that the thf is held more weakly than in these related compounds. [It was, however, not removed when **3** was heated to 150 °C for 6 h.] The crowding around aluminium in **3** is reflected in the wide Al–O–Si angles [163.7(2) and 170.4(2)°] (*cf.* 149.7(3) to 157.3(3)° in **4** and 160.4(3)° in **5**); the angles involving the Al–thf bonds are significantly less than the tetrahedral value. Crowding around the carbon of the C($SiMe_3$)$_3$ group is shown by the fact that the Si–C–Si angles are close to the tetrahedral value. Widening to alleviate intraligand strain is prevented.[26] The Al–O–Si angles in **3**, **4** and **5** become wider as the length of the Al–O bond increases.

We have found no evidence for cleavage of the Al–C bonds in **2** or **3** by the use of an excess of the reagents ArOH or Ph_3SiOH, suggesting that the metal centre is effectively protected from attack. In contrast, reaction of [($C_6H_2Bu^t_3$-2,4,6)AlH_2]$_2$ with $Ph_2Si(OH)_2$ yields mainly $C_6H_3Bu^t_3$,[27] indicating that only slightly less well protected centres are vulnerable.

The reactions between the lithium {tris(trimethylsilyl)-methyl} trihydroaluminate **1** and the compounds HX (X = halogen, OR, SR or NHPh) are summarised in Scheme 1.

When X is large, *e.g.* $OC_6H_3Pr^i_2$, SBu^t [13] or NHPh,[14] the reaction can be halted at the alkylhydridoaluminate stage (**A**) and,



Scheme 1

in the case of **2**, the crowding is shown by the crystal structure and the restricted rotation about C–O bonds detected by variable temperature NMR data. When X is a small alkoxo or alkanethiolato group, there is no barrier to attack by the third equivalent of HX but the reaction stops at the alkylaluminate stage to give an associated ion pair (**B**).[9,10,13] When X = F, a tetramer $[Li(thf)AlF_3R]_4$ is formed[9] and when X = OMe[10] or NHPh (with an excess of HX under forcing conditions[14]), products containing separated ion pairs (**C**) can be obtained. Elimination of LiX from **B** gives the complex **D**. This elimination is achieved cleanly when X is Cl, Br, or I,[14] probably because of the low solubility of LiX in hydrocarbons. When X contains a lipophilic organic group, the elimination, which relieves crowding in the species **B**, depends critically on the relative solubilities of LiX and $AlRX_2$. It is not achieved cleanly when X = $OC_6H_3Bu^t_2$ but when X = $OSiPh_3$ the compound **3** is formed quantitatively. The size of the $OSiPh_3$ group is not quite enough to squeeze out the thf, originally present in **1**, to give a compound like $AlMe(OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4)_2$ containing three-coordinate aluminium.[5] Attempts to prepare compounds of type **A** when X is small have resulted in complex mixtures containing products **B**.[10] This indicates that in the absence of significant steric hindrance the second and third Al–H bonds in **1** are more reactive than the first. The increasing reactivity of Al–H bonds with increasing substitution has also been observed in the preparation of $[AlH(OC_6H_3Pr^i_2\text{-}2,6)_2(thf)_2]$.[28]

Acknowledgements

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References

1 (*a*) J. Málek, *Org. React.*, 1985, **34**, 1; (*b*) J. Seyden-Penne, *Reductions by the Alumino- and Borohydrides in Organic Synthesis*, VCH, New York, 1991; (*c*) J. Málek, *Org. React.*, 1988, **36**, 249.

2 M. D. Healy, M. B. Power and A. R. Barron, *Coord. Chem. Rev.*, 1994, **130**, 63.

3 H. Nöth, A. Schlegel, J. Knizek, I. Krossing, W. Ponikwar and T. Seifert, *Chem. Eur. J.*, 1998, **4**, 2191.

4 H. Nöth, A. Schlegel, J. Knizek and H. Schwenk, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2640.

5 W. Clegg, E. Lamb, S. T. Liddle, R. Snaith and A. E. H. Wheatley, *J. Organomet. Chem.*, 1999, **573**, 305 and references therein.

6 S. Saito and H. Yamamoto, *Chem. Commun.*, 1997, 1585.

7 A. P. Shreve, R. Mulhaupt, W. Fultz, J. Calabrese, W. Robbins and S. D. Ittel, *Organometallics*, 1988, **7**, 409.

8 (*a*) O. Štrouf, B. Časenský and V. Kubánek, *J. Organomet. Chem. Libr.*, 1985, **15**, 5; (*b*) Z. Černý, J. Fusek, J. Macháček, O. Kříž and B. Časenský, *J. Organomet. Chem.*, 1996, **516**, 115.

9 A. G. Avent, W.-Y. Chen, C. Eaborn, I. B. Gorrell, P. B. Hitchcock and J. D. Smith, *Organometallics*, 1996, **15**, 4343.

10 W.-Y. Chen, C. Eaborn, I. B. Gorrell, P. B. Hitchcock, M. Hopman and J. D. Smith, *J. Chem. Soc., Dalton Trans.*, 1997, 4689.

11 (*a*) J. Pauls and B. Neumüller, *Z. Anorg. Allg. Chem.*, 2000, **626**, 270; (*b*) H. Nöth, A. Schlegel and M. Suter, *J. Organomet. Chem.*, 2001, **621**, 231; (*c*) S. M. Ivanova, B. G. Nolan, Y. Kobayashi, S. M. Miller, O. P. Anderson and S. H. Strauss, *Chem. Eur. J.*, 2001, **7**, 503; (*d*) T. J. Barbarich, S. M. Miller, O. P. Anderson and S. H. Strauss, *J. Mol. Catal. A: Chem.*, 1998, **128**, 289; (*e*) J. A. Francis, S. B. Bott and A. R. Barron, *J. Organomet. Chem.*, 2000, **597**, 29; (*f*) H. Nöth, A. Schlegel and S. R. Lima, *Z. Anorg. Allg. Chem.*, 2001, **627**, 1793; (*g*) J. Pauls and B. Neumüller, *Z. Anorg. Allg. Chem.*, 2001, **627**, 2127.

12 C. Eaborn, I. B. Gorrell, P. B. Hitchcock, J. D. Smith and K. Tavakkoli, *Organometallics*, 1994, **13**, 4143.

13 W.-Y. Chen, C. Eaborn, I. B. Gorrell, P. B. Hitchcock and J. D. Smith, *J. Chem. Soc., Dalton Trans.*, 2000, 2313.

14 S. S. Al-Juaid, C. Eaborn, I. B. Gorrell, S. A. Hawkes, P. B. Hitchcock and J. D. Smith, *J. Chem. Soc., Dalton Trans.*, 1998, 2411.

15 R. Mulhaupt, J. Calabrese and S. D. Ittel, *Organometallics*, 1991, **10**, 3403.

16 J. C. Huffman, R. L. Geerts and K. G. Caulton, *J. Crystallogr. Spectrosc. Res.*, 1984, **14**, 541.

17 G. M. Sheldrick, SHELXL 97, University of Göttingen, Germany, 1997.

18 M. B. Power, S. G. Bott, J. L. Atwood and A. R. Barron, *J. Am. Chem. Soc.*, 1990, **112**, 3446.

19 J. E. Huheey, E. A. Keiter and R. L. Keiter, *Inorganic Chemistry*, HarperCollins, New York, 4th edn., 1993, p. 292.

20 W. C. A. Wilisch, M. J. Scott and W. H. Armstrong, *Inorg. Chem.*, 1988, **27**, 4333.

21 M. M. Andrianarison, A. G. Avent, M. C. Ellerby, I. B. Gorrell, P. B. Hitchcock, J. D. Smith and D. R. Stanley, *J. Chem. Soc., Dalton Trans.*, 1998, 249.

22 J. H. Wengrovius, M. F. Garbauskas, E. A. Williams, R. C. Going, P. E. Donahue and J. F. Smith, *J. Am. Chem. Soc.*, 1986, **108**, 982.

23 A. W. Apblett, A. C. Warren and A. R. Barron, *Can. J. Chem.*, 1992, **70**, 771.

24 M. D. Healy and A. R. Barron, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 921.

25 C. Schnitter, K. Klimek, H. W. Roesky, T. Albers, H.-G. Schmidt, C. Röpken and E. Parisini, *Organometallics*, 1998, **17**, 2249.

26 (*a*) P. T. Brain, M. Mehta, D. W. H. Rankin, H. E. Robertson, C. Eaborn, J. D. Smith and A. D. Webb, *J. Chem. Soc., Dalton Trans.*, 1995, 349; (*b*) C. A. Morrison, D. W. H. Rankin, H. E. Robertson, C. Eaborn, A. Farook, P. B. Hitchcock and J. D. Smith, *J. Chem. Soc., Dalton Trans.*, 2000, 4312.

27 R. J. Wehmschulte and P. P. Power, *Polyhedron*, 2000, **19**, 1649.

28 J. P. Campbell and W. L. Gladfelter, *Inorg. Chem.*, 1997, **36**, 4094.