DALTON
FULL PAPER

Syntheses and crystal structures of some lithium di- and tri-(thiolato)[tris(trimethylsilyl)methyl]aluminates

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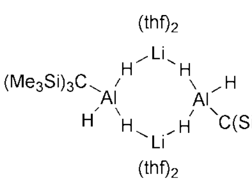
Received 29th March 2000, Accepted 31st May 2000
Published on the Web 22nd June 2000

The first organodi- and organotri-(thiolato)aluminates have been prepared and structurally characterised. They have been obtained by the reactions of $[Li(thf)_2\{AlH_3[C(SiMe_3)_3]\}]_2$ **1** (thf = tetrahydrofuran) with disulfides R_2S_2 (R = Me, Et or Ph) or thiols RSH (R = Pr^i, Bu^t or Ph). The structure of the methyl compound $[Li(thf)_2\{Al[C(SiMe_3)_3](SMe)_3\}]$ **2** has been determined by X-ray crystallography and shown to comprise lithium organotri(thiolato)aluminates each containing a folded four-membered LiS_2Al ring. NMR spectroscopy indicates that the Et, Pr^i and Ph derivatives have similar structures in solution. Treatment of compound **1** with a three-fold excess of Bu^{t}SH led to the replacement of only two of the available Al–H bonds and formation of $[Li(thf)\{AlH[C(SiMe_3)_3](SBu^t)_2\}]$ **6**, which contains an almost planar four-membered LiS_2Al ring. The derivatives $[Li(tmen)_2][Al\{C(SiMe_3)_3\}(SR)_3]$ (R = Bu^t or Ph) have been made by treatment of $[Li(tmen)_2][AlH_3\{C(SiMe_3)_3\}]$ **9** (tmen = *N*,*N*,*N*′,*N*′-tetramethylethane-1,2-diamine) with RSH, and the Bu^t derivative has been shown to crystallise in a lattice containing separated $[Li(tmen)_2]$ cations and $[Al\{C(SiMe_3)_3\}(SBu^t)_3]$ anions.

Lithium aluminium hydride and related compounds obtained by replacement of one or more hydrogen atoms by alkoxy or alkyl groups are widely used as reducing agents in organic synthesis. Some of the most important applications are in the reduction of carbonyl compounds; the intermediates are thought to be alkoxoaluminates of the form $LiAlH_n(OR)_{4-n}$ (n = 0–3),[1] but it is not easy to isolate and characterise them. With this background in mind we recently reported the synthesis and structures of a series of lithium trialkoxoaluminates $[Li(thf)_n\{Al[C(SiMe_3)_3](OR)_3\}]$ (n = 1, R = Me, Pr^i, Bu^t, CH_2Ph or $CHPh_2$; n = 2, R = Et or Ph; n = 4, R = Me), obtained by reaction of $[Li(thf)_2\{AlH_3[C(SiMe_3)_3]\}]_2$ **1**,[2] with alcohols, aldehydes and ketones.[3,4] The introduction of the bulky organic group greatly facilitates the isolation of stable species which may be structurally similar to the intermediates in the reduction process.



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Since thiolato groups are much softer than alkoxo groups and since the tendency of sulfur to adopt a more pyramidal coordination than oxygen should have a significant effect on the configuration of LiS_2Al rings we considered it worthwhile to extend our previous work by studying the reactions of the organotrihydroaluminate **1** with diorganodisulfides or thiols. We expected that these would give a class of compounds that have not previously been studied, *viz.* organotri(thiolato)-aluminates, related to the intermediates in the reduction of disulfides and thiocarbonyls by $LiAlH_4$.[5–7] Good yields of the organotri(thiolato)aluminates $[Li(thf)_2\{Al[C(SiMe_3)_3](SR)_3\}]$ with R = Me **2**; Et **3**; Pr^i **4** or Ph **5** were obtained, but the reaction of compound **1** with Bu^{t}SH gave only the dithiolato derivative $[Li(thf)\{AlH[C(SiMe_3)_3](SBu^t)_2\}]$ **6**. The ionic compounds $[Li(tmen)_2][Al\{C(SiMe_3)_3\}(SR)_3]$ (R = Bu^t **7** or Ph **8**) were made from $[Li(tmen)_2][AlH_3\{C(SiMe_3)_3\}]$ **9**[8] and RSH. The structures of the methanethiolato derivative **2**, the monohydroaluminate **6**, and the benzene solvate of **7** were determined. As far as we are aware, no structural data on lithium thioaluminates have previously been reported but the compounds $[Li(OEt_2)_2M(SC_6H_2Pr^i_3\text{-}2,4,6)_4]$ (M = Ga or In)[9] and $[RbAlMe_2\{SC_6H_3(C_6H_2Pr^i_3\text{-}2,4,6)_2\text{-}2,6\}]$[10] have been described.

Experimental

Air and moisture were excluded as far as possible from all reactions by the use of Schlenk techniques, flame-dried glassware and Ar as blanket gas. NMR spectra from samples dissolved in C_6D_6 (thf-d_8 for **7** and **8**) unless otherwise stated 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 given relative to $SiMe_4$ (H, C and Si), aqueous LiCl or $Al(NO_3)_3$. IR spectra were recorded as Nujol mulls. The compounds **1**[2] and **9**[8] were prepared as described previously. Microanalyses were by Medac Ltd; the C values for some compounds were low, possibly owing to difficulties associated with combustion of organoaluminium compounds.

Syntheses

$[Li(thf)_2\{Al[C(SiMe_3)_3](SMe)_3\}]$ 2. A solution of Me_2S_2 (0.11 g, 1.17 mmol) in toluene (10 cm^3) was added to a solution of **1** (0.32 g, 0.77 mmol as monomer) in toluene (20 cm^3) and the mixture stirred for 3 h. Gas was evolved. Most of the solvent was removed under vacuum and the remaining solution kept at room temperature for several hours. The colourless moisture-sensitive blocks which separated were washed with toluene to give **2** (0.20 g, 47%), mp 166–168 °C (Found: C, 45.4; H, 9.3. $C_{21}H_{52}AlLiO_2S_3Si_3$ requires C, 45.8; H, 9.5%); ν_{max}/cm^{-1} 1311w, 1260m, 1247 (sh), 1048s, 958m, 848m and 798m; δ_H 0.70 (27 H, s, Me_3Si),1.27 (8 H, m, thf), 2.21 (9 H, s, MeS) and 3.38 (8 H, m, thf); δ_C 6.6 (Me_3Si), 10.1 (MeS), 25.3 and 62.3 (thf); δ_{Li} 0.47; δ_{Al} 153, $\Delta\nu_{1/2}$ 3.3 kHz; δ_{Si} −1.51.

$[Li(thf)_2\{Al[C(SiMe_3)_3](SEt)_3\}]$ 3. Liquid Et_2S_2 (0.16 cm^3, 1.30 mmol) was slowly added to a stirred solution of **1** (0.35 g, 0.85 mmol) in toluene (20 cm^3) at room temperature. Gas was

DOI: 10.1039/b002489i

evolved. After 16 h the solvent was removed under vacuum and the sticky residue crystallised from light petroleum (bp 40–60 °C) to give **3** (0.25 g, 50%), mp 96 °C (Found: C, 45.0; H, 9.5. $C_{24}H_{58}AlLiO_2S_3Si_3$ requires C, 48.6; H, 9.8%); ν_{max}/cm^{-1} 1261s, 1179w, 1076m, 1035s, 972m, 919w, 861m and 801m; δ_H 0.66 (27 H, s, SiMe$_3$), 1.23 (8 H, m, thf), 1.33 (9 H, t, CH$_2$C*H*$_3$), 2.85 (6 H, q, C*H*$_2$CH$_3$) and 3.42 (8 H, m, thf); δ_C 6.6 (SiMe$_3$), 20.0 (*C*H$_2$CH$_3$), 22.3 (CH$_2$*C*H$_3$), 25.2 and 68.6 (thf); δ_{Li} 0.56; δ_{Al} 136, $\Delta\nu_{1/2}$ 4.6 kHz; δ_{Si} −3.4.

[Li(thf)$_2${Al[C(SiMe$_3$)$_3$](SPr^i)$_3$}] 4. A solution of Pr^{i}SH (0.11 g, 1.46 mmol) in toluene (10 cm^3) was added to a stirred solution of **1** (0.20 g, 0.49 mmol) in toluene (15 cm^3). Gas evolution was rapid. The mixture was kept at room temperature for 3 h, then solvent was removed under vacuum and the residue recrystallised from methylcyclohexane to give colourless moisture-sensitive crystals of **4** (0.24 g, 78%), mp 115–117 °C (Found: C, 51.0; H, 10.1. $C_{27}H_{64}AlLiO_2S_3Si_3$ requires C, 51.0; H, 10.1%); ν_{max}/cm^{-1} 1257s, 1150m, 1046s, 857vs, 666m and 632m; δ_H 0.69 (27 H, s, Me$_3$Si), 1.31 (8 H, m, thf), 1.47 [18 H, d, CH(C*H*$_3$)$_2$], 3.49 (8 H, m, thf) and 3.61 [6 H, sept, C*H*(CH$_3$)$_2$]; δ_C 6.8 (SiMe$_3$), 25.3 (CH$_2$), 29.7 [CH(*C*H$_3$)$_2$], 32.9 [*C*H(CH$_3$)$_2$] and 68.5 (OCH$_2$); δ_{Li} −0.11; δ_{Al} 125, $\Delta\nu_{1/2}$ 4.1 kHz; δ_{Si} −3.55.

[Li(thf)$_2${Al[C(SiMe$_3$)$_3$](SPh)$_3$}] 5. A solution of diphenyl disulfide (0.32 g, 1.46 mmol) in toluene (5 cm^3) was added slowly to a stirred solution of **1** (0.40 g, 0.97 mmol) in toluene (20 cm^3) at room temperature. Gas was evolved. After 20 h a white solid was filtered off and the filtrate was reduced to 5 cm^3 then cooled to −30 °C to give colourless crystals of **5** (0.16 g, 23%), mp 133 °C (Found: C, 56.8; H, 7.9. $C_{36}H_{58}AlLiO_2S_3Si_3$ requires C, 58.7; H, 7.9%); ν_{max}/cm^{-1} 1937w, 1858w, 1798w, 1731w, 1582s, 1344w, 1261s, 1173w, 1088s, 1025s, 800m and 732w; δ_H 0.63 (27 H, s, SiMe$_3$), 1.16 and 3.23 (8 H, m, thf), 6.88 (3 H, m, *p*-H), 6.98 (6 H, m, *m*-H), 7.86 (6 H, d, *o*-H); δ_C 6.9 (Me), 25.2, 68.5 (thf), 125.1 (*p*-C), 128.5 (*m*-C), 134.6 (*o*-C) and 137.9 (*ipso*-C); δ_{Li} −0.51; δ_{Al} 136, $\Delta\nu_{1/2}$ 6.2 kHz; δ_{Si} −3.4. When PhSH was used in this reaction, instead of Ph$_2$S$_2$, the product was contaminated with LiSPh.

[Li(thf){AlH[C(SiMe$_3$)$_3$](SBu^t)$_2$}] 6. This was made in the same way as **4** but from Bu^{t}SH (2.4 mmol) and **1** (0.8 mmol) and obtained from heptane as colourless moisture-sensitive needles (0.35 g, 85%), mp 132.5–133.5 °C (Found: C, 50.8; H, 10.5. $C_{22}H_{54}AlLiOS_2Si_3$ requires C, 51.1; H, 10.5%); ν_{max}/cm^{-1} 1809 (Al–H), 1387s, 1257s, 1164m, 1033m, 916m, 862s and 780m; δ_H 0.64 (27 H, s, Me$_3$Si), 1.11 (4 H, m, thf), 1.58 (18 H, s, Bu^t) and 3.31 (4 H, m, thf); δ_C 6.4 (SiMe$_3$), 25.2 (CH$_2$), 36.8 [(*C*H$_3$)$_3$C], 44.9 [(CH$_3$)$_3$*C*] and 68.7 (OCH$_2$); δ_{Li} 0.93; δ_{Al} 140, $\Delta\nu_{1/2}$ 3.4 kHz; δ_{Si} −1.3.

[Li(tmen)$_2$][Al{C(SiMe$_3$)$_3$}(SBu^t)$_3$] 7. Dry tmen (0.20 cm^3, 1.32 mmol) was added to a stirred solution of **1** (0.27 g, 0.65 mmol) in toluene (20 cm^3) at room temperature. After 16 h, Bu^{t}SH (0.23 cm^3, 2.04 mmol) was added and gas was evolved. The mixture was stirred for 22 h and the solvent then removed. The residue was crystallised from warm benzene to give **7** as colourless crystals (0.20 g, 40%), mp 176 °C. ν_{max}/cm^{-1} 1357s, 1288s, 1252s, 1158s, 1127m, 1094m, 1065m, 1029s, 1013s, 945s, 860s br, 804 (sh), 787 (sh), 665s, 610m, 578m; δ_H(thf-*d*$_8$) 0.29 (27 H, s, SiMe$_3$), 1.57 (27 H, s, Bu^t), 2.15 and 2.31 (32 H, s, free tmen displaced by thf solvent); δ_C 8.4 (SiMe$_3$), 37.8 (C*Me*$_3$), 44.4 (*C*Me$_3$), 46.2 and 58.9 (tmen); δ_{Li} −0.65; δ_{Al} 127, $\Delta\nu_{1/2}$ 600 Hz; δ_{Si} −4.6.

[Li(tmen)$_2$][Al{C(SiMe$_3$)$_3$}(SPh)$_3$] 8. PhSH (0.22 cm^3, 2.14 mmol) was slowly added to a stirred solution of **9** (0.35 g, 0.70 mmol) in toluene (20 cm^3) at room temperature. Gas was evolved rapidly. After 14 h two layers were present. The upper layer was removed by cannula and solvent was pumped away from the lower layer to leave a white solid, which was recrystallised from warm toluene to give colourless crystals of **8** (0.30 g, 52%), mp 152 °C (Found: C, 56.0; H, 8.9; N, 6.4. $C_{40}H_{74}AlLiN_4S_3Si_3$ requires C, 58.2; H, 9.0; N, 6.8%); ν_{max}/cm^{-1} 1578m, 1289m, 1245s, 1183w, 1159m, 1129m, 1095m, 1066w, 1031s, 1016 (sh), 947s, 850vs, 786 (sh), 742s, 698m, 661s and 629m; δ_H(C$_6$D$_6$) 0.63 (27 H, s, SiMe$_3$), 1.83 (32 H, s br, tmen), 7.03 (9 H, m, *m*- and *p*-H), 7.80 (6 H, m, *o*-H); δ_H(thf-*d*$_8$) 0.35 (SiMe$_3$), 2.15 and 2.31 (displaced tmen), 6.77 (*m*- and *p*-H), 7.08 (*o*-H); δ_C 7.4 (SiMe$_3$), 46.2 and 58.9 (tmen), 123.2 (*p*-C), 127.3 (*o*-C), 136.4 (*m*-C) and 141.7 (*ipso*-C); δ_{Li} −0.58; δ_{Al} 137, $\Delta\nu_{1/2}$ 1.8 kHz; δ_{Si} −4.2.

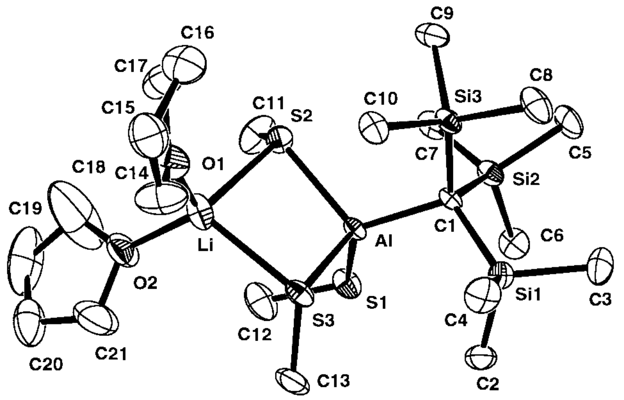

Fig. 1 Molecular structure of [Li(thf)$_2${Al[C(SiMe$_3$)$_3$](SMe)$_3$}] **2**.

Crystallography

Data were collected on a CAD4 diffractometer by use of Mo-Kα radiation (λ = 0.71073 Å) and details are given in Table 1. All non-hydrogen atoms were anisotropic and H atoms were included in riding mode. In compound **2**, the methyl groups attached to sulfur were fixed at idealised geometry but the torsion angle defining the H atom positions was refined. In **6**, hydride H atoms were freely refined isotropically. In **8**, the C(19) Bu^t group had methyl groups disordered equally over two orientations.

CCDC reference number 186/2009.

See http://www.rsc.org/suppdata/dt/b0/b002489i/ for crystallographic files in .cif format.

Discussion

The organotri(thiolato)aluminates 2–5

Reaction of **1** with the organic disulfides R$_2$S$_2$ (R = Me, Et or Ph) or propanethiol gave dihydrogen and the lithium organotri(thiolato)aluminates **2**–**5** [Li(thf)$_2$Al{C(SiMe$_3$)$_3$}(SR)$_3$] (R = Me **2**, Et **3**, Pr^i **4** or Ph **5**) analogous to the trialkoxoaluminates described previously.[3,4] The reductive cleavage of disulfides by organoaluminium hydrides to give thiolates is known[11] though (PhCH$_2$)$_2$S$_2$ and Ph$_2$S$_2$ were reported not to react with [Me$_3$NAlH$_3$]$_2$.[12] A few reactions between thiols and aluminium hydrides have been described,[13,14] but thiolatoaluminium compounds are usually prepared from triorganoaluminium compounds.[15,16] In the reactions described in this work the Al–C bond is apparently protected by the bulky alkyl group attached to aluminium.

The structure of **2** (Fig. 1) was confirmed by an X-ray diffraction study and bond lengths and angles are given in Table 2. The structure is analogous to that of [Li(thf)$_2$Al{C(SiMe$_3$)$_3$}(OEt)$_3$] **10**[4] but with a LiS$_2$Al rather than a LiO$_2$Al ring. The bridging Al–S bonds [mean 2.310(2) Å] are slightly shorter than those in other thiolato compounds (2.35–2.41 Å)[15,16] and the terminal Al–S bond length [2.239(2) Å] is similar to those in the only other previously reported four-co-ordinate thiolatoaluminium compounds, *viz.* [Al(SPh)(μ-Se)(NMe$_3$)]$_2$ [2.243(2)

Table 1 Crystal data and structural determinations for compounds **2**, **6** and **7**

	$[Li(thf)_2\{Al[C(SiMe_3)_3](SMe)_3\}]$ **2**	$[Li(thf)\{AlH[C(SiMe_3)_3](SBu^t)_2\}]$ **6**	$[Li(tmen)_2][Al\{C(SiMe_3)_3\}(SBu^t)_3]\cdot 2.5C_6H_6$ **7**·$2.5C_6H_6$
Chemical formula	$C_{21}H_{52}AlLiO_2S_3Si_3$	$C_{22}H_{54}AlLiOS_2Si_3$	$C_{34}H_{86}AlLiN_4S_3Si_3\cdot 2.5C_6H_6$
Formula weight	551.0	517.0	960.7
T/K	173(2)	173(2)	173(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$C2/c$ (no. 15)
a/Å	16.891(6)	21.737(4)	34.256(7)
b/Å	9.826(4)	14.610(3)	11.863(3)
c/Å	19.456(11)	23.040(4)	30.519(4)
β/°	98.45(4)	115.15(1)	99.88(2)
U/Å^3	3194(3)	6623(2)	12218(4)
Z	4	8	8
μ/mm^{-1}	0.39	0.31	0.23
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.071, 0.203	0.063, 0.157	0.086, 0.166
(all data)	0.092, 0.225	0.107, 0.204	0.191, 0.211
Measured/indep. rflns./R_{int}	4589/4426/0.073	11948/11632/0.038	8619/8468/0.082
Rflns. with $I > 2\sigma(I)$	3385	7701	4068

Table 2 Bond lengths (Å) and angles (°) in $[Li(thf)_2\{Al[C(SiMe_3)_3](SMe)_3\}]$ **2**, $[Li(thf)\{AlH[C(SiMe_3)_3](SBu^t)_2\}]$ **6** and the anion $[Al\{C(SiMe_3)_3\}(SBu^t)_3]^-$ of **7**

	2[a]	**6**[b]	Anion of **7**[c]
Al–C	2.008(5)	2.026(4)	2.090(7)
Al–S_b[d]	2.305(2), 2.314(2)	2.328(2)[e]	
Al–S_t[d]	2.239(2)		2.291(3)[e]
Al···Li	3.233(10)	3.032(9)	
Li–S	2.462(10), 2.483(11)	2.361(10), 2.389(10)	
Si–C1[e]	1.891(5)	1.885(5)	1.886(7)
Si–Me[e]	1.876(5)	1.881(5)	1.881(8)
S–C[e]	1.822(6)	1.866(6)	1.849(8)
C1–Al–S_t	115.1(2)		107.8(2), 108.7(2), 106.2(2)
C1–Al–S_b	113.3(2)[e]	108.97(14)[e]	
S_t–Al–$S_{b,t}$	107.77(9)[e]		111.27(11), 112.58(12), 110.07(11)
S_b–Al–S_b	98.04(8)	101.05(7)	
S–Li–S	89.7(3)	98.4(3)	
C–S_t–Al	102.8(2)		121.0(2), 116.8(3), 121.4(3)
C–S_b–Al	107.8(2), 106.9(2)	110.6(2), 117.7(2)	
Al–S–Li	85.1(3), 84.9(2)	80.6(3), 80.0(2)	
Li–S_b–C	114.9(3), 117.9(3)	108.3(3), 101.1(3)	
Si–C–Si[e]	110.2(2)	110.5(2)	109.3(3)
Me–Si–Me[e]	105.2(2)	104.8(2)	103.8(4)
C–Si–Me[e]	113.5(2)	113.8(2)	114.7(3)
LiS1S2/S1S2Al fold	17	1	

[a] Mean Li–O 1.903(11); O2–Li–S2 119.3(5), O1–Li–S2 110.1(5), O2–Li–S3 116.7(5), O1–Li–S3 109.4(5), O2–Li–O1 110.0(5). [b] Values for molecule 1 only: Li–O 1.856(10); O–Li–S1 133.0(6), O–Li–S2 125.6(5); Al–H 1.65(5); C1–Al–H 117(2), S1–Al–H 111(2), S2–Al–H 108(2). [c] Li–N mean 2.097(15); N–Li–N 90.4(6), 116.6(7), 119.4(7), 91.3(6), 119.4(7), 122.6(7). [d] S_b in bridge, S_t terminal. [e] Mean value. The precision of individual measurements, none of which differs significantly from the mean, is indicated in parentheses.

Å][12] and $[Al(SC_6H_2Pr^i_3\text{-}2,4,6)_3(thf)]$ [2.227(2) Å].[13] The five-coordinate aluminium compound $[\overline{AlH(SCH_2CH_2N}Et_2)_2]$ has a mean Al–S bond length of 2.275(1) Å.[14] The Li–S bond lengths in **2** [mean 2.473(11) Å] are at the upper end of the usual range (2.34–2.49 Å).[9,17] The compound is therefore best regarded as a lithium alkyl(methanethiolato)aluminate and the related compounds **3**–**5** can be assumed from spectroscopic evidence to have similar structures. Tetra(thiolato)aluminates do not appear to have been characterised [no details have been given about $LiAl(SC_6H_2Pr^i_3\text{-}2,4,6)_4$],[13] but the gallium analogues containing the species $[Ga(SR)_4]^-$ are known.[18] The mean Ga–S bond lengths (2.264(3) Å for R = Et, 2.2678(6) Å for R = Pr^i and 2.257(3) Å for R = Ph) are, as expected in view of the similar covalent radii of Al and Ga,[13] close to the Al–S bond lengths in **2**. The four-membered AlS_2Li ring in **2** is folded by 17° about the S···S axis [*cf.* a fold angle of 14° in $[Li(thf)\{Al[C(SiMe_3)_3](OBu^t)_3\}]$ **11** and an almost planar ring in **10**] and the bonds at sulfur are more strongly pyramidalised [sum of angles 307.8 at S(2) and 309.7° at S(3)] than those at oxygen [mean 348° in **10** and 345° in **11**]; *cf.* also the narrower angle at S(1) [102.8(2)°] in **2** compared with that at the oxygen of the terminal OEt group in **10** [130.1(8)°].[4] The methyl groups attached to sulfur are pushed to one side of the AlS_2Li ring and the bulky $C(SiMe_3)_3$ group is located on the other side, but there is still room for the co-ordination of two thf molecules at lithium, as found in **10**.[4] The Li–O bond distances are normal. The angles at the metal centres in **2** and **10** show that the terminal SMe group in **2** lies further over the ring than does the OEt group in **10**, and that the adjacent thf is pushed further away [mean S–Li–O(2) = 118.0(5), mean S–Li–O(1) = 109.8(5)°]. In contrast, in **10** it is the other thf molecule, *i.e.* that adjacent to the bulky organic group, that is pushed away from the ring. As far as we are aware, **2** is the first organotri(thiolato)aluminate to be structurally characterised. It is noteworthy that the analogous methoxo compound contained only one thf molecule per lithium, was insoluble in hydrocarbons, and is probably polymeric.[4]

The NMR spectra of **2** and **3** in toluene-d_8 at room temperature show only one set of signals attributable to SR groups, showing that bridging and terminal thiolato groups exchange rapidly on the NMR timescale. There was no separation of

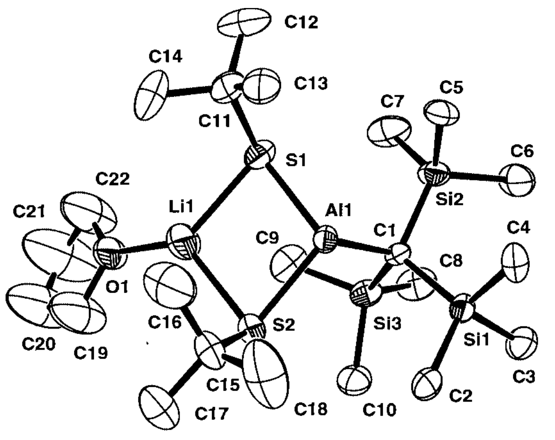

Fig. 2 Molecular structure of $[Li(thf)\{AlH[C(SiMe_3)_3](SBu^t)_2\}]$ **6**.

signals at temperatures down to −90 °C. In contrast, separate signals can be observed below room temperature from samples of the alkoxo derivatives *e.g.* **10**.[4] The faster exchange of thiolato than of alkoxo groups is consistent with weaker bridge bonds in the sulfur derivatives.

The organodi(thiolato)aluminate 6

After the characterisation of the methyl derivative **2** we decided to make the corresponding *tert*-butyl compound in order to compare it with the already reported alkoxo analogue $[Li(thf)Al\{C(SiMe_3)_3\}(OBu^t)_3]$ **11**.[3] In particular we wished to discover what effect the greater tendency to pyramidalisation at sulfur would have on the congestion at the Li and Al centres. The reaction of **1** with a three-fold excess of *tert*-butanethiol at room temperature gave dihydrogen and a solution from which colourless needles were isolated. NMR and IR spectroscopic data from these needles indicated that only two of the available Al–H bonds had been cleaved to give the organodi(thiolato)aluminate **6**. The third Al–H bond appeared to be stable and well protected from attack by the excess of thiol.

The asymmetric unit in the crystalline compound, the first organodi(thiolato)aluminate to be structurally characterised, consists of two independent lithium aluminate molecules, one of which is shown in Fig. 2, but, as the differences in bond lengths and angles between them are insignificant, values for molecule 1 only are given in Table 2. The thf and $C(SiMe_3)_3$ groups lie on one side of the central LiS_2Al ring and the hydride and SBu^t groups on the other. A comparison between the bond lengths and angles in **2** and those in **6** shows that the Al–C bonds are the same, within experimental uncertainty, and the Al–S bonds are only slightly longer in **6**. The Li–S bonds are, however, significantly shorter in **6**, suggesting that the lithium and aluminium fragments are more firmly held together than those in **2**. The shorter bonds in **6** may reflect the fact that there is only one thf rather than two, so that the coordination at Li is almost planar rather than tetrahedral (sum of angles 357° in one independent molecule and 359.7° in the other). The Bu^t groups are bent towards the Li to give narrow Li–S–C (105°) and wide Al–S–C angles (114°). The steric effect of the large Bu^t group is shown in the C–S distances [1.861(5) and 1.872(6) Å], which are significantly longer than those in **2** [1.816(6)–1.834(7) Å]. A similar effect is found in the compounds $[R_2Al\text{-}NR'_2]_2$, in which N–C bonds become longer as the size of R′ increases.[19] The tighter endocyclic bonding together with the steric hindrance provided by the large Bu^t group accounts for the difficulty in the displacement of the final hydrogen from aluminium to give a tri(thiolato) derivative analogous to **2**. The LiS_2Al ring is almost planar (fold angle along the S···S axis only 1°), a consequence, presumably, of repulsion between the *tert*-butyl groups in the bridging thiolato ligands. It is more distorted from square, with narrower Li–S–Al angles (80°, *cf.* 85° in **2**) and wider S–Li–S and S–Al–S angles (98.4 and 101.0, *cf.* 89.7 and 98.0°, respectively, in **2**) and closer metal centres. The shortest Li···Me contact (3.05 Å) in **6** is to C16; this is longer than the shortest Li···Me contacts in **11** (2.60 Å) or $[LiC(SiMe_3)_3]_2$ (2.47 Å),[20] and probably does not imply any significant agostic interaction.

Attempts to make the analogous isopropyl compound $[Li(thf)\{Al[C(SiMe_3)_3]H(SPr^i)_2\}]$ from **1** and two equivalents of Pr^iSH gave only complex mixtures which appeared from NMR data to include the trithiolato derivative, showing that the isopropyl group is not large enough to prevent access of thiol to the third Al–H bond in the starting hydride.

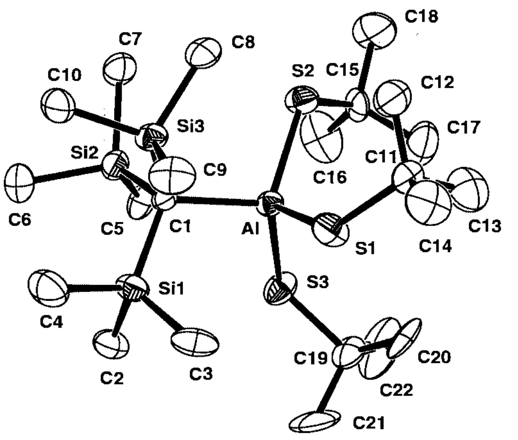

Fig. 3 The anion of $[Li(tmen)_2][Al\{C(SiMe_3)_3\}(SBu^t)_3]$ **7**.

The ionic organotri(thiolato)aluminate 7

The Li–S bond is significantly weaker than the Li–O bond so sulfur ligands are less able than oxygen ligands to compete with the commonly used bases having oxygen or nitrogen donor atoms. We therefore considered that the organotri(thiolato)-aluminates would be more likely to give solvent-separated ion pairs than the anlaogous alkoxo derivatives. Our attempts to obtain solvent-separated lithium trialkoxoorganoaluminates had been unsuccessful,[4] but when the ionic compound **9** was treated with a three-fold excess of Bu^tSH, the resulting solid, after crystallisation from benzene, showed no absorption in the Al–H stretching region of the IR spectrum and the NMR spectra also indicated that all three hydrogens had been displaced from aluminium to give a tri(thiolato)aluminate **7**. The implication is that the separated ions found in crystalline **9** remain separated in solution during attack by butanethiol molecules. There is thus room for reaction at all three Al–H bonds and the reaction is not inhibited, after only two have been attacked, by the formation of a tightly bound ring analogous to that in compound **6**. It was not possible to obtain C and H analyses for **7** but no impurities were detected by NMR spectroscopy. The structure was confirmed by an X-ray study, which revealed the presence in the crystal of separated cations and anions. The cation has been found in a number of structures and is not discussed further. Data for the anion are given in Table 2 and the structure is shown in Fig. 3. The Al–C bond lengths are significantly longer than those in **2** and **6**, and the Al–S bonds slightly shorter, though they are not as short as the terminal Al–S bond in **2**. The S–Al–S angles are only slightly wider and the C–Al–S angles slightly narrower than the tetrahedral value. Other bond lengths and angles are in the usual range but the S–Bu^t bonds [1.842(8)–1.858(7) Å] are again long. The Al–S–Bu^t angles (110–121°) in **6** and **7** are much larger than the Al–S–Me angles in **2** (102–107°), showing that the flexible pyramidalisation at sulfur is able to accommodate alkyl groups of various sizes. An analogous organotri(amido)aluminate was isolated from the reaction between compound **1** and an excess of aniline.[8]

In all three compounds the Si–C1 bond lengths are similar, as are the Si–Me bond lengths. The Si–C1 bonds are also of similar length to the Si–Me bond lengths, as in other compounds containing the $C(SiMe_3)_3$ group attached to aluminium.[21]

Acknowledgements

We thank the EPSRC for financial support, the Chinese Education Commission for the award of a scholarship to W.-Y. C., and Chengdu University of Science and Technology for granting him sabbatical leave.

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