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Polyhedron 22 (2003) 2655–2660

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Synthetic and structural studies on aluminium thiolate complexes

Claire J. Carmalt [a,*], John D. Mileham [a], Andrew J.P. White [b], David J. Williams [b], Simon Rushworth [c]

[a] *Department of Chemistry, Christopher Ingold Laboratories, University College London, 20 Gordon Street, London, WC1H 0AJ, UK*
[b] *Department of Chemistry, Imperial College London, South Kensington, London, SW7 2AZ, UK*
[c] *Epichem Limited, Power Road, Bromborough, Wirral, CH62 3QF UK*

Received 31 March 2003; accepted 12 May 2003

Abstract

The reaction between [$AlH_3(NMe_2Et)$] and 1 equiv. of *t*-BuSH resulted in the isolation of colourless crystals of [Al(S–*t*-Bu)$_3$(NMe_2Et)]. The reaction of [$AlH_3(NMe_2Et)$] and 1 equiv. of 2,6-$Me_2C_6H_3SH$ afforded colourless crystals of [$HNMe_2Et$][Al($SC_6H_3Me_2$-2,6)$_4$]. The related reaction of [$AlH_3(OEt_2)$] (generated in situ from $AlCl_3$ and 3 equiv. of $LiAlH_4$) and 2,6-$Me_2C_6H_3SH$ in diethyl ether resulted in the formation of [Al($SC_6H_3Me_2$-2,6)$_3$(OEt_2)]. However, the ionic compound [Li(OEt_2)$_3$][Al($SC_6H_3Me_2$-2,6)$_4$] can be isolated from the reaction between [$AlH_3(OEt_2)$] and 2,6-$Me_2C_6H_3SH$, when incomplete reaction of $AlCl_3$ with $LiAlH_4$ occurs before the addition of the thiol. The X-ray crystal structures of all the compounds have been determined.

Keywords: Aluminium; Thiolate; Hydride

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1. Introduction

Organometallic compounds, of the type [$R_nM(ER')_{3-n}$] (where M = Al–Tl; E = S–Te; R and R′ = alkyl or aryl) have been studied for many years [1]. More recently, structural information has shown that these complexes have a tendency to form dimeric or trimeric aggregates in the solid-state [1]. Monomeric derivatives, of the type [$M(ER)_3$], have only been studied to a limited extent. With reference to aluminium tris(thiolate) complexes, [$Al(SR)_3$], structurally characterised examples include [Al(SC_6H_2–*t*-Bu_3-2,4,6)$_3$] and [$Al(SR)_3$(L)] (L = $HNMe_2$, R = *i*-Pr; L = thf, R = *t*-Bu or C_6H_2–*i*-Pr_3-2,4,6) [2–4]. Lithium organo-tri(thiolato)aluminates, of the type [Li(thf)$_2$Al{C($SiMe_3$)$_3$}(SR)$_3$] (R = Me, Et, *i*-Pr or Ph) have been reported recently and some of the complexes structurally characterised [5]. Most of the aluminium thiolate complexes are prepared from salt elimination routes or triorganoaluminium compounds [1–6]. However, there are relatively few reports of reactions between thiols and aluminium hydrides [2,4,7,8].

We were interested in exploring the reactivity of alane with thiols in more detail in an attempt to obtain structural information on mixed hydrido-thiolate complexes of aluminium. In related reactions of alane with alcohols we isolated and structurally characterised some pentanuclear alkoxyaluminium hydrides [9]. We were also interested in hydridoaluminium thiolate complexes because materials containing a Group 13 metal (Al, Ga, In or Tl) and a chalcogen are reported to have applications as precursors to III/VI materials, which are potential alternatives to II/VI materials for photovoltaic and optoelectronic devices [10–12].

Herein we describe the reactivity of alane with *t*-BuSH and 2,6-$Me_2C_6H_3SH$. The structures of four new complexes, namely [Al(S–*t*-Bu)$_3$(NMe_2Et)], [Al($SC_6H_3Me_2$-2,6)$_3$(OEt_2)], [Li(OEt_2)$_3$][Al($SC_6H_3Me_2$-2,6)$_4$] and [$HNMe_2Et$][Al($SC_6H_3Me_2$-2,6)$_4$] are described.

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[*] Corresponding author. Tel: +44-20-7679-7528; fax: +44-20-7679-7463.

E-mail address: c.j.carmalt@ucl.ac.uk (C.J. Carmalt).

0277-5387/03/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/S0277-5387(03)00351-6

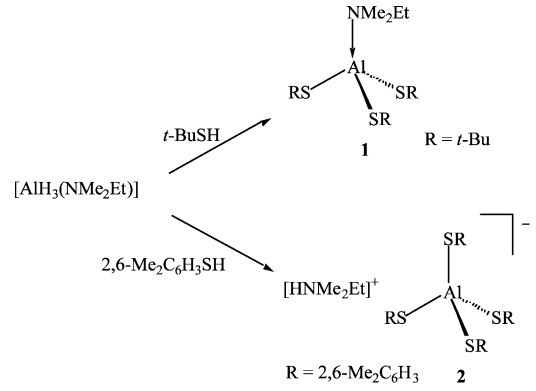
2. Results and discussion

The reaction of [$AlH_3(NMe_2Et)$] and 1 equiv. of *t*-BuSH in diethyl ether at room temperature resulted, after work up, in the isolation of colourless crystals of [Al(S–*t*-Bu)$_3$(NMe_2Et)] (**1**). Analytical and spectroscopic data for **1** were consistent with the formation of the tris(thiolate) complex [Al(S–*t*-Bu)$_3$(NMe_2Et)] rather than a hydridoaluminium thiolate. The X-ray structure of **1** (Fig. 1, Table 1) shows the coordination geometry at aluminium to be noticeably flattened tetrahedral, the N–Al–S angles ranging between 99.83(6)° and 104.00(6)°, whereas those for S–Al–S are between 115.68(3)° and 116.21(3)° with the aluminium atom lying 0.45 Å out of the S_3 plane. This geometry is directly analogous to that observed in [Al(S–*t*-Bu)$_3$(thf)] and [Al(S–*i*-Pr)$_3$($HNMe_2$)] where the geometry at aluminium was described as distorted trigonal pyramidal [3]. In the present structure the sum of the three S–Al–S angles is 348°, a value virtually identical to those reported for [Al(S–*t*-Bu)$_3$(thf)] and [Al(S–*i*-Pr)$_3$($HNMe_2$)] (348° and 345°, respectively [3]). Although the three Al–S distances are in a very narrow range (2.2337(8)–2.2366(8) Å) and there appears to be an essentially C_3-symmetric arrangement of the *t*-SBu ligands with respect to the Al–N axis, this symmetry does not extend to the torsion angles about the Al–S bonds, with the twists relative to the Al–N vector ranging between 109° and 137°. There are no intermolecular packing interactions of note.

Table 1
Selected bond lengths (Å) and angles (°) for **1**

Bond lengths			
Al–N(1)	2.038(2)	Al–S(1)	2.2366(8)
Al–S(2)	2.2356(8)	Al–S(3)	2.2337(8)
S(1)–C(6)	1.852(2)	S(2)–C(10)	1.862(2)
S(3)–C(14)	1.858(2)		
Bond angles			
N(1)–Al–S(3)	101.16(6)	N(1)–Al–S(2)	104.00(6)
S(3)–Al–S(2)	115.68(3)	N(1)–Al–S(1)	99.83(6)
S(3)–Al–S(1)	116.21(3)	S(2)–Al–S(1)	116.17(4)
C(6)–S(1)–Al	112.65(7)	C(10)–S(2)–Al	112.91(7)
C(14)–S(3)–Al	112.46(8)		

Compound **1** was the only species isolated from the reaction of [$AlH_3(NMe_2Et)$] with *t*-BuSH and the expected product [H_2Al(S–*t*-Bu)(NMe_2Et)] was not observed (Scheme 1). The formation of compound **1** is in contrast to a previous report where the alkylthiolatoalanes, [H_2Al(S–*t*-Bu)(NMe_3)] and [HAl(S–*t*-Bu)$_2$(NMe_3)], were isolated from the reaction of [$AlH_3(NMe_3)$] and 1 or 2 equiv. of *t*-BuSH, respectively [8]. However, the reaction temperature employed to prepare compound **1** was higher (room temperature vs. −15 °C) which may result in ligand redistribution reactions occurring. It is possible that [H_2Al(S–*t*-Bu)(NMe_2Et)] or [HAl(S–*t*-Bu)$_2$(NMe_2Et)] was formed during the reaction but ligand exchange occurred to give **1** and [AlH_3]. The formation of a tris(thiolate) complex has been observed previously in related gallium thiolate chemistry [13]. Thus, the reaction between [GaH_3(NMe_3)] and 2 equiv. of *t*-BuSH was reported to yield [Ga(S–*t*-Bu)$_3$(NMe_3)] and [HGa(S–*t*-Bu)$_2$(NMe_3)] [13]. Compound **1** can be prepared in higher yield from the reaction of [$AlH_3(NMe_2Et)$] and 3 equiv. of *t*-BuSH [3].



Scheme 1.

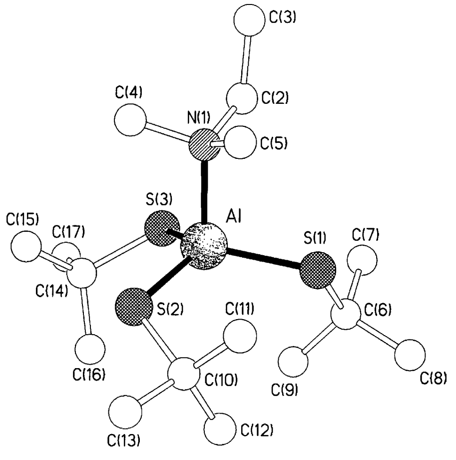


Fig. 1. The molecular structure of **1**.

In order to investigate the reactivity of alane with thiols in more detail, [$AlH_3(NMe_2Et)$] was treated with 1 equiv. of 2,6-$Me_2C_6H_3SH$ in diethyl ether (Scheme 1). After work up a colourless crystalline product (**2**) was obtained. The structure of **2** was established by X-ray crystallography and shown to be the *pseudo*-homoleptic complex [$HNMe_2Et$][Al($SC_6H_3Me_2$-2,6)$_4$], shown in Fig. 2 (Table 2). For the charges to balance either the complex or the co-crystallised NMe_2Et molecule has to be protonated, but unfortunately it was not possible to locate in difference electron maps a hydrogen atom on any of the four sulfur atoms or on the nitrogen atom of the NMe_2Et. Inspection of the Al–S bond lengths showed that three of these, those to S(1), S(3) and

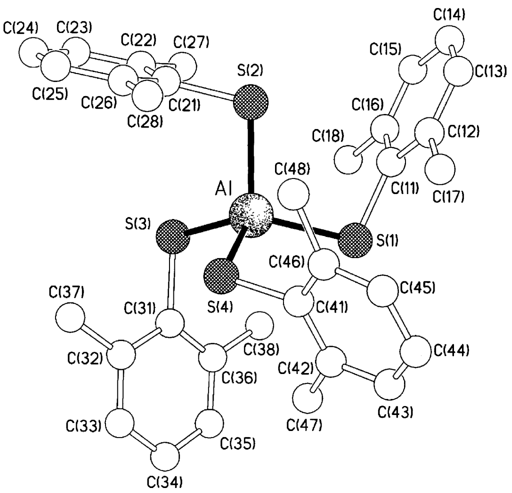


Fig. 2. The structure of the $[Al(SC_6H_3Me_2\text{-}2,6)4]^-$ anion in **2**.

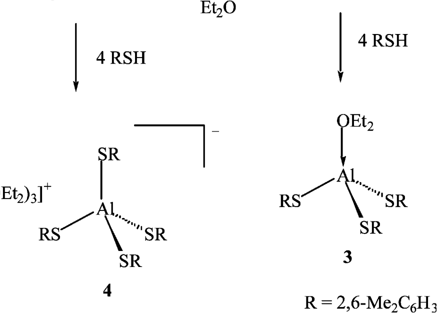
S(4), lie in the narrow range 2.250(2)–2.254(3) Å, whereas the fourth, to Al-(2), is significantly longer at 2.275(2) Å. Such a lengthening has been seen previously in the structure of [*i*-Pr_2NH_2][Al(S–*t*-Bu)$_4$] [3], where it was associated with the presence of weak N–H···S hydrogen bonds with N···S ca. 3.38 Å. Here in **2** the NMe_2Et nitrogen approaches S(2) at 3.37 Å, suggesting an analogous N–H···S hydrogen bonding interaction. We thus conclude that in the solid state structure of **2** the 'missing' proton most probably resides on the nitrogen of the NMe_2Et unit. The geometry at aluminium does not exhibit the flattening observed in **1**, though the S–Al–S angles cover a fairly wide range of between 103.79(7)° [S(4)/S(3)] and 119.45(10)° [S(1)/S(3)]. The molecule has superficially non-crystallographic S_4 symmetry, though on closer inspection it is found that the planes of the four 2,6-dimethylphenyl rings are inclined by between 49° and 64° to the vector bisecting the S(1)–Al–S(3) angle. Except for the already discussed weak N–H···S hydrogen bond, there are no noteworthy packing interactions. Analytical and spectroscopic data for **2** were consistent with the formation of a 1:1 mixture of **2** and the neutral complex $[Al(SC_6H_3Me_2\text{-}2,6)_3(NMe_2Et)]$.

Table 2
Selected bond lengths (Å) and angles (°) for **2**

Bond lengths			
Al–S(1)	2.250(2)	Al–S(2)	2.275(2)
Al–S(3)	2.254(3)	Al–S(4)	2.250(2)
S(1)–C(11)	1.771(6)	S(2)–C(21)	1.790(6)
S(3)–C(31)	1.792(6)	S(4)–C(41)	1.794(7)
Bond angles			
S(4)–Al–S(1)	108.28(9)	S(4)–Al–S(3)	103.79(9)
S(1)–Al–S(3)	119.45(10)	S(4)–Al–S(2)	116.49(9)
S(1)–Al–S(2)	104.65(8)	S(3)–Al–S(2)	104.78(9)
C(11)–S(1)–Al	102.5(2)	C(21)–S(2)–Al	103.7(2)
C(31)–S(3)–Al	101.9(2)	C(41)–S(4)–Al	107.0(2)

An alternative route was also investigated where $[AlH_3]$ in diethyl ether was reacted with thiols. Thus, the reaction between $[AlH_3(OEt_2)]$ (generated in situ according to Ref. [14]) and 1 equiv. of 2,6-$Me_2C_6H_3SH$ in diethyl ether at room temperature resulted, after work up, in a 30% yield of colourless crystalline **3**. Analytical and spectroscopic data for **3** were consistent with the formation of $[Al(SC_6H_3Me_2\text{-}2,6)_3(OEt_2)]$ rather than that of the expected product $[H_2Al(SC_6H_3Me_2\text{-}2,6)]_n$ (Scheme 2). Interestingly, the addition of 3 equiv. of 2,6-$Me_2C_6H_3SH$ to $[AlH_3(OEt_2)]$ resulted in the formation of a mixture of products rather than the isolation of compound **3**.

The X-ray analysis revealed compound **3** to be the tri(thiophenolato)aluminium-diethyl ether species depicted in Fig. 3 (Table 3). The structure, ignoring the two ethyl groups, has pseudo C_3 symmetry about the O–Al direction creating a propeller-like geometry. Viewed down the O–Al vector, the structure shown in Fig. 3 has a Λ-type conformation, but as the crystal is racemic the structure contains equal numbers of Δ and Λ forms. The three 2,6-dimethylphenyl ring systems are oriented approximately orthogonally (77°, 82° and 96°) to the S_3 plane. The 'all down' geometry observed here is in contrast to the 'one up, two down' conformation seen in the related $[Al(SC_6H_2\text{-}i\text{-}Pr_3\text{-}2,4,6)_3(thf)]$ species [2]. The geometry at aluminium is best described as flattened tetrahedral, the metal centre being displaced towards the 'basal' S_3 face, lying only 0.43 Å out of this plane in the direction of the oxygen atom (a deviation very similar to that seen in **1**). The angles subtended at aluminium are in the range 97.34(7)–120.81(5)°, and the sum of the three S–Al–S angles is 349°. The Al–S distances are unexceptional, ranging between 2.227(1) and 2.238(1) Å (the Al–O distance is 1.907(2) Å). The propeller-like geometry results in one of the methyl groups of each 2,6-dimethylphenyl ring system being directed into the face of its nearest neighbour aryl ring, the shortest H···π distance being 2.78 Å. There are no intermolecular



Scheme 2.

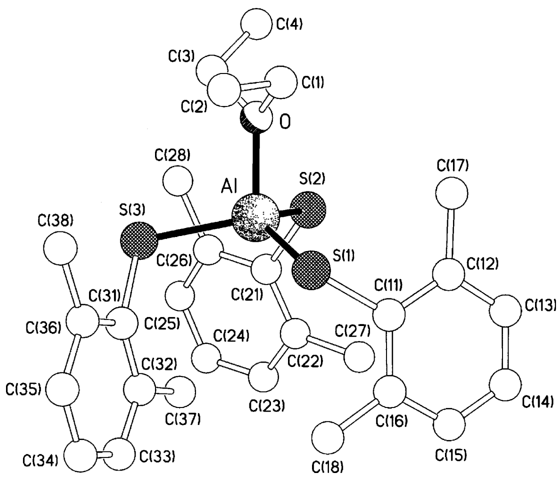


Fig. 3. The molecular structure of **3**.

interactions of note. The formation of **3** is similar to the isolation of [Al(S–*t*-Bu)$_3$(NMe$_2$Et)] (**1**) from the reaction between [AlH$_3$(NMe$_2$Et)] and 1 equiv. of *t*-BuSH (Scheme 1). In addition, the ^{1}H and ^{13}C NMR data for **1** and **3** indicate the presence of bound and uncoordinated ligand (NMe$_2$Et for **1** and Et$_2$O for **3**) suggesting that an exchange process is occurring.

In order to obtain compound **3**, the mixture of LiAlH$_4$ and AlCl$_3$ was stirred for 30 min before the addition of 2,6-Me$_2$C$_6$H$_3$SH. However, if 2,6-Me$_2$C$_6$H$_3$SH is added immediately to the slurry of LiAlH$_4$ and AlCl$_3$ in diethyl ether, colourless crystals of a new compound [Li(OEt$_2$)$_3$][Al(SC$_6$H$_3$Me$_2$-2,6)$_4$] (**4**) are obtained (Scheme 2). The formation of **4** is probably the result of incomplete reaction of aluminium(III) chloride with LiAlH$_4$ before the addition of the thiol. ^{1}H/^{13}C NMR data show only the formation of **4** rather than a mixture of products. A single crystal X-ray diffraction analysis showed the anion in **4** to be the S_4-symmetric homoleptic complex shown in Fig. 4. The geometry at aluminium is distorted tetrahedral with unique angles of 104.85(3)° and 119.16(6)°, reflecting a slight flattening of the tetrahedron about the S_4 axis (which bisects the S–Al–S(0A) angle), and an Al–S distance of 2.253(1) Å. This distance is similar to those seen for the three Al–S bonds in **2** where the sulfur is not involved in intermolecular hydrogen bonding (2.250(2)–2.254(3) Å, vide supra). The [(Et$_2$O)$_3$Li] cation is disordered. Attempts to prepare compound **4** from the reaction of LiAlH$_4$ and 4 equiv. of 2,6-Me$_2$C$_6$H$_3$SH under the same conditions (diethyl ether, room temperature) resulted in decomposition.

Table 3
Selected bond lengths (Å) and angles (°) for **3**

Bond lengths			
Al–O	1.907(2)	Al–S(1)	2.227(1)
Al–S(2)	2.238(1)	Al–S(3)	2.234(1)
S(1)–C(11)	1.794(3)	S(2)–C(21)	1.797(3)
S(3)–C(31)	1.796(3)		
Bond angles			
O–Al–S(1)	104.03(7)	O–Al–S(3)	102.01(7)
S(1)–Al–S(3)	112.73(4)	O–Al–S(2)	97.34(7)
S(1)–Al–S(2)	120.81(5)	S(3)–Al–S(2)	115.61(4)
C(11)–S(1)–Al	106.12(9)	C(21)–S(2)–Al	107.03(9)
C(31)–S(3)–Al	107.98(9)		

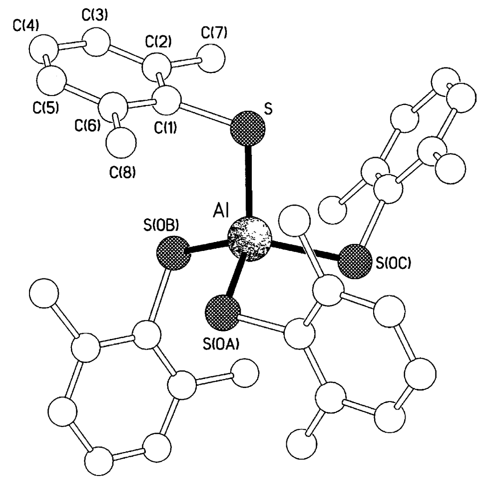


Fig. 4. The structure of the homoleptic, S_4-symmetric anion in the crystals of **4**. Selected bond length (Å) and angles (°); Al–S 2.2534(9), S–C(1) 1.784(4), S–Al–S(0A) 119.16(6), S–Al–S(0B) 104.85(3), C(1)–S–Al 107.42(12).

3. Summary

The aluminium tris(thiolate) complexes [Al(S–*t*-Bu)$_3$(NMe$_2$Et)] (**1**), and [Al(SC$_6$H$_3$Me$_2$-2,6)$_3$(OEt$_2$)] (**3**) have been synthesised from the 1:1 reaction of [AlH$_3$(L)] (L = NMe$_2$Et or Et$_2$O) and RSH (R = *t*-Bu or 2,6-Me$_2$C$_6$H$_3$SH). Compound **1** can be prepared in higher yields (~ 70%) from the 1:3 reaction of [AlH$_3$(NMe$_2$Et)] and *t*-BuSH [3]. These results suggest that [AlH$_3$(L)] reacts with thiols in a similar manner to alcohols (ROH) to produce not very well defined species of composition [AlH$_{3-n}$(ER)$_n$] (E = O, S) [14]. The formation of the aluminium tris(thiolate) complexes also suggests that compounds of the type [AlH$_{3-n}$(SR)$_n$] undergo ligand exchange reactions at ambient temperatures. Two ionic complexes containing the homoleptic anion [Al(SC$_6$H$_3$Me$_2$-2,6)$_4$]$^-$ (compounds **2** and **4**) have also been isolated. All the compounds have been structurally characterised. We are currently investigating reactions between AlH$_3$ and thiols under different conditions (e.g. low temperature), the results of which will be described in a future publication.

4. Experimental

4.1. General and physical measurements

All manipulations were performed under a dry, oxygen-free dinitrogen atmosphere using standard Schlenk techniques or in a Mbraun Unilab glove box. All solvents were distilled from appropriate drying agents prior to use (sodium/benzophenone for ether) and $\mathrm{AlH_3(OEt_2)}$ was prepared by literature methods [15]. $\mathrm{[AlH_3(NMe_2Et)]}$ was supplied by Epichem Ltd. All other reagents were procured commercially from Aldrich and used without further purification. Microanalytical data were obtained at University College London (UCL).

^{1}H and ^{13}C NMR spectra were recorded on Bruker AMX400 spectrometers at UCL. The NMR spectra are referenced to $\mathrm{CDCl_3}$ or $\mathrm{CD_2Cl_2}$, which was degassed and dried over molecular sieves prior to use; ^{1}H and ^{13}C chemical shifts are reported relative to $\mathrm{SiMe_4}$ (0.00 ppm). IR spectra were run on a Shimadzu FTIR-8200 instrument. Melting points were obtained in sealed glass capillaries under nitrogen and are uncorrected.

4.2. Preparations

4.2.1. $[\mathrm{Al(S{-}}t\mathrm{{-}Bu)_3(NMe_2Et)}]$ (1)

t-BuSH (0.43 cm^3, 3.77 mmol) was added dropwise to a solution of $\mathrm{[AlH_3(NMe_2Et)]}$ (0.5 cm^3, 3.77 mmol) in diethyl ether (20 cm^3) at room temperature. The evolution of hydrogen was observed and the mixture was stirred at room temperature for 1.5 h. The solution was reduced in volume to ~5 cm^3 under vacuum. Cooling to −20 °C for 24 h resulted in the formation of colourless crystals of **1** (0.19 g, 15% yield based on aluminium), m.p. 84–86 °C. *Anal.* Calc. for $\mathrm{C_{16}H_{38}NS_3Al}$: C, 52.27; H, 10.42; N, 3.81. Found: C, 51.38; H, 9.92; N, 3.46. ^{1}H NMR ($\mathrm{CD_2Cl_2}$): δ 1.12 (t, $J = 10$ Hz, 3H, $\mathrm{NCH_2C}\mathit{H}_3$), 1.14 (t, $J = 10$ Hz, $\mathrm{NCH_2C}\mathit{H}_3$), 1.57 (s, 27H, $\mathrm{SC(C}\mathit{H}_3)_3$), 2.56 (s, 6H, $\mathrm{N(C}\mathit{H}_3)_2$), 2.58 (s, $\mathrm{N(C}\mathit{H}_3)_2$), 3.08 (q, $\mathrm{NC}\mathit{H}_2\mathrm{CH_3}$), 3.22 (q, 2H, $\mathrm{NC}\mathit{H}_2\mathrm{CH_3}$). ^{13}C{^{1}H} NMR ($\mathrm{CD_2Cl_2}$): δ 5.9 (s, $\mathrm{NCH_2}\mathit{C}\mathrm{H_3}$), 35.1 (s, $\mathrm{SC(}\mathit{C}\mathrm{H_3)_3}$), 41.8 (s, $\mathrm{N(}\mathit{C}\mathrm{H_3)_2}$), 45.2 (s, $\mathrm{S}\mathit{C}\mathrm{(CH_3)_3}$), 50.7 (s, $\mathrm{N}\mathit{C}\mathrm{H_2CH_3}$). IR (nujol, cm^{-1}): 1463 s, 1425 m, 1377 m, 1360 m, 1216 w, 1169 m, 1150 m, 1078 m, 1019 m, 999 m, 915 w, 820 w, 764 m, 582 s, 504 s, 412 w.

4.2.2. $\mathrm{[HNMe_2Et][Al(SC_6H_3Me_2\text{-}2,6)_4]}$ (2)

2,6-$\mathrm{Me_2C_6H_3SH}$ (0.3 cm^3, 2.26 mmol) was added dropwise to a solution of $\mathrm{[AlH_3(NMe_2Et)]}$ (0.3 cm^3, 2.26 mmol) in diethyl ether (15 cm^3) at room temperature. Evolution of hydrogen was observed and a white precipitate formed. The solvent was removed under vacuum yielding a white powder (0.39 g, 27% yield based on aluminium). The white powder was dissolved in $\mathrm{CH_2Cl_2}$ (~5 cm^3) and over a period of days at room temperature colourless crystals of **2** were formed. *Anal.* Calc. for $\mathrm{C_{36}H_{48}NS_4Al}$: C, 66.52; H, 7.44; N, 2.15. Found: C, 64.20; H, 6.72; N, 2.35. ^{1}H NMR ($\mathrm{CD_2Cl_2}$): δ 1.10 (t, $J = 11$ Hz, $\mathrm{HNCH_2C}\mathit{H}_3$), 1.17 (t, $J = 11$ Hz, $\mathrm{NCH_2C}\mathit{H}_3$), 2.14 (s, $\mathrm{SC_6H_3(C}\mathit{H}_3\mathrm{)_2\text{-}2,6}$), 2.34 (s, $\mathrm{SC_6H_3(C}\mathit{H}_3\mathrm{)_2\text{-}2,6}$), 2.45 (s, $\mathrm{N(C}\mathit{H}_3)_2$), 2.73 (s, $\mathrm{HN(C}\mathit{H}_3)_2$), 2.77 (q, $J = 19$ Hz, $\mathrm{HNC}\mathit{H}_2\mathrm{CH_3}$), 3.31 (q, $J = 19$ Hz, $\mathrm{NC}\mathit{H}_2\mathrm{CH_3}$), 6.86–7.01 (m, $\mathrm{SC_6}\mathit{H}_3\mathrm{(CH_3)_2\text{-}2,6}$), 7.70 (br, $\mathrm{N}\mathit{H}$). ^{13}C{^{1}H} NMR ($\mathrm{CD_2Cl_2}$): δ 6.0 (s, $\mathrm{NCH_2}\mathit{C}\mathrm{H_3}$), 9.9 (s, $\mathrm{HNCH_2}\mathit{C}\mathrm{H_3}$), 23.8 (s, $\mathrm{SC_6H_3\text{-}(}\mathit{CH}_3\mathrm{)_2\text{-}2,6}$), 24.1 (s, $\mathrm{SC_6H_3(}\mathit{CH}_3\mathrm{)_2\text{-}2,6}$), 42.7 (s, $\mathrm{N}\mathit{C}\mathrm{H_2\text{-}CH_3}$), 43.2 (s, $\mathrm{HN}\mathit{C}\mathrm{H_2CH_3}$), 51.8 (s, $\mathrm{N(}\mathit{C}\mathrm{H_3)_2}$), 54.0 (s, $\mathrm{HN(}\mathit{C}\mathrm{H_3)_2}$), 125.2 (s, m-$\mathrm{SC_6}\mathit{H}_3\mathrm{(CH_3)_2\text{-}2,6}$), 126.0 (s, m-$\mathrm{SC_6}\mathit{H}_3\mathrm{(CH_3)_2\text{-}2,6}$), 127.3 (s, *ipso*-$\mathrm{SC_6}\mathit{H}_3\mathrm{(CH_3)_2\text{-}2,6}$), 127.9 (s, *ipso*-$\mathrm{SC_6}\mathit{H}_3\mathrm{(CH_3)_2\text{-}2,6}$), 133.1 (s, p-$\mathrm{SC_6}\mathit{H}_3\mathrm{\text{-}(CH_3)_2\text{-}2,6}$), 136.2 (s, p-$\mathrm{SC_6}\mathit{H}_3\mathrm{(CH_3)_2\text{-}2,6}$), 142.7 (s, o-$\mathrm{SC_6}\mathit{H}_3\mathrm{(CH_3)_2\text{-}2,6}$)142.8 (s, o-$\mathrm{SC_6}\mathit{H}_3\mathrm{(CH_3)_2\text{-}2,6}$). IR (nujol, cm^{-1}): 3143 m, 1581 m, 1375 s, 1161 m, 1115 m, 1082 m, 1062 m, 1021 m, 988 s, 914 s, 812 m, 764 vs, 720 s, 586 s, 544 s, 469 s, 458 m, 442 w.

4.2.3. $\mathrm{[Al(SC_6H_3Me_2\text{-}2,6)_3(OEt_2)]}$ (3)

Following literature routes, [15] $\mathrm{AlCl_3}$ (0.22 g, 1.60 mmol) was dissolved in diethyl ether (10 cm^3) and added slowly to a stirred slurry of $\mathrm{LiAlH_4}$ (0.19 g, 5.0 mmol) in diethyl ether (15 cm^3). After stirring for 1 h, 2,6-$\mathrm{Me_2C_6H_3SH}$ (0.88 cm^3, 6.65 mmol) was added dropwise and the immediate evolution of hydrogen was observed. The resulting grey slurry was stirred at room temperature for 24 h. After filtering through celite the solvent was reduced in vacuo to ca. 5 cm^3 and cooled to −20 °C. After 24 h at this temperature colourless crystals of **3** formed (1.09 g, 28% yield based on aluminium, m.p. 103–104 °C). *Anal.* Calc. for $\mathrm{C_{28}H_{37}O_1S_3Al}$: C, 65.59; H, 7.27. Found C, 65.51; H, 7.41. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 1.12 (t, $J = 11$ Hz, 6H, $\mathrm{O(CH_2C}\mathit{H}_3)_2$), 1.35 (t, $J = 11$ Hz, 3H, $\mathrm{O(CH_2C}\mathit{H}_3)_2$), 2.25 (s, 18H, $\mathrm{SC_6H_3(C}\mathit{H}_3\mathrm{)_2\text{-}2,6}$), 3.42 (q, $J = 21$ Hz, 4H, $\mathrm{O(C}\mathit{H}_2\mathrm{CH_3)_2}$), 4.37 (q, $J = 21$ Hz, 2H, $\mathrm{O(C}\mathit{H}_2\mathrm{CH_3)_2}$), 6.77–6.95 (m, 9H, $\mathrm{SC_6}\mathit{H}_3\mathrm{(CH_3)_2\text{-}2,6}$). ^{13}C{^{1}H} NMR ($\mathrm{CDCl_3}$): δ 13.4 (s, $\mathrm{O(CH_2}\mathit{C}\mathrm{H_3)_2}$), 15.1 (s, $\mathrm{O(CH_2\text{-}}\mathit{C}\mathrm{H_3)_2}$), 23.6 (s, $\mathrm{SC_6H_3(}\mathit{C}\mathrm{H_3)_2\text{-}2,6}$), 65.8 (s, $\mathrm{O(}\mathit{C}\mathrm{H_2\text{-}CH_3)_2}$), 68.8 (s, $\mathrm{O(}\mathit{C}\mathrm{H_2CH_3)_2}$), 125.5 (s, m-$\mathrm{SC_6}\mathit{H}_3\mathrm{\text{-}(CH_3)_2\text{-}2,6}$), 127.5 (s, *ipso*-$\mathrm{SC_6}\mathit{H}_3\mathrm{(CH_3)_2\text{-}2,6}$), 132.4 (s, p-$\mathrm{SC_6}\mathit{H}_3\mathrm{(CH_3)_2\text{-}2,6}$), 142.0 (s, o-$\mathrm{SC_6}\mathit{H}_3\mathrm{(CH_3)_2\text{-}2,6}$). IR (KBr disc, cm^{-1}): 3057 m, 2977 m, 2922 w, 1460 s, 1436 m, 1371 m, 1323 w br, 1262 w, 1188 m, 1162 m, 1149 m, 1088 m, 1051 s, 1009 s, 989 m, 878 s, 831 w, 760 vs, 718 s, 588 m, 528 s, 496 s, 480 s, 413 m.

4.2.4. $\mathrm{[Li(OEt_2)_3][Al(SC_6H_3Me_2\text{-}2,6)_4]}$ (4)

Compound **4** was prepared using the same procedure described above for **3**, except that 2,6-$\mathrm{Me_2C_6H_3SH}$ was added immediately to the slurry of $\mathrm{LiAlH_4}$ and $\mathrm{AlCl_3}$. Colourless crystals of **4** formed from a concentrated diethyl ether solution at −20 °C (0.24 g, 10% yield based on aluminium, decomposed without melting below 230 °C). *Anal.* Calc. for $C_{44}H_{66}O_3S_4LiAl$: C, 65.63; H, 8.26. Found C, 63.71; H, 7.51. ^{1}H NMR ($CDCl_3$): δ 2.00 (t, $J = 14$ Hz, $O(CH_2CH_3)_2$), 2.27 (s, 24H, $SC_6H_3(CH_3)_2$-2,6), 3.53 (q, $J = 21$ Hz, 4H, $O(CH_2CH_3)_2$), 6.86–6.97 (m, 9H, $SC_6H_3(CH_3)_2$-2,6). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 14.8 (s, $O(CH_2CH_3)_2$), 23.8 (s, $SC_6H_3(CH_3)_2$-2,6), 66.0 (s, $O(CH_2CH_3)_2$), 125.0 (s, *m*-$SC_6H_3(CH_3)_2$-2,6), 127.1 (s, *ipso*-$SC_6H_3(CH_3)_2$-2,6), 134.8 (s, *p*-$SC_6H_3(CH_3)_2$-2,6), 142.3 (s, *o*-$SC_6H_3(CH_3)_2$-2,6). IR (KBr disc, cm^{-1}): 1583 w, 1303 w, 1257 w, 1161 m, 1092 m, 1051 s, 1022 m, 912 m, 838 w, 798 m, 771 s, 759 m, 587 m, 521 m, 492 m, 468 m, 436 m, 408 m.

4.3. *X-ray crystallography*

Crystals of **1**, **3** and **4** were grown from diethyl ether solutions at −20 °C and crystals of **2** were grown from CH_2Cl_2 at room temperature.

Crystal data for **1**: $C_{16}H_{38}NS_3Al$, $M = 367.6$, orthorhombic, *Pbca* (no. 61), $a = 11.668(1)$, $b = 16.626(1)$, $c = 22.468(2)$ Å, $V = 4358.5(5)$ Å^3, $Z = 8$, $D_{calc} = 1.121$ g cm^{-3}, μ (Cu Kα) = 3.45 mm^{-1}, $T = 183$ K, colourless prisms; 3226 independent measured reflections, F^2 refinement, $R_1 = 0.034$, $wR_2 = 0.076$, 2668 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max} = 120°$], 191 parameters. CCDC 194439.

4.3.1. *Crystal data for* **2**

$C_{32}H_{36}S_4Al \cdot C_4H_{12}N$, $M = 650.0$, triclinic, $P\bar{1}$ (no. 2), $a = 11.034(7)$, $b = 11.485(2)$, $c = 16.618(2)$ Å, $\alpha = 81.65(1)°$, $\beta = 74.18(2)°$, $\gamma = 62.92(1)°$, $V = 1804(1)$ Å^3, $Z = 2$, $D_{calc} = 1.197$ g cm^{-3}, μ (Cu Kα) = 2.83 mm^{-1}, $T = 183$ K, colourless blocks; 5091 independent measured reflections, F^2 refinement, $R_1 = 0.086$, $wR_2 = 0.232$, 3658 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max} = 120°$], 379 parameters. The somewhat high final value of *R* is a reflection of the poor quality of the crystals (including the presence of significant twinning) with consequent diffuse diffraction. CCDC 194438.

4.3.2. *Crystal data for* **3**

$C_{28}H_{37}OS_3Al \cdot Et_2O$, $M = 586.9$, monoclinic, $P2_1/c$ (no. 14), $a = 15.946(3)$, $b = 14.182(2)$, $c = 14.984(4)$ Å, $\beta = 104.13(1)°$, $V = 3286(1)$ Å^3, $Z = 4$, $D_{calc} = 1.186$ g cm^{-3}, μ (Mo Kα) = 0.28 mm^{-1}, $T = 183$ K, colourless prisms; 5780 independent measured reflections, F^2 refinement, $R_1 = 0.048$, $wR_2 = 0.105$, 4218 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max} = 50°$], 344 parameters. CCDC 194436.

Crystal data for **4**: $[C_{32}H_{36}S_4Al][C_{12}H_{30}O_3Li] \cdot C_4H_{10}O$, $M = 879.3$, tetragonal, $I\bar{4}$ (no. 82), $a = 12.186(1)$, $c = 17.693(3)$ Å, $V = 2627.3(4)$ Å^3, $Z = 2$ (S_4 symmetry), $D_{calc} = 1.111$ g cm^{-3}, μ (Cu Kα) = 2.11 mm^{-1}, $T = 183$ K, colourless tetrahedra; 1242 independent measured reflections, F^2 refinement, $R_1 = 0.042$, $wR_2 = 0.114$, 1130 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max} = 128°$], 224 parameters. The absolute structure of **4** was determined by a combination of *R*-factor tests [$R_1^+ = 0.0417$, $R_1^- = 0.0508$] and by use of the Flack parameter [$x^+ = -0.07(5)$]. Disorder was observed in both the included solvent diethyl ether molecule and in those coordinated to the lithium centre. CCDC 194437.

5. Supplementary material

Supplementary data are available from the CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK on request, quoting the deposition numbers CCDC 194436–194439 (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

We thank EPSRC for a studentship (J.D.M.).

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