Aluminium amides derived from metallation of N,N'-di-tert-butyl-ethylenediamine

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The metallation of N,N'-di-tert-butylethylenediamine by $AlH_3 \cdot NMe_3$ has been investigated and shown to proceed via the formation of the unstable secondary amine-stabilised amidoalane $[AlH_2(Bu^tNCH_2CH_2NBu^tH)]$. This compound reacted with an additional equivalent of $AlH_3 \cdot NMe_3$ to yield the dibridging amidoalane complex $[(AlH_2)_2\{\mu-N(Bu^t)CH_2CH_2N(Bu^t)\}]$ or a molecule of the diamine to give the triamidoaluminium species $[Al(Bu^tNCH_2CH_2NBu^t)(Bu^tNCH_2CH_2NBu^tH)]$. In the absence of an excess of $AlH_3 \cdot NMe_3$ or N,N'-di-tert-butylethylenediamine, $[AlH_2(Bu^tNCH_2CH_2NBu^tH)]$ eliminates molecular hydrogen to give the trans isomer of the dimeric diamidoalane complex trans-$[\{AlH[\mu-N(Bu^t)CH_2CH_2NBu^t]\}_2]$ which is stable toward reaction with either of the reactants. A stable analogue of the intermediate $[AlH_2(Bu^tNCH_2CH_2NBu^tH)]$ was made by replacing a hydride by a chloride, achieved by using $AlH_2Cl \cdot NMe_3$ as the metallating agent. The cis isomer of the dimeric diamidoalane cis-$[AlH\{[\mu-N(Bu^t)CH_2CH_2NBu^t]\}_2]$ was prepared from the unstable lithium diamido aluminium hydride species $[\{Li[N(Bu^t)CH_2CH_2NBu^t]AlH_2\}_n]$ via elimination of lithium hydride. The aluminium triamide and the cis and trans isomers of the dimeric aluminium diamide have been structurally authenticated.
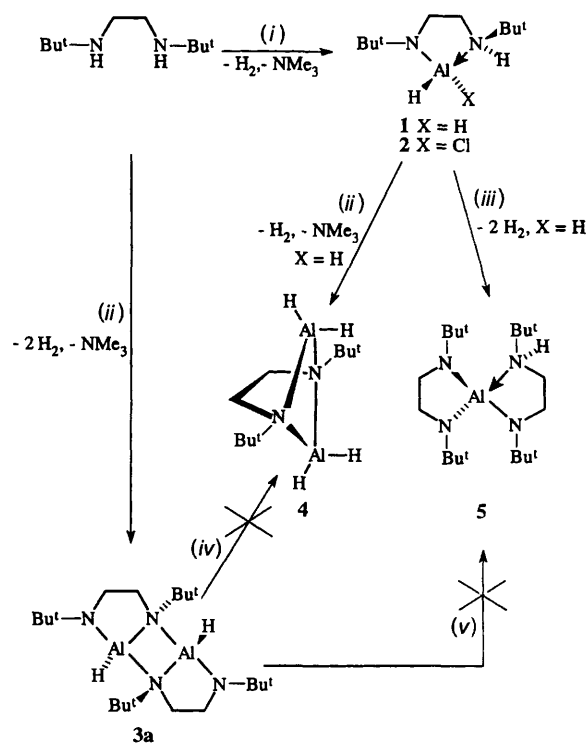
In recent publications we have reported our findings on the metallation and hydrometallation of various secondary amines and imines by some aluminium and gallium hydride sources, as an extension of our research on the reactivity of Group 13 metal hydrides.[1,2] We have focused attention on substituted ethylenediamines bearing Bu^t [3,4] and trimethylsilyl substituents at N,[5] 1,4-di-tert-butyl-1,4-diazabutadiene[6–10] and related 1,4-diazabut-1-enes,[11] as well as bulky monofunctional secondary amines.[12,13] In this paper we report the full details of the reaction of N,N'-di-tert-butylethylenediamine with $AlH_3 \cdot NMe_3$ including the mechanism of the formation of the various products, some aspects of which have been previously reported.[3]

Results and Discussion

Syntheses

N,N'-Di-tert-butylethylenediamine is readily metallated by $AlH_3 \cdot NMe_3$ affording three aluminium amide species, trans $[\{AlH[\mu-N(Bu^t)CH_2CH_2NBu^t]\}_2]$ **3a**,† $[(AlH_2)_2\{\mu-N(Bu^t)CH_2CH_2N(Bu^t)\}]$ **4** and $[Al(Bu^tNCH_2CH_2NBu^t)(Bu^tNCH_2CH_2NBu^tH)]$ **5** depending on the stoichiometry of the reaction, as outlined in Scheme 1.

The metallation of the substituted ethylenediamine proceeds via the formation of an unstable secondary amine-stabilised amidoalane $[AlH_2(Bu^tNCH_2CH_2NBu^tH)]$ **1**. Although this species could not be isolated, the preparation of a stable analogue was possible by replacement of a hydride with a chloride substituent on the aluminium centre. Using $AlH_2Cl \cdot NMe_3$ as the metallating agent, the chlorohydrido-species $[AlH(Cl)(Bu^tNCH_2CH_2NBu^tH)]$ **2** was isolated. This is only stable at low temperature and eliminates molecular hydrogen on warming to room temperature to give the dimeric diamidoaluminium hydride **3a** which is stable toward reaction
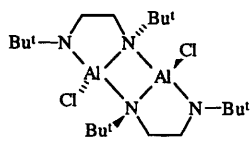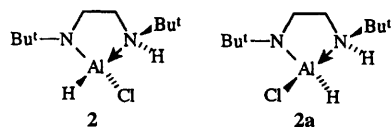
† The hydride $[\{AlH[\mu-N(Bu^t)CH_2CH_2NBu^t]\}_2]$ was incorrectly identified in ref. 3 as the amidoaluminium dihydride species $[AlH_2\{HN(Bu^t)CH_2CH_2NBu^t\}]$.

Scheme 1 (i) $AlH_2X \cdot NMe_3$, Et_2O, $-80\ ^\circ C$; (ii) $AlH_3 \cdot NMe_3$, Et_2O, $-80\ ^\circ C$; (iii) $HBu^tNCH_2CH_2NBu^tH$, $-80\ ^\circ C$; (iv) $AlH_3 \cdot NMe_3$, Et_2O, $25\ ^\circ C$; (v) $HBu^tNCH_2CH_2NBu^tH$, $25\ ^\circ C$

with either the substituted ethylenediamine or $AlH_3 \cdot NMe_3$ in diethyl ether at 25 °C. In contrast, the reaction of the ethylenediamine with 2 equivalents of $AlH_3 \cdot NMe_3$ in diethyl ether at $-80\ ^\circ C$ yields the bridging dialuminium diamide complex **4**. Increasing the amount of the ethylenediamine to 2 equivalents leads to the formation of the aluminium triamide species **5**.

Compounds **2**, **3a**, **4** and **5** were obtained as air- and

Bu^t—N   N$^{Bu^t}$
    Al   H
   H   Cl

2

Bu^t—N   N$^{Bu^t}$
    Al   H
   Cl   H

2a

Bu^t—N   N$^{Bu^t}$
          Cl
    Al   Al
   Cl   N—Bu^t
      N
    Bu^t

2b (*cis* or *trans* isomer)

moisture-sensitive colourless crystalline solids in high yield. Characterisation was achieved using ^{1}H and ^{13}C NMR, infrared spectroscopy, microanalysis and X-ray diffraction studies on all four compounds.[3]

The structurally authenticated chlorohydride species **2**[3] was obtained from a mixture of two compounds most likely to be diastereoisomers in hexane solution having different relative chiralities at both the metal and amine centres. The structure determination revealed a monomeric species with the bidentate monometallated ligand chelating a four-co-ordinate aluminium centre. The co-ordination environment of the aluminium comprises one hydride, one chloride, and N (amido) and N (amine) centres, with the chloride group and the N (amine) proton on the same side of the chelate ring. The decreased activity of the hydride in this chloride-substituted species relative to the dihydride **1** is responsible for its stability. The stability of the other enantiomer of the chlorohydride species, **2a**, may be considerably reduced relative to **2** given the aluminium hydride and the acidic secondary amine proton are on the same side of the chelate ring and may spontaneously eliminate hydrogen to form a chloroaluminium diamide. Owing to this, we also offer the alternative identity of the compound in the mixture as *cis*- or *trans*-[{AlCl[μ-N(Bu^t)CH$_2$CH$_2$NBu^t]}$_2$] **2b**. The results of the crystal structure determination of the chlorohydride species **2** provide a means of substantiating the structure of the unstable intermediate dihydride **1** in the metallation reaction of the substituted ethylenediamine with AlH$_3$·NMe$_3$.

Proton and ^{13}C NMR spectroscopic studies in benzene solution of the reaction mixture from which the chlorohydride species **2** was isolated are consistent with the presence of two compounds in solution, **2**, and **2a** or **2b**. The ^{13}C NMR resonances of the two compounds are more distinctive than those of the ^{1}H NMR spectra which are complex due to overlapping multiplet resonances. There are clearly four ^{13}C NMR resonances for both the methyl and quaternary carbons of the Bu^t groups and also four resonances which were assigned to the methylene carbons in the mixture. The infrared spectrum of the chlorohydride **2** displays an Al–H stretching absorption band at 1841 cm^{-1} in the region characteristic for alane amides.[14] An N–H stretching absorption at 3186 cm^{-1} confirms the formation of an intramolecularly co-ordinated secondary amine-complexed amidoaluminium hydride species. Satisfactory elemental analysis was obtained for the mixture of complexes **2**, and **2a** or **2b**.

Hydrogen elimination from the intermediate dihydride species **1** followed by association of the resulting monomers results in the formation of the aluminium diamide **3a** with bridging amido groups. The crystal structure determination of **3a** shows a dimeric species with C_i symmetry. The complex possesses a planar four-membered Al$_2$N$_2$ ring in which both aluminium centres are tetrahedrally co-ordinated. The bidentate dimetallated ethylenediamide ligands are positioned in a *trans* arrangement with respect to the planar Al$_2$N$_2$ core. The diamidogallium hydride obtained from the hydrogallation of 1,4-diisopropyl-1,4-diazabutadiene with GaH$_3$·NMe$_3$,
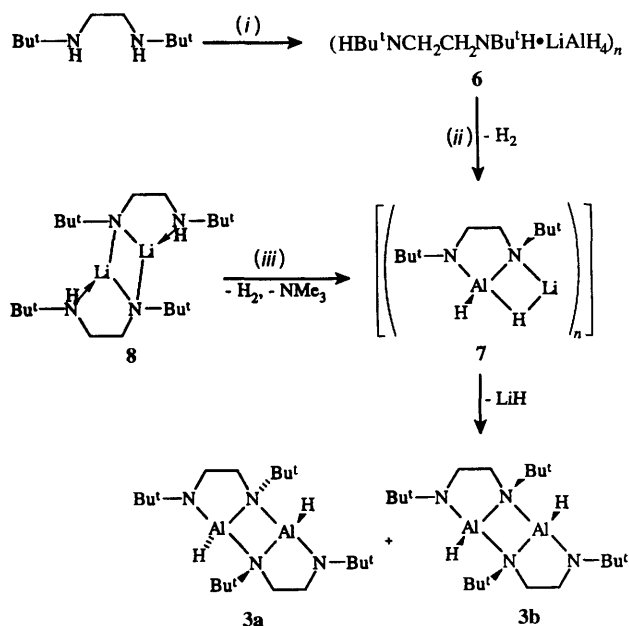
trans-[{GaH[μ-N(Pr^i)CH$_2$CH$_2$NPr^i]}$_2$], has a similar structure to that of **3a**.[9] The metallation of the less-hindered N,N'-diethylethylenediamine by AlH$_3$·NMe$_3$ gives the trialuminium species[15] [Al$_3$H$_5$(EtNCH$_2$CH$_2$NEt)$_2$] which has a similar structure to that of a gallium diamide [Ga$_3$H$_5$(MeNCH$_2$CH$_2$NMe)$_2$] also prepared by metallation of the ethylenediamine by GaH$_3$·NMe$_3$.[9]

The ^{1}H and ^{13}C NMR data of the aluminium diamide **3a** are consistent with the solid-state structure being retained in solution. The ^{1}H NMR spectrum shows the presence of two singlets at δ 1.30 and 1.32 of equal intensity corresponding to the protons of the Bu^t groups and two areas of unresolved multiplet resonances centred at δ 2.8 and 3.5 arising from the four inequivalent methylene protons. The hydride resonance was indistinguishable from the baseline which is typical for amidoaluminium hydride species. The ^{13}C NMR spectrum also supports a dimeric structure in solution with two separate resonances for the methyl protons of the Bu^t groups, the quaternary carbons and the methylene carbons. The infrared spectrum exhibits an absorption at 1840 cm^{-1} attributable to an Al–H stretching mode which is within the established range for aluminium amide species.

Treatment of isolated samples of the aluminium diamide **3a** with either AlH$_3$·NMe$_3$ or the substituted ethylenediamine in diethyl ether at 25 °C resulted in the recovery of **3a** and no evidence of the formation of either the dialuminium diamide **4** or the aluminium triamide **5**. This lack of reaction of **3a** further implicates the unstable amidoaluminium dihydride **1** as an intermediate in the formation of **4** or **5**. The aluminium diamide **3a** has high thermal stability, having a melting point of 198 °C, decomposing only above 292 °C to an orange oil.

The reaction of the substituted ethylenediamine with 2 equivalents of AlH$_3$·NMe$_3$ yields the dialuminium diamide species **4**. The formation of compound **4** most likely proceeds *via* the intermediate amidoaluminium dihydride species **1** which then binds AlH$_3$·NMe$_3$ or AlH$_3$ at the amido-centre prior to the metallation of the secondary amine. The diminished steric hindrance of the ethylenediamine relative to the C-alkylated substituted amines **1**, N,N'-tri-*tert*-butyl- and *rac*-N,N'-di-*tert*-butyl-1,2-dimethyl-ethylenediamine facilitates the second metallation by AlH$_3$·NMe$_3$ to give dialuminium amides. In those cases the reactivity of the amidoaluminium dihydride is reduced and the additional equivalent of AlH$_3$·NMe$_3$ is converted into AlH$_3$·2NMe$_3$ which is slow to react with the ethylenediamines.[4] The gallium analogue of **4**, [(GaH$_2$)$_2${μ-N(Bu^t)CH$_2$CH$_2$N-(Bu^t)}], has been prepared by the hydrometallation pathway involving 1,4-di-*tert*-butyl-1,4-diazabutadiene and GaH$_3$·NMe$_3$.[7] The crystal structure determination of the dialuminium diamide **4** reveals a monomeric species of pseudo-C_{2v} symmetry with a butterfly-shaped Al$_2$N$_2$ ring. The AlH$_2$ units form a dibridging structure which attains a four-fold co-ordination environment for the aluminium centres, analogous to that in the gallium complex.[7]

The ^{1}H and ^{13}C NMR spectra of the dialuminium diamide **4** in benzene solution support the existence of a symmetrical molecule. The ^{1}H NMR spectrum displays a single resonance at δ 1.06 corresponding to the protons of the Bu^t groups and a singlet at δ 2.78 attributable to the methylene protons. The hydride resonance at δ 4.30 is characteristic of aluminium hydride species. The ^{1}H NMR data for the gallium analogue show inequivalent gallium hydride resonances corresponding to an AB spin system for the chemically distinct hydride groups on each gallium centre.[7] However, **4** displays only one broad hydride resonance rather than an AB spin system. The infrared spectrum shows two strong broad absorption bands at 1752 and 1860 cm^{-1} consistent with symmetric and antisymmetric aluminium hydride stretching modes for the AlH$_2$ unit. Similar Ga–H bands were observed for the gallium analogue at 1870 and 1920 cm^{-1}.[7] Compound **4** displays high thermal stability, decomposing above 215 °C after melting at 136–137 °C.

Bu^t—N(H)—CH_2CH_2—N(H)—Bu^t $\xrightarrow{(i)}$ $(HBu^tNCH_2CH_2NBu^tH{\cdot}LiAlH_4)_n$ **6**

$(ii) \downarrow -H_2$

8 $\xrightarrow[-H_2, -NMe_3]{(iii)}$ **7**

$\downarrow -LiH$

3a + **3b**

Scheme 2 (*i*) $LiAlH_4$, Et_2O, $-80\,°C$; (*ii*) C_6D_6, $50\,°C$, 1 d; (*iii*) $AlH_3{\cdot}NMe_3$, Et_2O, $-80\,°C$

The formation of the aluminium triamide **5** results from the reaction of 2 equivalents of the substituted ethylenediamine with $AlH_3{\cdot}NMe_3$ in diethyl ether at $-80\,°C$. The crystal structure determination revealed a monomeric species possessing a central four-co-ordinate aluminium centre devoid of hydrides. The aluminium is co-ordinated by two bidentate ligands with one having both acidic protons removed and the other having one remaining amine proton. Spectroscopic data support the identity of the compound with the ^1H NMR spectrum displaying four inequivalent Bu^t proton resonances and complex splitting patterns for the methylene proton resonances. The broad resonance at δ 1.62 can be assigned to the co-ordinated secondary amine proton. The N–H absorption stretch for the secondary amine occurs at $3246\,cm^{-1}$ and there is no Al–H absorbance present confirming the removal of all of the hydride substituents.

The dimeric diamidoaluminium hydrides **3a** and **3b** have subsequently been prepared *via* an alternative metallation reaction of the lithium amide *cis*-[{Li[μ-N(Bu^t)CH₂CH₂-NBu^tH]}₂] **8** by $AlH_3{\cdot}NMe_3$, as shown in Scheme 2. The aluminium diamides were obtained as a *ca.* 9:1 ratio of *cis*:*trans* isomers which are not interconvertible in diethyl ether. In contrast, **3a** was obtained solely as the *trans* isomer according to the reaction in Scheme 1.

The crystal structure determination of compound **3b** shows a dimeric species with C_2 symmetry. The complex possesses a planar four-membered Al_2N_2 ring in which both aluminium centres are tetrahedrally co-ordinated. The bidentate dimetallated ethylenediamine ligands are positioned in a *cis* arrangement with respect to the planar Al_2N_2 core. The ^1H and ^{13}C NMR data for the aluminium diamide **3b** are consistent with the solid-state structure being retained in solution. The ^1H NMR spectrum shows the presence of two singlets at δ 1.29 and 1.32 of equal intensity corresponding to the protons of the Bu^t groups and three areas of unresolved multiplet resonances centred at δ 2.8, 3.0 and 4.0 arising from the four inequivalent methylene protons. The hydride resonance was indistinguishable from the baseline which is typical for amidoaluminium hydride species. The ^{13}C NMR spectrum also supports a dimeric structure in solution with two separate resonances for the methyl protons of the Bu^t groups, the quaternary carbons and the methylene carbons. The infrared spectrum exhibits an absorption at $1843\,cm^{-1}$ attributable to an Al–H stretching

mode which is within the established range for four-co-ordinate aluminium amides and similar to that of the *trans* isomer **3a**.

The two dimeric aluminium diamide isomers **3a** and **3b** are not interconvertible in Et_2O at room temperature over several weeks. Treatment of isolated samples of **3b** with either $AlH_3{\cdot}NMe_3$ or the substituted ethylenediamine in diethyl ether at $25\,°C$ resulted in the recovery of **3b** and no formation of either the dialuminium diamide **4** or the aluminium triamide **5**. This lack of reactivity of **3b** and the absence of any **3b** being formed in the reactions of the ethylenediamine with $AlH_3{\cdot}NMe_3$ shows that **3b** is not involved in the reaction mechanism for the formation of **3a**, **4** or **5**. The aluminium diamide **3b** is much less stable than the *trans* isomer **3a**, decomposing above $115\,°C$ to an orange oil after melting at 75–$77\,°C$, possibly due to the *cis* arrangement of the hydrides with respect to the Al_2N_2 ring facilitating further decomposition.

Presumably, the formation of the diamidoaluminium hydride **3b** from the reaction of the lithium amide **8** with $AlH_3{\cdot}NMe_3$ proceeds *via* unstable lithium diamide–aluminium dihydride $[\{Li[N(Bu^t)CH_2CH_2NBu^t]AlH_2\}_n]$ **7**, which eliminates LiH to give **3b**. In contrast the tetrameric C-alkylated analogue of **7**, $[\{Li[N(Bu^t)CH(Bu^t)CH_2NBu^t]AlH_2\}_4]$, is stable to above $115\,°C$, which can be accounted for by the added steric bulk of the ethylenediamine in that case.[4,11] The aluminium diamides **3a** and **3b** were also prepared from the thermal decomposition of an adduct of the substituted ethylenediamine and $LiAlH_4$, $(HBu^tNCH_2CH_2NBu^tH{\cdot}Li-AlH_4)_n$, **6**, in benzene solution which presumably initially involves elimination of hydrogen by metallation of the secondary amines to give **7** which then spontaneously further eliminates LiH to give **3a** and **3b**. Given that the latter do not interconvert in diethyl ether and the *cis* isomer **3b** is not formed from the reaction of the substituted ethylenediamine with $AlH_3{\cdot}NMe_3$, the decomposition of **7** must involve an oligomer which assembles into the *cis* isomer **3b** as a consequence of the structure of **7**. The adduct **6** was obtained as an insoluble white powder which slowly decomposes in benzene solution at room temperature over several weeks or overnight at $50\,°C$. The insolubility is in contrast to the behaviour of the related dimeric ethylenediamine[4] and 1,4-diazabut-1-ene[11] adducts $[\{[HBu^tNCH(Bu^t)CH_2NBu^tH]-Li(\mu-H)_2AlH_2\}_2]$ and $[\{[HBu^tNCH(Bu^t)CHNBu^t]Li(\mu-H)_2-AlH_2\}_2]$[16] which are highly soluble. Presumably the less bulky ethylenediamine results in the adduct forming some higher oligo- or poly-meric structure in the solid state or the compound is ionic. Attempts to characterise this compound were unsuccessful.

Crystal structures

The structure determinations of the chloroaluminium amide **2** and the dibridging amidoalane compound **4** were described in our previous communication[3] and will not be described here.

Compounds 3a and 3b. Compound **3a** crystallises as prismatic crystals in the monoclinic space group $P2_1/n$ with two molecules in the unit cell, the asymmetric unit comprising one half of a centrosymmetric dimeric molecule, Fig. 1. Compound **3b** crystallises as prismatic crystals in the monoclinic space group $P2_1/c$ with four molecules in the unit cell, the asymmetric unit comprising one discrete molecule, Fig. 2. It has non-crystallographic C_2 symmetry. The aluminium centres achieve four-fold co-ordination by binding to a terminal hydride atom.

Compounds **3a** and **3b** are best described as centrosymmetric and C_2 symmetric nitrogen-bridged diamidoaluminium hydride dimers, respectively, containing planar Al_2N_2 four-membered ring systems with tetrahedrally co-ordinated aluminium centres. The dimetallated ethylenediamines act as bidentate ligands to one aluminium atom and bridge the other aluminium atom through one of the amido-nitrogen centres giving it both
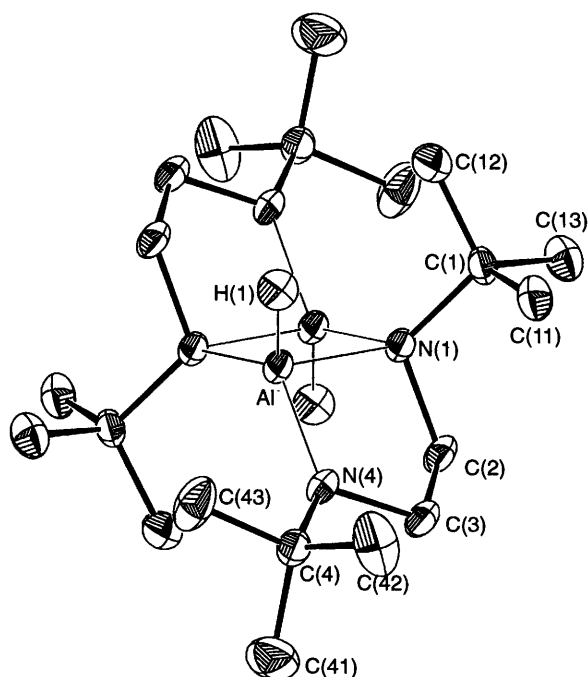
Fig. 1 Molecular structure of *trans*-[{AlH[μ-N(Buᵗ)CH₂CH₂N-Buᵗ]}₂] **3a**, showing the atom labelling scheme. Thermal ellipsoids are drawn at the 20% probability level. For clarity methyl and methylene hydrogen atoms are omitted
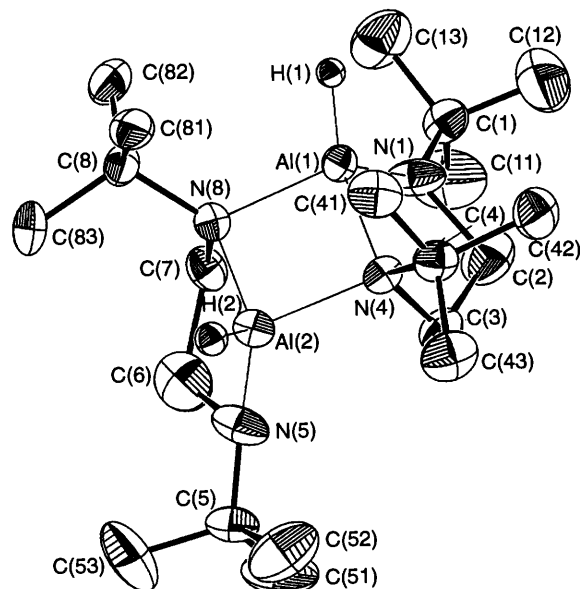
Fig. 2 Molecular structure of *cis*-[{AlH[μ-N(Buᵗ)CH₂CH₂NBuᵗ]}₂] **3b**, showing the atom labelling scheme. Details as in Fig. 1

three- and four-co-ordinate nitrogen centres. Oligomerisation of aluminium amides *via* nitrogen bridging to form dimers and trimers is common with four-membered Al₂N₂ rings being favoured for bulky amines. Four-fold co-ordination of the aluminium centres in **3a** and **3b** is achieved by one hydride, two bridging amido-nitrogen centres and a terminally bound amido-nitrogen, giving a distorted tetrahedral N (terminal amide)N (dibridging amide)₂H environment.

Selected geometrical parameters are given in Tables 1 and 2. The Al–N bond distances vary considerably, with those between the terminally bound amido-nitrogens and the aluminium atoms of 1.781(7) (**3a**) and 1.756(9) and 1.766(8) Å (**3b**) being much shorter than the cyclic ones of 1.960(6) and 1.968(7) (**3a**) and 1.944(7)–1.981(7) Å (**3b**) as expected for a terminal sp²-hybridised nitrogen centre. The latter are close to the established range for bridging amides, for example,

Table 1 Selected bond lengths (Å) and angles (°) for *trans*-[{AlH-[μ-N(Buᵗ)CH₂CH₂NBuᵗ]}₂] **3a**

Al–N(1)	1.960(6)	N1–C(2)	1.509(9)
Al–N(4)	1.781(7)	C(2)–C(3)	1.53(1)
Al–N(1ⁱ)	1.968(7)	N(4)–C(3)	1.468(9)
Al–H(1)	1.39(7)	N(4)–C(4)	1.47(1)
N(1)–C(1)	1.54(1)		
N(1)–Al–N(4)	94.6(3)	C(1)–N(1)–C(2)	114.1(5)
N(1ⁱ)–Al–N(4)	125.0(3)	C(1)–N(1)–Alⁱ	122.2(5)
N(1)–Al–N(1ⁱ)	86.8(3)	C(2)–N(1)–Alⁱ	104.9(5)
N(1)–Al–H(1)	109(3)	Al–N(4)–C(3)	112.1(5)
N(4)–Al–H(1)	112(3)	Al–N(4)–C(4)	132.7(5)
N(1ⁱ)–Al–N(1)	119(3)	C(3)–N(4)–C(4)	113.8(6)
Al–N(1)–C(1)	118.7(5)	N(1)–C(2)–C(3)	114.7(6)
Al–N(1)–C(2)	99.9(4)	N(4)–C(3)–C(2)	108.8(6)
Al–N(1)–Alⁱ	93.2(2)		

Symmetry relation: I −*x*, 1 − *y*, 1 − *z*.

Table 2 Selected bond lengths (Å) and angles (°) for *cis*-[{AlH-[μ-N(Buᵗ)CH₂CH₂NBuᵗ]}₂] **3b**

Al(1)–N(1)	1.766(8)	N(1)–C(2)	1.54(1)
Al(1)–N(4)	1.951(7)	N(4)–C(3)	1.50(1)
Al(1)–N(8)	1.958(7)	N(4)–C(4)	1.50(1)
Al(1)–H(1)	1.42(6)	N(5)–C(5)	1.42(1)
Al(2)–N(4)	1.944(7)	N(5)–C(6)	1.58(2)
Al(2)–N(5)	1.756(9)	N(8)–C(7)	1.50(1)
Al(2)–N(8)	1.981(7)	N(8)–C(8)	1.53(1)
Al(2)–H(2)	1.54(6)	C(2)–C(3)	1.61(1)
N(1)–C(1)	1.40(1)	C(6)–C(7)	1.60(2)
N(1)–Al(1)–N(4)	97.8(4)	Al(1)–N(4)–C(4)	119.8(6)
N(1)–Al(1)–N(8)	115.8(4)	Al(2)–N(4)–C(3)	108.1(6)
N(1)–Al(1)–H(1)	120(2)	Al(2)–N(4)–C(4)	119.5(6)
N(4)–Al(1)–N(8)	89.1(3)	C(3)–N(4)–C(4)	112.1(7)
N(4)–Al(1)–H(1)	121(2)	Al(2)–N(5)–C(5)	136.9(8)
N(8)–Al(1)–H(1)	110(2)	Al(2)–N(5)–C(6)	105.4(8)
N(4)–Al(2)–N(5)	112.7(4)	C(5)–N(5)–C(6)	112(1)
N(4)–Al(2)–N(8)	88.7(3)	Al(1)–N(8)–Al(2)	90.2(3)
N(4)–Al(2)–H(2)	113(2)	Al(1)–N(8)–C(7)	107.4(5)
N(5)–Al(2)–N(8)	98.7(4)	Al(1)–N(8)–C(8)	120.5(6)
N(5)–Al(2)–H(2)	118(2)	Al(2)–N(8)–C(7)	103.2(6)
N(8)–Al(2)–H(2)	121(2)	Al(2)–N(8)–C(8)	118.4(6)
Al(1)–N(1)–C(1)	136.8(8)	C(7)–N(8)–C(8)	113.8(7)
Al(1)–N(1)–C(2)	108.1(7)	N(1)–C(2)–C(3)	109(1)
C(1)–N(1)–C(2)	112(1)	N(4)–C(3)–C(2)	110.8(8)
Al(1)–N(4)–Al(2)	91.5(3)	N(5)–C(6)–C(7)	111(1)
Al(1)–N(4)–C(3)	103.2(5)	N(8)–C(7)–C(6)	109.4(8)

[(Me₂NAlH₂)₃][17] 1.936(3) Å and [{CH₂[CH₂C(H)Me]₂-NAlH₂}₂][18] 1.952(3) Å. The former compare well to the Al–N bond distances in monomeric aluminium triamides possessing terminally bound amide ligands, for example, [Al{N-(SiMe₃)₂}₃][19] 1.78(2) Å and [Al(NPrⁱ₂)₃][20] 1.79(5) Å. The distortion from the tetrahedral environment of the aluminium atoms is noted from the acute N–Al–N ligand bite angles of 94.6(3) (**3a**) and 97.8(4) and 98.7(4)° (**3b**), N–Al–N angles within the Al₂N₂ rings of 86.8(3) (**3a**) and 89.1(3) and 88.7(3)° (**3b**), and the large exocyclic N–Al–N angles of 125.0(3) (**3a**) and 115.8(4) and 112.7(4)° (**3b**). Other bond angles within the molecules are unexceptional.

Compound 5. Compound **5** crystallises as prismatic crystals in the monoclinic space group C2/c with four molecules in the unit cell, the asymmetric unit comprising one half of a molecule, Fig. 3. It was shown to be monomeric exhibiting a central four-co-ordinate aluminium centre in a distorted-tetrahedral N (amido)₃N (amine) environment. The mono- and di-metallated ethylenediamine ligands chelate the aluminium centre.

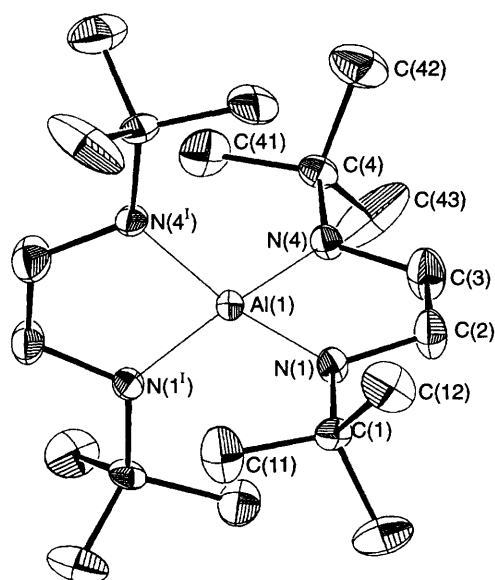Compound **5** has crystallographic C₂ symmetry which implies a disorder of the unique amine nitrogen centre over at

Fig. 3 Molecular structure of disordered [Al(Bu^{t}NCH$_2$CH$_2$NBu^t)-(Bu^{t}NCH$_2$CH$_2$NBu^{t}H)] **5** showing the atom labelling scheme. Thermal ellipsoids are drawn at the 50% probability level. For clarity hydrogen atoms are omitted

Table 3 Selected bond lengths (Å) and angles (°) for [Al(Bu^{t}NCH$_2$-CH$_2$NBu^t)(Bu^{t}NCH$_2$CH$_2$NBu^{t}H)] **5**

Al(1)–N(1)	1.850(5)	N(4)–C(3)	1.41(1)
Al(1)–N(4)	1.870(5)	N(4)–C(4)	1.466(7)
N(1)–C(1)	1.455(7)	C(2)–C(3)	1.45(1)
N(1)–C(2)	1.43(1)		
N(1)–Al(1)–N(1^I)	120.0(3)	C(1)–N(1)–C(2)	116.6(5)
N(1)–Al(1)–N(4)	91.5(2)	Al(1)–N(4)–C(3)	108.5(4)
N(1)–Al(1)–N(4^I)	119.3(2)	Al(1)–N(4)–C(4)	133.3(5)
N(4)–Al(1)–N(4^I)	117.8(3)	C(3)–N(4)–C(4)	118.2(6)
Al(1)–N(1)–C(1)	134.4(5)	N(1)–C(2)–C(3)	114.6(7)
Al(1)–N(1)–C(2)	109.1(4)	N(4)–C(3)–C(2)	115.7(7)

Symmetry relation: I 1 − x, y, $\frac{3}{2}$ − z.

least two positions and is extended to all four nitrogen centres here. The structure was also refined in the acentric space group *Cc*, however the disorder was also present and correlation problems are problematic to the refinement and lead to higher final residuals. As a consequence of the disorder, the Al–N distances are midway between those expected for the covalent and dative bonds and approximately planar co-ordination geometries [Σ(C–N–Al,C) = 360°]. The disorder also accounts for the large thermal parameters of the ligand atoms in the − 100 °C data set. The structure is analogous to that of the trimethylsilyl-substituted analogue [Al(Me$_3$SiNCH$_2$CH$_2$-NSiMe$_3$){Me$_3$SiNCH$_2$CH$_2$N(SiMe$_3$)H}], however that structure is not disordered, crystallising in the space group *C2/c* and exhibits distinct Al–N distances for the amide and amine nitrogen centres.[5]

Selected geometrical parameters are given in Table 3. The Al–N bond distances of 1.850(5) and 1.870(5) Å can be compared to the terminal Al–N (amide) distances in [CH$_2$(CH$_2$CMe$_2$)$_2$-NAlH$_2$·NMe$_3$][13] 1.838(2) Å, **2** 1.80(1) Å, [{Al(μ-H)[N(C-Me$_2$CH$_2$)$_2$CH$_2$]$_2$}$_2$][18] 1.836(3) Å and [{[(Me$_3$Si)$_2$N]HAl(μ-H)$_2$Li(OEt$_2$)$_2$}$_2$][21] 1.857(8) Å, and the Al–N (amine) distances in [AlH$_3$·HN(CH$_2$CMe$_2$)$_2$CH$_2$][13] 2.04(1) Å and **2** 2.00(1) Å. The Al–N (amine) bond distance in the trimethylsilyl-substituted analogue [Al(Me$_3$SiNCH$_2$CH$_2$NSiMe$_3$){Me$_3$-SiNCH$_2$CH$_2$N(SiMe$_3$)H}] was found to be 2.004(5) Å and the Al–N (amide) bond distances average to 1.815(9) Å.[5] Other bond angles within the molecule are unexceptional.

Conclusion

The reaction of *N*,*N*′-di-*tert*-butylethylenediamine with AlH$_3$·NMe$_3$ yields a number of aluminium amides depending on the stoichiometry of the reaction. The reaction proceeds *via* an unstable intermediate [AlH$_2$(Bu^{t}NCH$_2$CH$_2$NBu^{t}H)] **1**, which in the absence of either of the starting materials eliminates hydrogen to yield the dimeric aluminium diamide *trans*-[{AlH[μ-N(Bu^t)CH$_2$CH$_2$NBu^t]}$_2$] **3a**. In the presence of an equivalent of either the ethylenediamine or AlH$_3$·NMe$_3$ this intermediate yields [Al(Bu^{t}NCH$_2$CH$_2$NBu^t)(Bu^{t}NCH$_2$CH$_2$N-Bu^{t}H)] **5** or [(AlH$_2$)$_2${μ-N(Bu^t)CH$_2$CH$_2$N(Bu^t)}] **4**, respectively, by either metallating the ethylenediamine or by metallation of the remaining acidic secondary amine proton of the aluminium amide **1** by AlH$_3$·NMe$_3$. Replacement of a hydride on the aluminium centre leads to stabilisation of the intermediate aluminium amide **1**, [AlH(Cl)(Bu^{t}NCH$_2$CH$_2$N-Bu^{t}H)] **2** being isolated from the reaction of the ethylenediamine with AlH$_2$Cl·NMe$_3$. The preparation of the dimeric *cis*-[{AlH[μ-N(Bu^t)CH$_2$CH$_2$NBu^t]}$_2$] **3b** was achieved *via* metallation of the secondary amine-functionalised lithium amide *cis*-[{Li[μ-N(Bu^t)CH$_2$CH$_2$NBu^{t}H]}$_2$] **8** by AlH$_3$·NMe$_3$ and also by thermal decomposition of the adduct (HBu^{t}NCH$_2$CH$_2$N-Bu^{t}H·LiAlH$_4$)$_n$ **6**.

Experimental

All manipulations were carried out using standard Schlenk and glove-box techniques under an atmosphere of high-purity argon. Solvents were dried then freeze–thaw degassed prior to use. *N*,*N*′-Di-*tert*-butylethylenediamine,[22] *cis*-[{Li[μ-N(Bu^t)CH$_2$CH$_2$NBu^t(H)]}$_2$][23] and AlH$_3$·NMe$_3$[24] were prepared according to literature procedures, distilled and sublimed, respectively, under reduced pressure before use. The compound AlH$_2$Cl·NMe$_3$ was prepared by the addition of HgCl$_2$ to AlH$_3$·NMe$_3$ and sublimed prior to use. All other reagents were obtained from Aldrich. Lithium aluminium hydride was recrystallised from diethyl ether before use. Proton NMR spectra were recorded on a Varian Gemini-200 spectrometer in deuteriated benzene or toluene and referenced to the residual ^{1}H resonances of the solvent (δ 7.15 or 6.98), ^{13}C NMR spectra in deuteriated benzene on a Varian Gemini-200 spectrometer operating at 50.3 MHz using broad-band proton decoupling and referenced to the ^{13}C resonance of the solvent (δ 128.00). Elemental analyses were performed by the Chemical and Micro Analytical Services Pty. Ltd., Melbourne. Melting points were determined in sealed glass capillaries under argon and are uncorrected. Infrared spectra were recorded as thin films or Nujol mulls on NaCl plates, as appropriate, using a Perkin-Elmer 1725X Fourier-transformed spectrometer. Unless detailed in the following sections, the reactions described were conducted in sealable NMR tubes under an atmosphere of argon using glove-box techniques. The general procedure adopted for the NMR reactions was portionwise addition of the substrate (*ca.* 20 mg) to a (C$_2$D$_5$)$_2$O, C$_6$D$_6$ or CD$_3$C$_6$D$_5$ solution of the aluminium hydride reagent at 0 °C. Thermal stability investigations were carried out by heating a prepared NMR sample of the compound in a sealed NMR tube at the described temperature. The products from the NMR reactions/thermal decompositions were identified by spectroscopic comparison with authentic samples.

Syntheses

[AlH(Cl)(Bu^{t}NCH$_2$CH$_2$NBu^{t}H)] 2. *N*,*N*′-Di-*tert*-butylethyl-enediamine (0.26 g, 1.51 mmol) was added to a solution of AlH$_2$Cl·NMe$_3$ (0.19 g, 1.54 mmol) in diethyl ether (40 cm^3) at −80 °C. The reaction mixture was stirred at −80 °C for 2 h and then warmed to room temperature and stirred for 3 h. The solution was filtered and the volatiles were removed *in vacuo*.

The white product was recrystallised from hexane (15 cm³) on storing at −30 °C for 10 d (0.23 g, 65%), m.p. 114–115 °C, 265 °C (decomp.) (Found: C, 51.0; H, 10.3; Cl, 15.3; N, 11.9. $C_{10}H_{24}AlClN_2$ requires C, 51.2; H, 10.3; Cl, 15.1; N, 11.9%); $\tilde{v}_{max}/cm^{-1}$ (Nujol) 3186m (NH), 1841 (br) (AlH); $\delta_H(C_6D_6)$ 0.84, 0.87 (9 H, s, CH₃), 1.38, 1.39 (9 H, s, CH₃), 2.06 (2 × 1 H, br, NH) and 2.32, 2.70 (2 × 4 H, m, CH₂); $\delta_C(C_6D_6)$ 27.5, 27.7, 30.2, 30.5 (CCH_3), 41.4, 42.4, 44.2, 44.9 (CH₂) and 51.0, 51.3, 54.9, 55.9 (CCH_3).

trans-[{AlH[μ-N(Buᵗ)CH₂CH₂NBuᵗ]}₂] 3a. N,N'-Di-tert-butylethylenediamine (0.75 g, 4.39 mmol) was added to a solution of AlH₃·NMe₃ (0.39 g, 4.39 mmol) in Et₂O (40 cm³) at −80 °C. After 1 h at ca. 20 °C the solution was filtered and concentrated in vacuo to ca. 20 cm³ affording colourless crystals after 7 d at −26 °C (0.74 g, 85%), m.p. 198 °C, 292 °C (decomp.) (Found: C, 60.1; H, 12.4; N, 14.1. $C_{20}H_{46}Al_2N_4$ requires C, 60.6; H, 11.7; N, 14.1%); $\tilde{v}_{max}/cm^{-1}$ (Nujol) 1840 (br) (AlH); $\delta_H(C_6D_6)$ 1.30, 1.32 (2 × 18 H, s, CH₃), 2.8 (2 × 3 H, m, CH₂) and 3.5 (2 × 1 H, m, CH₂); $\delta_C(C_6D_6)$ 29.9, 31.1 (CCH_3), 45.4, 45.8 (CH₂) and 51.7, 55.5 (CCH_3).

cis-[{AlH[μ-N(Buᵗ)CH₂CH₂NBuᵗ]}₂] 3b. To a stirred solution of cis-[{Li[μ-N(Buᵗ)CH₂CH₂NBuᵗH]}₂] 8 (0.50 g, 1.41 mmol) in diethyl ether (10 cm³) was added dropwise a diethyl ether (5 cm³) solution of AlH₃·NMe₃ (0.25 g, 2.81 mmol) over 5 min at −50 °C. The colourless solution was allowed to warm to room temperature during which time gas evolution commenced; it was left to stir overnight after which time gas evolution had ceased. The solution was filtered and volatiles were removed in vacuo to yield a paste, from which 3a and 3b were sublimed under reduced pressure (10⁻¹ mmHg, ca. 13.3 Pa) at 140 °C. The sublimate comprised ca. 90% 3b. Toluene (5 cm³) was added, the solution filtered, concentrated in vacuo and cooled to −30 °C, whereupon colourless prisms of 3a deposited overnight (0.03 g, 7%), m.p. 192 °C (Found: C, 59.9; H, 12.6; N, 15.4. Calc. for $C_{20}H_{46}Al_2N_4$: C, 60.6; H, 11.7; N, 14.1%); this product was spectroscopically identical to that of the previous independent synthesis. Subsequent cropping of the crystals yielded crystals of 3b (0.34 g, 76%), m.p. 75–77 °C, 115 °C (decomp.) (Found: C, 58.0; H, 11.5; N, 14.2. $C_{20}H_{46}Al_2N_4$ requires C, 60.6; H, 11.7; N, 14.1%); $\tilde{v}_{max}/cm^{-1}$ (Nujol) 1843 (br) (AlH); $\delta_H(C_6D_6)$ 1.29, 1.32 (2 × 18 H, s, CH₃), 2.8 (2 × 2 H, m, CH₂), 3.0 (2 × 1 H, m, CH₂) and 4.0 (2 × 1 H, m, CH₂); $\delta_C(C_6D_6)$ 29.4, 31.0 (CCH_3), 45.4, 46.9 (CH₂) and 51.1, 56.4 (CCH_3).

[(AlH₂)₂{μ-N(Buᵗ)CH₂CH₂N(Buᵗ)}] 4. N,N'-Di-tert-butylethylenediamine (0.15 g, 0.84 mmol) in diethyl ether (10 cm³) was added to a solution of AlH₃·NMe₃ (0.15 g, 1.69 mmol) in diethyl ether (20 cm³) over 15 min at −80 °C. After 2 h at room temperature the solution was filtered and concentrated in vacuo to ca. 10 cm³ affording colourless crystals on storing at −30 °C for 3 d (0.11 g, 60%), m.p. 136–137 °C, 215 °C (decomp.) (Found: C, 49.7; H, 11.0; N, 13.0. $C_{20}H_{46}Al_2N_4$ requires C, 52.6; H, 11.5; N, 12.3%); $\tilde{v}_{max}/cm^{-1}$ (Nujol) 1860 (br), 1752 (br) (AlH); $\delta_H(C_6D_6)$ 1.06 (18 H, s, CH₃), 2.78 (4 H, s, CH₂) and 4.30 (4 H, br, AlH₂); $\delta_C(C_6D_6)$ 29.3 (CCH_3), 39.1 (CH₂) and 52.1 (CCH_3).

[Al(BuᵗNCH₂CH₂NBuᵗ)(BuᵗNCH₂CH₂NBuᵗH)] 5. N,N'-Di-tert-butylethylenediamine (0.78 g, 4.49 mmol) was added to a solution of AlH₃·NMe₃ (0.20 g, 2.25 mmol) in diethyl ether (50 cm³) at −80 °C. After 30 min at −80 °C then 2.5 h at ca. 20 °C the solution was filtered and volatiles were removed in vacuo. The pale yellow powder was recrystallised from hexane (15 cm³) at −30 °C over 9 d (0.74 g, 89%), m.p. 175 °C, 279 °C (decomp.) (Found: C, 64.1; H, 12.6; N, 15.5. $C_{20}H_{45}AlN_4$ requires C, 65.2; H, 12.3; N, 15.2%); $\tilde{v}_{max}/cm^{-1}$ (Nujol) 3246 (br) (AlH); $\delta_H(C_6D_6)$ 1.03, 1.27, 1.37, 1.39 (4 × 9 H, s, CH₃), 1.62 (1 H, br,

Table 4 Diffraction data for trans-[{AlH[μ-N(Buᵗ)CH₂CH₂NBuᵗ]}₂] 3a, cis-[{AlH[μ-N(Buᵗ)CH₂CH₂NBuᵗ]}₂] 3b and [Al(BuᵗNCH₂-CH₂NBuᵗ)(BuᵗNCH₂CH₂NBuᵗH)] 5

	3a	3b	5
Formula	$C_{20}H_{46}Al_2N_4$	$C_{20}H_{46}Al_2N_4$	$C_{20}H_{45}AlN_4$
M	396.57	396.57	368.58
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)	$C2/c$ (no. 15)
a/Å	9.952(5)	9.890(2)	16.715(7)
b/Å	9.802(4)	13.648(2)	9.450(6)
c/Å	12.611(6)	19.432(1)	16.401(5)
β/°	98.80(2)	94.872(8)	113.60(2)
U/Å³	1216(1)	2613.4(5)	2374(1)
T/K	298	298	173
Z	2	4	4
D_c/g cm⁻³	1.083	1.008	1.031
F(000)	440	880	824
Crystal size/mm	0.3 × 0.3 × 0.5	0.2 × 0.4 × 0.4	0.3 × 0.3 × 0.5
μ/cm⁻¹	1.3	1.2	1.0
Absorption correction	None	None	None
Scan type	2θ–ω	ω–2θ	ω–2θ
2θ Limit/° (+h, +k, ±l)	50	54.6	50
Crystal decay	None	None	6% (linear)
No. unique reflections	2122	4819	2231
No. observed reflections	1209 [$I > 2.5\sigma(I)$]	1623 [$I > 3.0\sigma(I)$]	930 [$I > 3.0\sigma(I)$]
$R(F_o)$ᵃ	0.092	0.078	0.069
$R'(F_o)$ᵇ	0.096	0.071	0.076
Weighting scheme	Unit	σ	σ
Goodness of fit	1.63	4.04	2.70
Final residuals/ e Å⁻³	−0.6, 1.2	−0.3, 0.6	−0.2, 0.3

ᵃ $\Sigma||F_o| - |F_c||/\Sigma|F_o|$. ᵇ $(\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2)^{\frac{1}{2}}$.

NH), 2.3 (2 × 1 H, m, CH₂), 2.65 (3 × 1 H, m, CH₂), 3.1 (1 H, s, CH₂) and 3.2 (2 × 1 H, s, CH₂); $\delta_C(C_6D_6)$ 28.9, 30.0, 30.8, 31.0 (CCH_3), 42.4, 43.9, 45.9, 46.0 (CH₂) and 51.2, 51.4, 51.5, 54.6 (CCH_3).

Crystallography

Colourless prismatic crystals of compounds 3a, 3b and 5 suitable for structure determination were grown from diethyl ether, toluene and hexane solutions, respectively, at −30 °C. Crystals of 3a and 3b were mounted in sealed capillaries under an argon atmosphere. Crystals of 5 were coated with a 1:1 mixture of Riedel-de Haën Perfluoropolyether RS 3000 and Perfluoropolyether 216 oils and placed directly into the cold stream of dry nitrogen for data collection. Unique diffractometer data sets were measured using Enraf-Nonius CAD4 (3a) or Rigaku AFC7R (3b and 5) diffractometers and graphite-monochromated Mo-Kα radiation (λ 0.710 69 Å). Reflections with $I > 2.5\sigma(I)$ (3a) or >3.0σ(I) (3b and 5) were considered 'observed' and used in the full-matrix least-squares refinements, minimising $\Sigma w\Delta^2$ after solution of the structures by direct methods (SHELXS 86²⁵) which located most of the non-hydrogen atoms; the remainder were located by subsequent Fourier-difference maps and refined with no constraints or restraints to convergence (maximum shift over e.s.d. <0.001). Conventional residuals on F at convergence are quoted (observed data only). No extensive, significant extinction effects were found. Neutral-atom complex scattering factors were employed.²⁶ Computation used the XTAL 3.0,²⁷ TEXSAN 1.6²⁸ and SHELXS 86²⁵ program systems implemented on Sun SPARCstation 2 and Silicon Graphics Indy computers. Crystal data are given in Table 4.

Averaged structural parameters are used in the comparisons where appropriate and are distinguished by the absence of the least-squares error term from the determined quantity.

Anisotropic thermal parameters were refined for all non-hydrogen atoms in all three structure determinations. Methyl and methylene hydrogen atoms were calculated and constrained at estimated values and all aluminium hydride atoms were located and refined in x, y, z and U_{iso}. Thermal parameters for methyl hydrogen atoms were estimated at $1.5U_{ii}$(average) (3a) and $1.2U_{ii}$(average) (3b and 5) of the attached carbon atom. Those for methylene hydrogen atoms were estimated at $1.2U_{ii}$(average) of the attached carbon atom.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/218.

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