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Aluminium compounds containing bidentate ligands: ligand base strength and remote geometric control over degree of association

C. Niamh McMahon,[a] Julie A. Francis,[a] Simon G. Bott *[b] and Andrew R. Barron *[a]

[a] *Department of Chemistry, Rice University, Houston, Texas 77005, USA*
[b] *Department of Chemistry, University of Houston, Houston, Texas 77204, USA*

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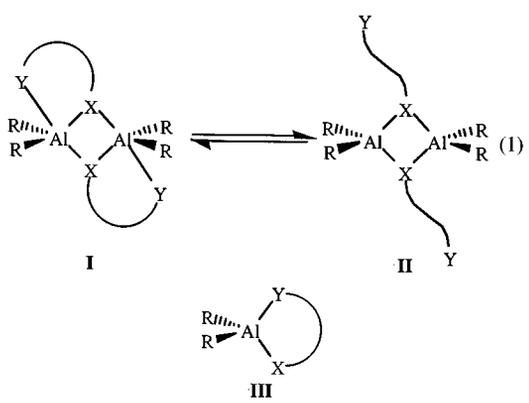
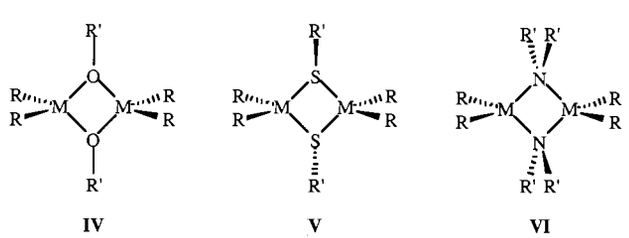
Dialkylaluminium compounds with bi-functional ligands, $[E(CH_2)_xNR_2]^-$ (x = 2, 3; E = S, NR′) have been prepared, and compared to those that contain $[O(CH_2)_xNR_2]^-$, in order to investigate the effect of the anionic termini on the structure of the aluminium compounds, $[R_2Al\{E(CH_2)_xNR'_2\}]_n$. The reaction of $R_2NCH_2CH_2SH{\cdot}HCl$ with Li[Al(ᵗBu)$_3$Me], formed *in situ* from Al(ᵗBu)$_3$ with MeLi, yields (ᵗBu)$_2$Al(SCH$_2$CH$_2$NR$_2$), R = Me **1** and Et **2**. Reaction of Al(ᵗBu)$_3$ with HN(Me)CH$_2$CH$_2$NMe$_2$ and HN(Me)CH$_2$CH$_2$CH$_2$NMe$_2$ ultimately yields (ᵗBu)$_2$Al[N(Me)CH$_2$CH$_2$NMe$_2$] **3** and (ᵗBu)$_2$Al[N(Me)CH$_2$CH$_2$CH$_2$NMe$_2$] **4**, respectively. Reaction of HAl(ᵗBu)$_2$ with HN(Me)CH$_2$CH$_2$NMe$_2$ yields [(ᵗBu)$_2$Al{μ-N(Me)CH$_2$CH$_2$NMe$_2$}]$_2$ **5**, while [H$_2$Al{μ-N(R)CH$_2$CH$_2$NMe$_2$}]$_2$, R = Me **6** and Et **7**, are formed from the reaction of AlH$_3$(NMe$_3$) with HN(R)CH$_2$CH$_2$NMe$_2$. The molecular structures of compounds **1**, **2**, **6** and **7** have been determined by X-ray crystallography. Compounds **1**–**4** are monomeric with five (**1**–**3**) and six (**4**) membered chelate heterocyclic rings. Compound **5** exists as a monomer/dimer equilibrium in solution, in contrast, compounds **6** and **7** exist as bridged dimers. The formation of monomeric chelate structures for compounds **1** and **2**, rather than the bridged dimers found for the alkoxide analogs is due to the relative ligand base strength. However, the formation of monomers in the case of compounds **3** and **4** is found to be due to a combination of the steric bulk of the aluminium alkyl and the geometry at the potentially bridging amide group. These results demonstrate a remote geometric control over the degree of association.

Introduction

Although aluminium compounds of non-delocalized ligands that contain both anionic and neutral Lewis base termini, and their solution chemistry, have been known for over twenty years,[1–3] recent research within our group has been aimed at gaining a detailed understanding of the steric and geometric factors that control the extent of oligomerization and co-ordination number in such compounds. We have been able to rationalize the observation that alkoxide compounds, $[R_2Al(OCH_2CH_2ER'_x)]_n$ (where R = Me, Et, ⁱBu, ᵗBu and ER'_x = OMe, SMe, NMe$_2$), exist as dimers in which an equilibrium exists between 5- and 4-coordinate compounds (**I** and **II**, respectively, where X = O and Y = OR′, SR′, NR′$_2$), eqn. (1).[4] The extent of coordination of the neutral donor is controlled by the steric bulk of the substituents at aluminium (R) and the neutral Lewis base donor (R′). Contrary to expectations, increased steric bulk does not result in the formation of a monomer (**III**) but a four-coordinate dimer is formed instead (**II**).



In the case of the alkoxide derived compounds, we have demonstrated that the formation of the four-coordinate monomer is preferred over the equilibrium in eqn. (1) only when either: (a) the potentially bidentate ligand is too rigid to allow dissociation, in which case the monomeric compounds are formed when sufficient steric bulk is placed on the aluminium alkyl groups,[5] or (b) sufficient steric bulk is placed on the alkoxide β-carbon, *i.e.*, R$_2$Al[OC(CH$_2$Ph)(Ph)CH(Me)CH$_2$NMe$_2$]. Given this latter effect we are interested in determining whether the geometry about the bridging atom (*i.e.*, planar *versus* tetrahedral) affects the relative stability of monomer *versus* 5-coordinate dimer *versus* 4-coordinate dimer. The oxygen atom bridges in the alkoxide compounds are planar (as is common for all Group 13 alkoxide compounds[6]), which orients the bridging ligand between the aluminium's alkyl groups (*cf.*, **IV** where M = Al, Ga, In). In contrast, thiolate compounds of Group 13 are known to have a pyramidal sulfur bridging atom,[7] which we have shown causes significant inter-ligand steric interactions (**V**).[8] Similarly, amide bridged compounds result in the substituents on nitrogen and aluminium being eclipsed, also exacerbating any steric effects (**VI**). However, whereas the formation of monomeric compounds with thiolate derived ligands may be attributed to the weakness of the thiolate bridge unit, "Al(μ-SR)Al", bridging amides, "Al(μ-NR$_2$)Al", are generally less readily cleaved than their alkoxide analogs.



We are therefore interested in determining if the geometry about the sulfur and nitrogen bridge affects the degree of association. In both cases it was decided to limit the neutral Lewis base termini to an amine group, *i.e.*, $[SCH_2CH_2NR_2]^-$, and $[N(Me)CH_2CH_2NR_2]^-$. Beachley and Racette[1] have previously reported several compounds in this series and these are

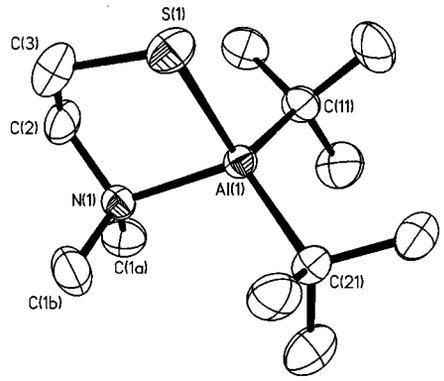


Fig. 1 Molecular structure of $(^tBu)_2Al(SCH_2CH_2NMe_2)$ **1**. Thermal ellipsoids shown at the 30% level, and hydrogen atoms are omitted for clarity.

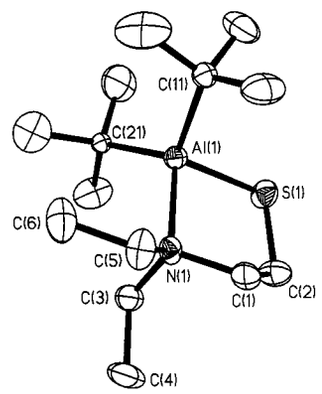


Fig. 2 Molecular structure of $(^tBu)_2Al(SCH_2CH_2NEt_2)$ **2**. Thermal ellipsoids shown at the 30% level, and hydrogen atoms are omitted for clarity.

discussed as part of the development of a cohesive view of this class of compounds.

Results and discussion

Amino-thiolate ligands

A common synthetic approach for the synthesis of thiolate compounds of aluminium is the reaction of the aluminium alkyl with the parent thiol.[9] However, in the present case, $R_2NCH_2CH_2SH$ (R = Me, Et) are commercially available as the hydrogen chloride salts, *i.e.*, $R_2NCH_2CH_2SH{\cdot}HCl$. In order to simplify work-up, instead of isolating $R_2NCH_2CH_2SH$, the salt was reacted with a tetraalkyl aluminate anion prepared from the reaction of MeLi with $Al(^tBu)_3$, *i.e.*, eqn. (2) and (3)

$$Al(^tBu)_3 + MeLi \longrightarrow Li[Al(^tBu)_3Me] \quad (2)$$

$$Li[Al(^tBu)_3Me] + R_2NCH_2CH_2SH{\cdot}HCl \longrightarrow (^tBu)_2Al(SCH_2CH_2NR_2) + MeH + {}^tBuH + LiCl \quad (3)$$

R = Me **1**, Et **2**

Compounds **1** and **2** have been characterized by NMR spectroscopy and mass spectrometry. The ^{27}Al NMR spectra of compounds **1** and **2** show a single broad resonance (*ca.* δ 160) consistent with a 4-coordinate aluminium in a AlR_2XY coordination environment.[10] Although no parent ion is observed in the mass spectra of either compound, the presence of $M^+ - {}^tBu$ ions are consistent with monomeric structures for both compounds, which have been confirmed by X-ray crystallography. The methyl analog, $Me_2Al(SCH_2CH_2NMe_2)$, has already been reported to be monomeric by solution molecular weight measurements.[1]

The molecular structures of $(^tBu)_2Al(SCH_2CH_2NMe_2)$ **1** and $(^tBu)_2Al(SCH_2CH_2NEt_2)$ **2** are shown in Fig. 1 and 2, respectively: selected bond lengths and angles are given in Table 1. The structures consist of discrete monomers in which the amino-thiolate serves as a chelate ligand. As can be seen from Table 1, the presence of ethyl *versus* methyl groups on the amine has no effect on the geometry of the $AlSC_2N$ cycle. The Al–N distances in $(^tBu)_2Al(SCH_2CH_2NR_2)$ [2.044(4) (**1**) and 2.061(7) Å (**2**)] are shorter than observed in the trigonal bipyramidal complex $HAl(SCH_2CH_2NEt_2)_2$ [2.175(2) and 2.182(2) Å].[3] This is expected based upon the relative s and p character in the respective Al–N bonds, trigonal bipyramidal axial (p) *versus* tetrahedral (sp^3).[11] However, the Al–S bond distances in compounds **1** and **2**, 2.262(2) and 2.272(4) Å, respectively, are similar to those in $HAl(SCH_2CH_2NEt_2)_2$ [2.271(1) and 2.278(1) Å].[3] The coordination about aluminium atoms in compounds **1** and **2** is distorted from an ideal tetrahedral geometry due to the small bite angle of the amino-thiolate ligand [90.1(1)° (**1**) and 90.2(3)° (**2**)]. The five membered cycle in both compounds is puckered with the ring carbon adjacent to the amine nitrogen twisted out of the plane (**VII**) resulting in an envelope conformation [S(1)–Al(1)–N(1)–C = 33.5° (**1**), 29.9° (**2**)]. It can be clearly seen from Fig. 3 that this distortion is necessary for the substituents about aluminium and nitrogen to attain a staggered arrangement about the Al–N bond.

Table 1 Selected bond lengths (Å) and angles (°) in $(^tBu)_2Al(SCH_2CH_2NR_2)$

	R = Me **1**	R = Et **2**
Al(1)–S(1)	2.262(2)	2.272(4)
Al(1)–N(1)	2.044(4)	2.061(7)
Al(1)–C(11)	2.019(4)	2.020(9)
Al(1)–C(21)	2.006(5)	2.019(8)
S(1)–Al(1)–N(1)	90.1(1)	90.2(3)
S(1)–Al(1)–C(11)	110.0(2)	109.2(3)
S(1)–Al(1)–C(21)	115.2(1)	110.6(3)
N(1)–Al(1)–C(11)	110.7(2)	112.1(3)
N(1)–Al(1)–C(21)	111.2(2)	114.4(3)
C(11)–Al(1)–C(21)	116.6(2)	117.0(3)
Al(1)–S(1)–C	96.4(2), C(3)	96.3(3), C(2)

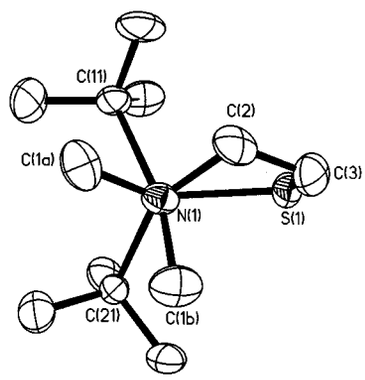
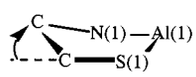


Fig. 3 Structure of $(^tBu)_2Al(SCH_2CH_2NMe_2)$ **1** viewed along the Al(1)–N(1) vector. The S(1)–Al(1)–N(1)–C_{ring} torsion angle = 33.5° compared to 29.9° in compound **2**. Thermal ellipsoids shown at the 30% level, and hydrogen atoms are omitted for clarity.

48.1° **1**, 49.7° **2**



VII

Amino-amide ligands

We have previously reported the synthesis and structural characterization of the Lewis acid base adduct $(^tBu)_3Al[NH(Me)CH_2CH_2NMe_2]$ from the reaction of $Al(^tBu)_3$ with $HN(Me)CH_2CH_2NMe_2$.[12] Extended thermolysis (48 hours) of this complex in toluene solution results in alkane elimination to

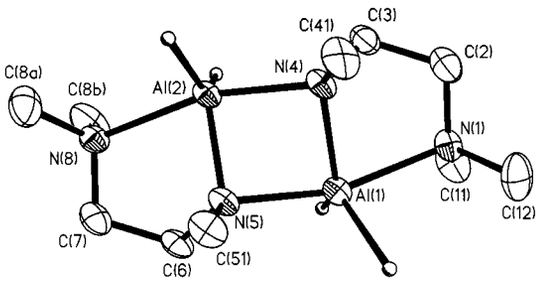


Fig. 4 Molecular structure of $[H_2Al\{\mu\text{-}N(Me)CH_2CH_2NMe_2\}]_2$ **6**. Thermal ellipsoids shown at the 30% level, and the hydrogens atoms are omitted for clarity.

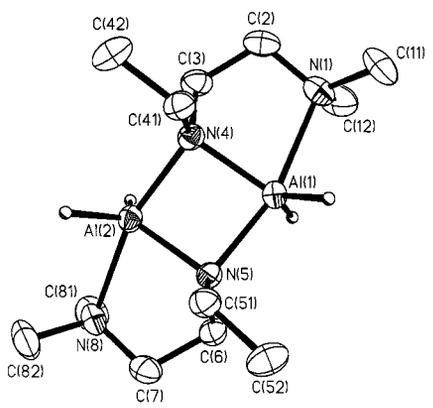
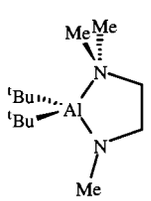


Fig. 5 Molecular structure of $[H_2Al\{\mu\text{-}N(Et)CH_2CH_2NMe_2\}]_2$ **7**. Thermal ellipsoids shown at the 30% level, and the hydrogens atoms are omitted for clarity.

yield $(^tBu)_2Al[N(Me)CH_2CH_2NMe_2]$ **3**. Direct synthesis of the propanediamine analog, $(^tBu)_2Al[N(Me)CH_2CH_2CH_2NMe_2]$ **4**, is possible without isolation of the Lewis acid–base complex (see Experimental section). Compounds **3** and **4** are monomeric chelate compounds, based upon molecular weight and mass spectrometry measurements. Zaworotko and Atwood have previously published the crystal structure of monomeric $Cl_2Al[N(Et)CH_2CH_2NMe_2]$.[13]



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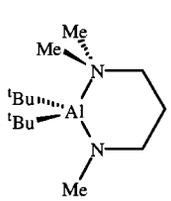

4

The reaction of $H(^iBu)_2Al$ and $AlH_3(NMe_3)$ with $NH(Me)CH_2CH_2NMe_2$ results in the formation of the amide compounds, $[R_2Al\{\mu\text{-}N(Me)CH_2CH_2NMe_2\}]_2$, R = ^{i}Bu **5** and H **6**, see Experimental section. Similarly, the reaction of $AlH_3(NMe_3)$ with $NH(Et)CH_2CH_2NMe_2$ results in the formation of $[H_2Al\{\mu\text{-}N(Et)CH_2CH_2NMe_2\}]_2$ **7**. Beachley and Racette have previously determined that compound **6** is dimeric in solution,[1] this is confirmed by the X-ray crystallographic structural determination, as is the structure of compound **7**. Compound **5** is found to exist as a dimer/monomer equilibrium based on solution molecular weight studies, see Experimental section.

The molecular structures of $[H_2Al\{\mu\text{-}N(Me)CH_2CH_2NMe_2\}]_2$ **6** and $[H_2Al\{\mu\text{-}N(Et)CH_2CH_2NMe_2\}]_2$ **7** are shown in Figs. 4 and 5; selected bond lengths and angles are given in Table 2. As may be seen from the comparison in Table 2, there is little effect of the substitution of the amide methyl group for an ethyl group. This is clearly not the case for the aluminium–methyl compounds, see below. Molecules of compounds **6** and **7** adopt

Table 2 Selected bond lengths (Å) and angles (°) in $[H_2Al\{\mu\text{-}N(R)CH_2CH_2NMe_2\}]_2$

	R = Me **6**	R = Et **7**
Al(1)–N(4)	1.970(3)	1.968(2)
Al(2)–N(4)	2.037(4)	2.044(3)
Al(1)–N(5)	2.044(4)	2.042(2)
Al(2)–N(5)	1.959(4)	1.973(2)
Al(1)–N(1)	2.290(4)	2.333(3)
Al(2)–N(8)	2.289(4)	2.308(3)
N(4)–Al(1)–N(5)	83.1(1)	84.3(1)
N(4)–Al(2)–N(5)	83.5(1)	84.2(1)
N(4)–Al(1)–N(4)	81.4(1)	81.5(1)
N(5)–Al(2)–N(8)	81.8(1)	82.1(1)
N(1)–Al(1)–N(5)	163.3(2)	164.1(1)
N(4)–Al(2)–N(8)	163.7(1)	164.3(1)
Al(1)–N(4)–Al(2)	91.4(1)	90.9(1)
Al(1)–N(5)–Al(2)	91.4(1)	90.8(1)
Al(1)–N(4)–C(41)	115.1(3)	113.9(2)
Al(2)–N(5)–C(51)	114.9(3)	113.2(2)
Al(1)–N(4)–C(3)	109.0(3)	107.5(2)
Al(2)–N(5)–C(6)	108.2(3)	107.1(2)

cis conformations in the solid state, *i.e.*, both of the amido alkyl groups are on the same face of the Al_2N_2 core. As a consequence of this orientation, the Al_2N_2 core adopts a "butterfly" geometry, with a fold of the amide "wings" of 144.5° (**6**) and 145.6° (**7**). Similar geometries have been previously observed for a small number of Group 13 amide compounds,[14] however, the majority of structurally characterized Group 13 amide compounds have been of the *trans* isomer.[15] Beachley and Tessier-Youngs[16] were the first to suggest that the *cis* isomers of aluminium amide dimers, $[R_2Al(\mu\text{-}NR'R'')]_2$, are favored by kinetic effects, while the *trans* isomers are favored by thermodynamic effects. Park *et al.*, have more recently demonstrated this to be true for the gallium amide compound, $[Me_2Ga\{\mu\text{-}N(H)^tBu\}]_2$.[17] It is worth noting that since the aluminium hydrides are not observed in the ^{1}H NMR spectra of compounds **6** and **7** (due to the quadrupolar broadening of the aluminium[18]), it is not possible to determine if the *cis* isomer is maintained in solution. However, it should be noted that the ^{1}H and ^{13}C NMR spectra of compound **5** exhibit two resonances for the aluminium isobutyl groups CH_3 resonances. Although molecular weight studies indicates that compound **5** exists as a monomer/dimer equilibrium in solution, the presence of single resonances for all the proton and carbon sites, except for the aluminium isobutyl groups CH_3 resonances, suggests that the NMR spectra are due to either hindered rotation about the Al–C bond or the retention of a *cis*-isomer in solution. However, in both cases anisochronous methylene (Al–CH_2) groups would be expected, which is not observed in the ^{1}H and ^{13}C NMR spectra, precluding definitive assignment of the solution structure.

Remote geometric control over degree of association

As was noted in the Introduction, in the absence of significant steric hindrance, dialkylaluminium compounds with bifunctional ligands, $[X(CH_2)_nY]^-$ (X = anionic Lewis base, Y = neutral Lewis base), exist as dimers in which the aluminium centers are 5-coordinate (**I**). With increased steric bulk of the aluminium alkyl groups, either the neutral Lewis base dissociates (**II**) or the dimer dissociates to two monomers (**III**).

We have previously shown that for alkoxide derived compounds (*i.e.*, X = O) cleavage does not generally occur, irrespective of the potential Lewis basicity of the neutral termini. Thus, while it is known that alkoxide dimers, $[R_2Al(\mu\text{-}OR')]_2$, may be readily cleaved by amines,[19] compounds of the type, "$R_2Al[O(CH_2)_nNMe_2]$", do not form monomers (Table 3). Thus, the amine would appear to be of insufficient basicity to cleave the alkoxide bridge. The measurement of surprisingly weak bonding interactions for the amine adducts in $[Me_2$-

Table 3 Summary of the extent of oligomerization for $R_2Al(XCH_2CH_2NMe_2)$ (X = S, O, NMe, NEt) compounds

R	$R_2Al(SCH_2CH_2NMe_2)$	$R_2Al(OCH_2CH_2NMe_2)$	$R_2Al[N(Me)CH_2CH_2NMe_2]$	$R_2Al[N(Et)CH_2CH_2NMe_2]$
H	—	—	dimer (5-coord.)[a,b]	dimer (5-coord.)[b]
Me	monomer[a]	dimer (5-coord.)[c]	dimer/monomer[a,e]	monomer[a]
Et	—	dimer (5-coord.)[d]	dimer/monomer[a,e]	—
^{i}Bu	—	dimer (5-coord.)[d]	dimer/monomer[b]	—
^{t}Bu	monomer[b]	dimer (4-coord.)[d]	monomer[b]	—

[a] Ref. 1. [b] This work. [c] Ref. 2(*g*). [d] Ref. 4. [e] Structure assigned as a dimer/monomer equilibrium based upon solution molecular weight measurements.

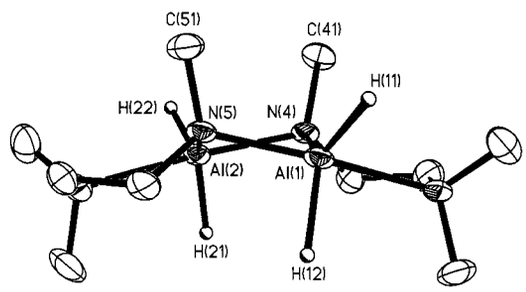

Fig. 6 Molecular structure of $[H_2Al\{\mu\text{-}N(Me)CH_2CH_2NMe_2\}]_2$ **6** viewed along the Al_2N_2 core, showing eclipsed orientation of the amide methyl groups [C(41) and C(51)] and the substituents on aluminium.

$Al(\mu\text{-}OCH_2CH_2NMe_2)]_2$ ($\Delta H = 7.4$ kJ mol^{-1}) and $[(^tBu)_2\text{-}Al(\mu\text{-}OCH_2CH_2NMe_2)]_2$ ($\Delta H = 2.3$ kJ mol^{-1}) confirms this proposal.[4] Since thiolate bridges are known to be weaker than those of alkoxides it would be expected that compounds of the type, "$R_2Al[S(CH_2)_nNMe_2]$", are monomers; which, as can be seen from Table 3 is indeed the case. The report[1] of a monomeric structure for $Me_2Al(SCH_2CH_2NMe_2)$ indicates that the amine termini is of sufficient basicity to cleave thiolate bridges irrespective of the additional weakening of a bridged thiolate through the steric bulk of the ancillary ligands.

The antithesis of this observation is that the amide derivatives, "$R_2Al[NMe(CH_2)_nNMe_2]$", are monomeric (*i.e.*, **III**), rather than 4-coordinate dimeric (*i.e.*, **II**), when sufficient steric bulk is placed around the aluminium. This is contrary to expectations since amide bridges are significantly stronger than their alkoxide analogs.[20] Thus, while the formation of monomeric chelate structures for compounds **1** and **2** is due to the relative ligand base strength, the formation of monomers in the case of compounds **3** and **4** must be due to other factors.

As is shown in Table 3, Beachley and Racette[1] reported $Me_2Al[N(Me)CH_2CH_2NMe_2]$ to exist as a monomer/dimer equilibrium in solution while $Me_2Al[N(Et)CH_2CH_2NMe_2]$ is a monomer. This result suggests that the steric bulk at the amine has a significant effect in determining the relative stability of the monomer and dimer. A consideration of the structure of compound **6** viewed along the Al_2N_2 plane (Fig. 6) shows the methyl groups [C(41) and C(51)] are eclipsed with respect to the substituents on aluminium. The eclipsed orientation is irrespective of whether the amido groups adopt *cis* or *trans* conformations. When the aluminium substituents are hydrides (as in compound **6**) only minimal inter-ligand steric hindrance is present, however, with increased steric bulk (*i.e.*, H < Me < Et < ^{i}Bu < ^{t}Bu) the extent of inter-ligand repulsion is dramatically increased, so that a monomer is formed when the substituent is *tert*-butyl. It should be noted that electronic effects of substituting hydrides for methyl *etc.* may play a role. However, we have previously shown that steric effects far outweigh electronic effects for alkylaluminium compounds.[21] In this regard we believe that the electronic effects while present are not significant. Thus, we propose that the formation of monomers for compounds **3** and **4** is due to the inter-ligand steric repulsion as a result of the geometry at the bridging amide. Clearly increased steric bulk at the amide will enhance this effect, thus, explaining the relative oligomerization of $Me_2Al[N(Me)CH_2\text{-}CH_2NMe_2]$ (monomer/dimer) and $Me_2Al[N(Et)CH_2CH_2NMe_2]$ (monomer).

Experimental

Mass spectra were obtained on a Finnigan MAT 95 mass spectrometer operating with an electron beam energy of 70 eV for EI mass spectra. IR spectra (4000–400 cm^{-1}) were obtained using a Nicolet 760 FT-IR infrared spectrometer; samples were prepared as Nujol mulls between KBr plates unless otherwise stated. NMR spectra were obtained on Bruker AM-250, AM-300 and Avance-200 spectrometers using (unless otherwise stated) d_6-benzene solutions. Chemical shifts are reported relative to internal solvent resonances (^{1}H and ^{13}C), and external $[Al(H_2O)_6]^{3+}$ (^{27}Al). Molecular weight measurements were obtained using the method of Clark.[22] Elemental analyses were performed using a Perkin-Elmer Magna 400 ICP atomic emission spectrometer. All compounds were digested in concentrated nitric acid to enable analysis. **CAUTION**: digestion of organoaluminium compounds in acidic solutions should be undertaken with care. Microanalyses were performed by Oneida Research Services, Inc., Whitesboro, NY, U.S.A. The synthesis of $Al(^tBu)_3$ and $(^tBu)_3Al[NH(Me)CH_2CH_2NMe_2]$ were performed according to a literature method.[12,23] $Me_2\text{-}NCH_2CH_2SH\cdot HCl$ and $Et_2NCH_2CH_2SH\cdot HCl$ were obtained from Aldrich and used without further purification. $HAl(^iBu)_2$ was donated by Akzo Nobel, Inc.

Preparations

$(^tBu)_2Al(SCH_2CH_2NMe_2)$ 1. A solution of $Al(^tBu)_3$ (4.2 g, 21.17 mmol) and MeLi (15.2 mL, 1.4 M in Et_2O, 21.28 mmol) in hexane (50 mL) was added to a suspension of $Me_2NCH_2\text{-}CH_2SH\cdot HCl$ (3.00 g, 21.18 mmol) in hexane (40 mL) at −78 °C. The reaction was allowed to stir overnight. The clear solution was filtered from a white milky residue and reduced to dryness under vacuum. The resulting solid was recrystallized from hexane to give colorless crystals. Yield: 21%. Mp 66–68 °C. Analysis (calc): Al, 10.1 ± 0.05 (11.0%). MS (EI, %): *m*/*z* 188 ($M^+ - {}^tBu$, 59), 146 ($M^+ - {}^tBu - NMe_2$, 94), 58 (^tBu, 100). IR (cm^{-1}): 2696s, 1406m, 1359m 1295s, 1167m, 1111s, 1096s, 1017s, 940s, 807s (br), 765s, 647s, 575s, 547s. ^{1}H NMR (C_6D_6): δ 2.40 [2 H, t, J(H–H) = 6.2, NCH_2], 2.06 [2 H, t, J(H–H) = 6.2, SCH_2], 1.74 [6 H, s, $N(CH_3)_2$], 1.21 [18 H, s, $C(CH_3)_3$]. ^{13}C NMR (C_6D_6): δ 63.4 (NCH_2), 45.5 [$N(CH_3)_2$], 32.2 [$C(CH_3)_3$], 23.0 (SCH_2). ^{27}Al NMR (C_7H_8/C_6D_6): δ 160 ($W_{1/2}$ = 2116 Hz).

$(^tBu)_2Al(SCH_2CH_2NEt_2)$ 2. Prepared in an analogous manner to compound **1** using $Al(^tBu)_3$ (4.0 g, 20.2 mmol), MeLi (14.5 mL, 1.4 M in Et_2O, 20.3 mmol), and $Et_2NCH_2CH_2SH\cdot HCl$ (3.43 g, 20.2 mmol). Yield: 43%. Mp 123–128 °C. Analysis (calc): C, 60.76 (61.49); H, 11.85 (11.79); N, 4.77 (5.12); Al, 10.1 (9.9%). MS (EI, %): *m*/*z* 216 ($M^+ - {}^tBu$, 100), 174 [$AlS(^tBu)_2$, 58]. IR (cm^{-1}): 1348m, 1204m, 1112m, 1016s, 1001s, 730s, 683m, 569s, 543s. ^{1}H NMR ($CDCl_3$): δ 2.97 [6 H, m, NCH_2, $N(CH_2CH_3)_2$], 2.70 [2 H, t, J(H–H) = 6.4, SCH_2], 1.14 [6 H, t, J(H–H) = 7.3 Hz, $N(CH_2CH_3)_2$], 0.99 [18 H, s, $C(CH_3)_3$]. ^{13}C NMR (C_6D_6): δ 55.5 (NCH_2), 43.4 [$N(CH_2CH_3)_2$], 33.0

Table 4 Summary of X-ray diffraction data

	1	**2**	**6**	**7**
Compound	$(^tBu)_2Al(SCH_2CH_2NMe_2)$	$(^tBu)_2Al(SCH_2CH_2NEt_2)$	$[H_2Al\{\mu\text{-}N(Me)CH_2CH_2NMe_2\}]_2$	$[H_2Al\{\mu\text{-}N(Et)CH_2CH_2NMe_2\}]_2$
Empirical formula	$C_{12}H_{28}AlNS$	$C_{14}H_{32}AlNS$	$C_{10}H_{30}Al_2N_4$	$C_{12}H_{34}Al_2N_4$
M	245.41	273.46	260.34	288.39
Crystal size/mm	0.7 × 0.11 × 0.17	0.08 × 0.21 × 0.22	0.14 × 0.22 × 0.43	0.12 × 0.13 × 0.23
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	*Pbca*	*Pbca*	*Pbca*	*Pbca*
a/Å	15.162(1)	15.047(1)	23.012(3)	11.797(2)
b/Å	12.118(1)	13.171(1)	9.730(2)	15.464(3)
c/Å	17.121(1)	17.520(2)	14.792(5)	20.420(4)
V/Å^3	3145.7(3)	3472.2(6)	3312(1)	3725(1)
Z	8	8	8	8
D_c/g cm^{-3}	1.036	1.046	1.044	1.028
μ/cm^{-1}	2.29	2.13	1.60	1.50
T/K	298	298	298	298
2θ range/°	3.0–44.0	3.0–44.0	5.0–45.0	4.6–45.0
No. collected	2212	2425	2678	2436
No. independent	2212	2425	2164	2428
No. observed	1294 ($\|F_o\| > 4.0\sigma\|F_o\|$)	898 ($\|F_o\| > 4.0\sigma\|F_o\|$)	1719 ($\|F_o\| > 4.0\sigma\|F_o\|$)	1862 ($\|F_o\| > 4.0\sigma\|F_o\|$)
Weighting scheme	$w^1 = 0.04(\|F_o\|)^2 + \sigma(\|F_o\|)^2$	$w^{-1} = 0.04(\|F_o\|)^2 + \sigma(\|F_o\|)^2$	$w^{-1} = 0.04(\|F_o\|)^2 + \sigma(\|F_o\|)^2$	$w^{-1} = \sigma(\|F_o\|)^2$
R	0.0442	0.0513	0.089 (0.115)	0.051 (0.128)
Rw	0.0455	0.0599	0.226 (0.259)	0.128 (0.189)
Largest (smallest) difference peak/e Å^{-3}	0.20 (−0.18)	0.22 (−0.22)	0.56 (−0.89)	0.31 (−0.22)

[C(CH_3)$_3$], 22.3 (SCH_2), 8.0 [N(CH_2CH_3)$_2$]. ^{27}Al NMR (C_7H_8/C_6D_6): δ 160 ($W_{1/2}$ = 2653 Hz).

(^tBu)$_2$Al[N(Me)CH$_2$CH$_2$NMe$_2$] 3. A toluene (40 mL) solution of (^tBu)$_3$Al[NH(Me)CH$_2$CH$_2$NMe$_2$] (1.2 g, 4 mmol) was refluxed for 48 hours. After removal of solvent under vacuum, the resultant oil was purified by vacuum sublimation (*ca.* 100 °C). Yield: 40%. Mp 137–139 °C. MS (EI, %): *m*/*z*: 243 (M^+, 22), 198 ($M^+ - NMe_2$, 14), 185 ($M^+ - {}^tBu$, 8), 141 ($M^+ - {}^tBu - NMe_2$, 30), 57 (^tBu, 100). IR (cm^{-1}): 1344m, 1286m, 1179s, 1046m, 945s, 881s, 809s, 621m. ^{1}H NMR (C_6D_6): δ 2.88 (3 H, s, NCH_3) 2.74 [2 H, t, J(H–H) = 5.9, N(Me)CH_2], 2.23 [2 H, t, J(H–H) = 5.9 Hz, NCH_2], 1.79 [6 H, s, N(CH_3)$_2$], 1.20 [18 H, s, C(CH_3)$_3$]. ^{13}C NMR ($CDCl_3$): δ 61.20 (NCH_2), 51.32 (NCH_2), 45.67 [N(CH_3)$_2$], 39.77 [N(CH_3)], 32.46 [C(CH_3)$_3$]. ^{27}Al NMR (C_7H_8/C_6D_6): δ 140 ($W_{1/2}$ = 1507 Hz).

(^tBu)$_2$Al[N(Me)CH$_2$CH$_2$CH$_2$NMe$_2$] 4. A mixture of Al(^tBu)$_3$ (2.56 g, 12.9 mmol) and Me$_2$NCH$_2$CH$_2$CH$_2$NH(Me) (1.5 g, 12.9 mmol) was refluxed overnight in a toluene solution (50 mL). After removal of the solvent and volatiles, the resultant oil was purified by vacuum sublimation (*ca.* 100 °C). Yield: 71%. Mp 183–185 °C. Molecular weight determination (calc.): 264.8 (256.4). MS (EI, %): *m*/*z* 199 ($M^+ - {}^tBu$, 100), 141 ($M^+ - {}^tBu - NMe_2$, 20), 57 (^tBu, 80). IR (cm^{-1}): 1231s, 1174s, 1157s, 1136s, 1071s, 1032s, 1005s, 924s, 850s, 809s, 770s, 611s, 570s. ^{1}H NMR (C_6D_6): δ 2.96 [2 H, t, J(H–H) = 5.7, CH_2NMe], 2.89 [3 H, s, N(CH_3)$_2$], 2.11 [2 H, t, J(H–H) = 5.8 Hz, CH_2NMe$_2$], 1.88 [6 H, s, N(CH_3)$_2$], 1.37 (2 H, m, CH_2), 1.25 [18 H, s, C(CH_3)$_3$]. ^{13}C NMR (C_6D_6): δ 62.1 (NCH_2), 55.2 (NCH_2), 46.9 [N(CH_3)$_2$], 42.9 [N(CH_3)], 33.4 [C(CH_3)$_3$], 27.0 (NCH_2CH_2). ^{27}Al NMR (C_7H_8/C_6D_6): δ 136 ($W_{1/2}$ = 1564 Hz).

[(^{i}Bu)$_2$Al{μ-N(Me)CH$_2$CH$_2$NMe$_2$}]$_2$ 5. To a solution of HAl(^{i}Bu)$_2$ (6.94 g of 2.75% Al heptane solution) in hexane (50 mL) at −78 °C was added HN(Me)CH$_2$CH$_2$NMe$_2$ (0.72 g, 7.0 mmol) *via* syringe. The solution was allowed to reach room temperature and stirred overnight. All volatiles were removed *in vacuo* leaving a pale yellow oil, which was distilled under vacuum to produce a clear oil. Yield: 42%. Molecular weight determination (calc.): 351 (monomer = 242.4, dimer = 484.8). MS (EI, %): *m*/*z* 243 (M^+, 18), 185 ($M^+ - {}^iBu$, 100), 129 ($M^+ - 2\,{}^iBu$, 48), 58 (^{i}BuH, 18). IR (cm^{-1}): 1466s, 1344s, 1286s, 1178s (br), 1044s. ^{1}H NMR (C_6D_6): δ 2.86 [3 H, s, N(CH_3)], 2.73 [2 H, t, J(H–H) = 5.8, NCH_2], 2.21 [2 H, m, J(H–H) = 5.8, NCH_2] 2.21 [2 H, m, J(H–H) = 6.5, $CH_2CH(CH_3)_2$], 1.67 [6 H, s, N(CH_3)$_2$], 1.27 [6 H, d, J(H–H) = 6.5, $CH_2CH(CH_3)_2$], 1.22 [6 H, d, J(H–H) = 6.5, $CH_2CH(CH_3)_2$], 0.13 [4 H, d, J(H–H) = 7.3 Hz, Al–CH_2]. ^{13}C NMR (C_6D_6): δ 60.8 (NCH_2), 51.3 (NCH_2), 44.7 [N(CH_3)$_2$], 38.8 [N(CH_3)], 29.5, 29.0 [$CH_2CH(CH_3)_2$], 27.4 [$CH_2CH(CH_3)_2$]. ^{27}Al (C_7H_8/C_6D_6): δ 150 ($W_{1/2}$ = 3131 Hz).

[H$_2$Al{μ-N(Me)CH$_2$CH$_2$NMe$_2$}]$_2$ 6. A solution of Me(H)NCH$_2$CH$_2$NMe$_2$ (1.15 g, 11.3 mmol) in degassed hexane (10 mL) was added to a hexane solution of $AlH_3(NMe_3)$ (1.0 g, 11.2 mmol) that was cooled to −78 °C. The mixture was allowed to warm to room temperature while stirring and was then refluxed for 1 h. After filtration, the solution was then placed in the freezer for crystallization. Yield: 60%. Mp 88–89 °C. MS (EI, %): *m*/*z* 102 [HN(Me)C$_2$H$_4$NMe$_2$, 100]. IR (cm^{-1}): 1762s, 1378s, 1280w, 1147w, 1086w, 850m, 778w, 691s. ^{1}H NMR (C_6D_6): δ 2.95 [2 H, t, J(H–H) = 4.9, N(Me)CH_2], 2.68 (3 H, s, NCH_3), 2.49 [2 H, t, J(H–H) = 4.9 Hz, NCH_2], 2.07 [6 H, s, N(CH_3)$_2$]. ^{13}C NMR (C_6D_6): δ 57.6 (NCH_2), 51.4 (NCH_2), 48.4 [N(CH_3)$_2$], 41.9 [N(CH_3)]. ^{27}Al NMR (C_6D_6): δ 86 ($W_{1/2}$ = 2250 Hz).

[H$_2$Al{μ-N(Et)CH$_2$CH$_2$NMe$_2$}]$_2$ 7. AlH_3·NMe_3 (0.32 g, 3.6 mmol) was dissolved in hexane (50 mL) and EtHNCH$_2$CH$_2$NMe$_2$ (0.40 g, 3.5 mmol) was dissolved in hexane (30 mL). The two solutions were added together at 0 °C. The solution was allowed to reach room temperature and stirred for one hour. The solvent was removed *in vacuo* and the white product recrystallised from hexane at −23 °C. Yield: 80%. Mp 114–116°C. Molecular weight determination (calc.): 288.7 (dimer = 288.4). MS (EI, %): *m*/*z* 143 (M^+, 55), 129 ($M^+ - Me$, 32), 58 (^{t}BuH, 100). IR (cm^{-1}): 1762 (ν_{AlH}), 1276w, 1143w, 1023m. ^{1}H NMR (C_6D_6): δ 3.11 (4 H, br s, NCH_2), 2.88 (4 H, br s, NCH_2), 2.09 [12 H, s, N(CH_3)$_2$], 2.05 (4 H, br s, NCH_2CH_2N), 1.19 [6 H, t, J(H–H) = 7.2 Hz, NCH_2CH_3]. ^{13}C NMR (C_6D_6): δ 57.1 (NCH_2), 48.7 [N(CH_3)$_2$], 43.9 (NCH_2), 43.5 (NCH_2), 12.7 (NCH_2CH_3). ^{27}Al (C_7H_8/C_6D_6): δ 110 ($W_{1/2}$ = 2020 Hz).

Crystallographic studies

Crystals of compounds **1**, **2**, **6** and **7** were sealed in glass capillaries under argon. Crystal and data collection and solution details are given in Table 4. Standard procedures in our

laboratory have been described previously.[24] Data were collected on either an Enraf-Nonius CAD-4 (**1** and **2**) or Rigaku four-circle (**6** and **7**) diffractometers equipped with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) and corrected for Lorentz and polarization effects. The structures were solved by using direct methods (**1** using SIR,[25] **2**, **6** and **7** using SHELXS-86[26]), and difference Fourier synthesis and refined using full-matrix least squares.[27,28] The non-hydrogen atoms, except the quaternary carbons in compound **2**, were refined anisotropically. All the hydrogen atoms attached to carbon were placed in calculated positions [$U_{iso} = 0.08$; d(C–H) = 0.96 Å] for refinement. The position and isotropic thermal parameters of the aluminium hydrogen atoms in compounds **6** and **7** were allowed to refine freely. Neutral-atom scattering factors were taken from the usual source.[29] Refinement of positional and anisotropic thermal parameters led to convergence, see Table 4.

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