

Reaction of $\text{Al}(\text{tBu})_3$ with $[\text{R}_2\text{Al}\{\mu\text{-O}(\text{CH}_2)_n\text{NMe}_2\}]_2$: dependence on the extent of intra-molecular $\text{Al}\cdots\text{N}$ coordination

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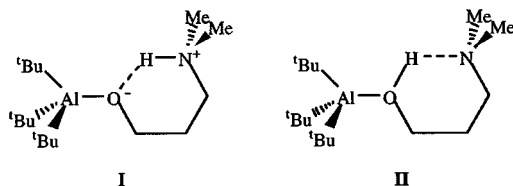
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Received 6th May 1998, Accepted 24th July 1998

Reaction of $\text{Al}(\text{tBu})_3$ with $(\text{tBu})_3\text{Al}[\text{O}(\text{H})\text{CH}_2\text{CH}_2\text{CH}_2\text{NMe}_2]$ yielded the Lewis acid–base complex $[(\text{tBu})_2\text{-Al}\{\mu\text{-OCH}_2\text{CH}_2\text{CH}_2\text{N}(\text{Me})_2\text{Al}(\text{tBu})_3\}]_2$ **1**. Compound **1** is also formed directly when 2 equivalents of $\text{Al}(\text{tBu})_3$ reacts with 1 equivalent of $[(\text{tBu})_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2)]_2$. In contrast, the reaction of 2 equivalents of $\text{Al}(\text{tBu})_3$ with 1 equivalent of $[\text{Me}_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{NMe}_2)]_2$ yielded $\text{Me}_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{NMe}_2)\text{Al}(\text{tBu})_3$ **2**. The molecular structure of compound **2** shows the AlMe_2 moiety chelate bound to the anionic bidentate ligand, while the $\text{Al}(\text{tBu})_3$ unit is bonded to the anionic terminus of the ligand. The formation of compound **1** is proposed to occur via the *tert*-butyl analog of compound **2**, *i.e.*, $(\text{tBu})_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2)\text{Al}(\text{tBu})_3$, which is unstable due to significant $\text{tBu}\cdots\text{tBu}$ inter-ligand interactions. The implications of the differences in products is discussed with respect to the extent of intra-molecular $\text{Al}\cdots\text{N}$ coordination in compounds of the general formula $[\text{R}_2\text{Al}\{\mu\text{-O}(\text{CH}_2)_n\text{NMe}_2\}]_2$.

Introduction

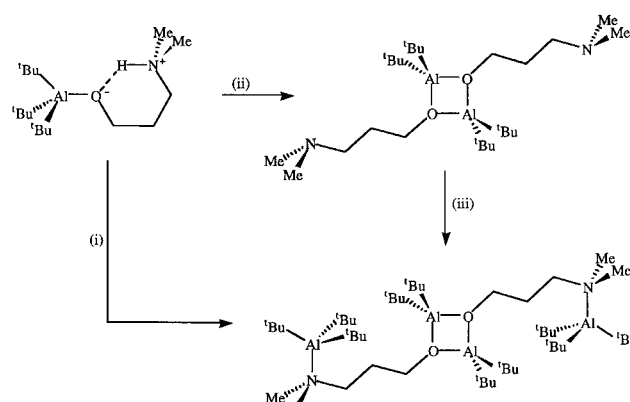
We have recently reported¹ that the reaction of $\text{Al}(\text{tBu})_3$ with less than 2 equivalents of $\text{HOCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2$ allows for the isolation of the surprisingly stable Lewis acid–base complex, $(\text{tBu})_3\text{Al}[\text{O}(\text{H})\text{CH}_2\text{CH}_2\text{CH}_2\text{NMe}_2]$, in which a strong intra-ligand hydrogen bond and unusually short $\text{Al}\text{-O}$ bond length suggests that it exists as a zwitterionic alkoxide⁻/ammonium⁺ form (**I**) instead of the alcohol/tertiary amine form (**II**). Given the apparent competition between the Lewis base sites (O and N) for the Lewis acid proton, we are interested in the site of reactivity of $(\text{tBu})_3\text{Al}[\text{O}(\text{H})\text{CH}_2\text{CH}_2\text{CH}_2\text{NMe}_2]$ with additional Lewis acids, in particular trialkylaluminium compounds.



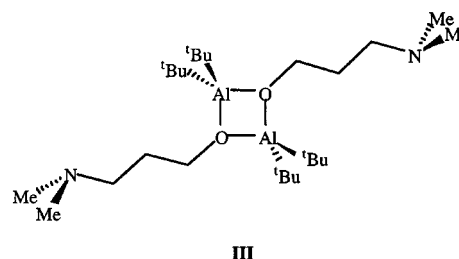
Results and discussion

Reaction of $(\text{tBu})_3\text{Al}[\text{O}(\text{H})\text{CH}_2\text{CH}_2\text{CH}_2\text{NMe}_2]$ with 2 equivalents of $\text{Al}(\text{tBu})_3$ allows for the isolation of the Lewis acid–base complexes, $[(\text{tBu})_2\text{Al}\{\mu\text{-OCH}_2\text{CH}_2\text{CH}_2\text{N}(\text{Me})_2\text{Al}(\text{tBu})_3\}]_2$ **1** and the concomitant elimination of isobutane, see Scheme 1(i). Compound **1** has been characterized by NMR spectroscopy and mass spectrometry. The ²⁷Al NMR spectrum of compound **1** shows two overlapping broad signals at δ 126 and 47. Based on their relative shifts,² and in comparison to the ²⁷Al NMR spectrum of $[(\text{tBu})_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2)]_2$ **III** which shows a single resonance at δ 143 ($\nu_3 = 4400$ Hz), we can assign the peak at δ 126 to the “ $(\text{tBu})_2\text{Al}$ ” moiety.

A comparison of the ¹H NMR spectrum of compound **1** with that of $[(\text{tBu})_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2)]_2$ **III** shows that there is essentially no change in the chemical shifts for the OCH_2CH_2 and *tert*-butyl resonances, but a significant downfield shift for the $\text{CH}_2\text{N}(\text{CH}_3)_2$ peaks: δ 2.89 (**1**) versus 1.98 for the methylene and δ 2.11 (**1**) versus 1.97 for the methyl groups. These shifts are consistent with the coordination of an $\text{Al}(\text{tBu})_3$ moiety to the amine nitrogen.³ Furthermore, the ¹H NMR



Scheme 1 Synthetic routes to $[(\text{tBu})_2\text{Al}\{\mu\text{-OCH}_2\text{CH}_2\text{CH}_2\text{N}(\text{Me})_2\text{-Al}(\text{tBu})_3\}]_2$ **1**: (i) 2 equivalents $\text{Al}(\text{tBu})_3$; (ii) heat, 45 °C in benzene; (iii) 2 equivalents $\text{Al}(\text{tBu})_3$ in hexane.



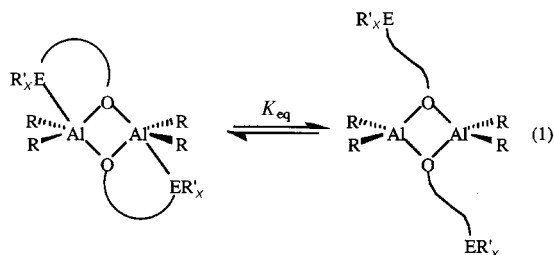
resonance of the *tert*-butyl groups of the $\text{Al}(\text{tBu})_3$ unit in compound **1** (δ 1.18) is shifted downfield relative to that of uncomplexed $\text{Al}(\text{tBu})_3$ (δ 1.07) in a similar manner to that observed for other Lewis acid–base complexes of $\text{Al}(\text{tBu})_3$.⁴

Clearly, compound **1** is best considered as the Lewis acid–base complex of $\text{Al}(\text{tBu})_3$ with the previously reported alkoxide amine derivative, $[(\text{tBu})_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2)]_2$, which is formed from the thermolysis of $(\text{tBu})_3\text{Al}[\text{O}(\text{H})\text{CH}_2\text{CH}_2\text{CH}_2\text{NMe}_2]$, see Scheme 1(ii). In fact, compound **1** is readily prepared by the direct reaction of 2 equivalents of $\text{Al}(\text{tBu})_3$ with $[(\text{tBu})_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2)]_2$, see Scheme 1(iii).

We have previously reported that in common with other compounds of aluminium containing bidentate anionic ligands,

Table 1 Selected bond lengths (Å) and angles (°) in Me₂Al(μ-OCH₂-CH₂NMe₂)Al(^tBu)₃ **2**

Al(1)–O(1)	1.929(4)	Al(1)–C(11)	2.020(5)
Al(1)–C(21)	2.037(7)	Al(1)–C(31)	2.019(6)
Al(2)–O(1)	1.837(4)	Al(2)–N(4)	2.013(6)
Al(2)–C(101)	1.946(8)	Al(2)–C(102)	1.902(8)
O(1)–C(2)	1.482(9)		
O(1)–Al(1)–C(11)	105.6(2)	O(1)–Al(1)–C(21)	105.3(2)
O(1)–Al(1)–C(31)	105.9(2)	C(11)–Al(1)–C(21)	112.8(2)
C(11)–Al(1)–C(31)	113.7(3)	C(21)–Al(1)–C(31)	112.7(3)
O(1)–Al(2)–N(4)	74.4(2)	O(1)–Al(2)–C(101)	114.3(3)
O(1)–Al(2)–C(102)	113.2(3)	N(4)–Al(2)–C(101)	106.2(3)
N(4)–Al(2)–C(102)	104.4(3)	C(101)–Al(2)–C(102)	122.7(4)
Al(1)–O(1)–Al(2)	135.5(2)	Al(1)–O(1)–C(2)	112.0(4)
Al(2)–O(1)–C(2)	112.4(4)		

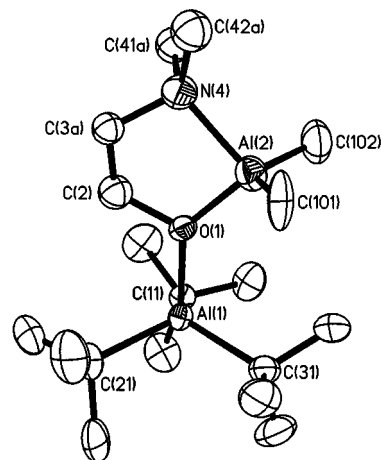
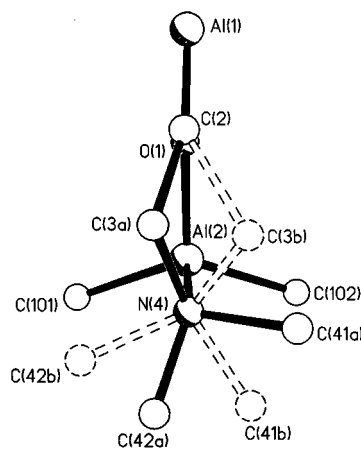


[O(CH₂)_nER'_x][−] (E = O, S or N; *n* = 2 or 3), [(^tBu)₂Al(μ-OCH₂-CH₂CH₂NMe₂)₂ **III** exists as an equilibrium in solution between the dimeric five-coordinate and dimeric four-coordinate isomers, where $K_{eq} = [4\text{-coord}]/[5\text{-coord}]$, eqn. (1).⁵ Due to the steric bulk of the aluminium *tert*-butyl groups in [(^tBu)₂Al(μ-OCH₂CH₂CH₂NMe₂)₂ the amine is predominantly dissociated ($K_{eq} \approx 6.60$).⁵ Thus, it is perhaps expected that the reaction of [(^tBu)₂Al(μ-OCH₂CH₂CH₂NMe₂)₂ with Al(^tBu)₃ yields compound **1**. In contrast, the amine in [Me₂Al(μ-OCH₂CH₂NMe₂)₂ is predominantly associated ($K_{eq} = 0.250$). Given this difference, can the reaction with a Lewis acid (*e.g.*, AlR₃) be used as a probe of the extent of coordination?

Reaction of [Me₂Al(μ-OCH₂CH₂NMe₂)₂ with 2 equivalents of Al(^tBu)₃ yields Me₂Al(μ-OCH₂CH₂NMe₂)Al(^tBu)₃ **2** (see Experimental section), in which the Al–N_(amine) intra-molecular interaction is retained but at the expense of the Al₂O₂ dimeric core (see below). Thus, the Lewis acid has cleaved the dimeric alkoxide bridged unit suggesting that in compounds with stronger intra-molecular coordination a monomer/dimer rather than a “on/off” equilibrium may be present, see below.

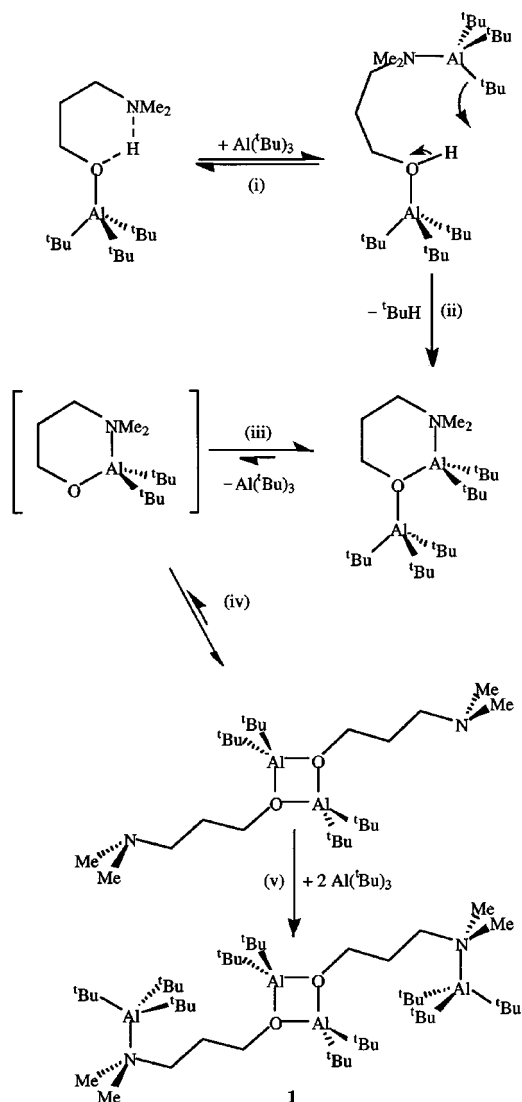
The molecular structure of Me₂Al(μ-OCH₂CH₂NMe₂)Al(^tBu)₃ **2** is shown in Fig. 1; selected bond lengths and angles are given in Table 1. The geometry of compound **2** is similar to Me₂Al[μ-OCH₂CH(CH₂Ph)NH₂]₂AlMe₃,⁶ Me₂Al[μ-OCMe₂-C(H)=N(^tBu)]AlMe₃,⁷ Me₂Al[μ-ON(Me)NO]AlMe₃⁸ and Me₂Al[μ-OC(H)(Me)N(Ph)C(Ph)=O]AlMe₃⁹ in that the anionic bidentate ligand is chelate bound to the AlR₂ moiety, while the AlR₃ unit bonds to the anionic end of the ligand. The Al(2)–O(1) and Al(2)–N(4) bond lengths to the AlMe₂ units [1.837(4) and 2.013(6) Å, respectively] are significantly shorter than the analogous values in the dimeric compounds [R₂Al(μ-OCH₂CH₂NR'₂)₂] [1.833(6)–1.958(5) and 2.126(9)–2.340(3) Å, respectively]. However, the Al(2)–O(1) distance is longer than in compounds without the AlR₃ units. The AIOCCN heterocycle in compound **2**, exhibited static disorder resulting from two different chain conformations (the so-called “slinky effect”¹⁰), and the disorder of the carbons attached to nitrogen. As can be seen from Fig. 2, both conformations relieve the steric strain caused by an eclipsed orientation of the amine methyl groups with the methyl substituents on the Al(2).

It is worth noting the relationship of compound **2** to (^tBu)₃Al[O(H)CH₂CH₂CH₂NMe₂] **I** in which an Al(^tBu)₃ unit is complexed to a formally anionic oxygen in a heterocyclic ring.

**Fig. 1** Molecular structure of Me₂Al(μ-OCH₂CH₂NMe₂)Al(^tBu)₃ **2**. Thermal ellipsoids shown at the 30% level, and hydrogen atoms are omitted for clarity. Only one confirmation of the cyclic ring is shown.**Fig. 2** Partial coordination sphere of Me₂Al(μ-OCH₂CH₂NMe₂)Al(^tBu)₃ **2** showing the site disorder of the OCH₂CH₂NMe₂ group. Hydrogen atoms are omitted for clarity.

In each compound the oxygen is also bonded to a carbon and the formal cationic moiety (H⁺ in (^tBu)₃Al[O(H)CH₂CH₂CH₂NMe₂]⁺ and [AlMe₂]⁺ in compound **2**). The analogy has some precedent since we have previously shown by ¹⁷O NMR spectroscopy that aluminium and a proton have similar electro-negatives with regard to oxygen.¹¹

Although the differences in reactivity of [Me₂Al(μ-OCH₂-CH₂NMe₂)₂ and [(^tBu)₂Al(μ-OCH₂CH₂CH₂NMe₂)₂ with Al(^tBu)₃ may be explained by the relative strength of the Al–N intra-molecular interaction, it is not readily apparent why the reaction of (^tBu)₃Al[O(H)CH₂CH₂CH₂NMe₂]⁺ with Al(^tBu)₃ yields compound **1**. If one considers this latter reaction it would ordinarily be supposed that the first product would result from the binding of the aluminium Lewis acid to the strongest Lewis base (the amine), Scheme 2(i). Subsequent alkane elimination would result in the *tert*-butyl analog of compound **2**, *i.e.*, (^tBu)₂Al(μ-OCH₂CH₂CH₂NMe₂)Al(^tBu)₃, Scheme 2(ii). Initially this compound would be expected to be stable. However, upon consideration of the space filling representation of compound **2**, and an equivalent (calculated) view of the unknown (^tBu)₂Al(μ-OCH₂CH₂NMe₂)Al(^tBu)₃ (Fig. 3), it is readily seen that the latter is highly sterically crowded, with the *tert*-butyl groups on each aluminium being close to van der Waals interactions. Thus, given this de-stabilization, it is likely that the Al(^tBu)₃ moiety will dissociate, Scheme 2(iii). Once “(^tBu)₂Al(OCH₂CH₂CH₂NMe₂)” is formed it will dimerize [Scheme 2(iv)] to give the previously isolated [(^tBu)₂Al(μ-OCH₂CH₂-CH₂NMe₂)₂], which we have shown, above, reacts with free Al(^tBu)₃ to yield compound **1**, Scheme 2(v). Therefore, we pro-



Scheme 2 Proposed pathway for the reaction of $(\text{tBu})_3\text{Al}[\text{O}(\text{H})\text{CH}_2\text{CH}_2\text{CH}_2\text{NMe}_2]$ with $\text{Al}(\text{tBu})_3$ to yield compound **1**.

pose that the isolation of compound **1** versus **2** is due to the relative stability of each of the species in a multiple equilibria, and that stability is determined by the steric bulk of the aluminium alkyl groups.

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 ($4000\text{--}400\text{ cm}^{-1}$) were obtained using a Nicolet 760 FT-IR infrared spectrometer. IR samples were prepared as Nujol mulls between KBr plates unless otherwise stated. NMR spectra were obtained on Bruker AM-250 and Avance-200 spectrometers using (unless otherwise stated) C_6D_6 solutions. Chemical shifts are reported relative to internal solvent resonances (^1H and ^{13}C), and external $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ (^{27}Al). The synthesis of $\text{Al}(\text{tBu})_3$ was performed according to modification of the literature methods.¹² $[\text{Me}_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2)]_2$,¹³ $(\text{tBu})_3\text{Al}[\text{O}(\text{H})\text{CH}_2\text{CH}_2\text{CH}_2\text{NMe}_2]$ ¹ and $[(\text{tBu})_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2)]_2$ ¹ were prepared as previously reported.

Synthesis

$[(\text{tBu})_2\text{Al}\{\mu\text{-OCH}_2\text{CH}_2\text{CH}_2\text{N}(\text{Me})_2\text{Al}(\text{tBu})_3\}]_2$ **1**. *Method 1*.—To a solution of $[(\text{tBu})_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2)]_2$ (0.47 g, 0.97 mmol) in hexane (40 mL), cooled to -78°C , was added

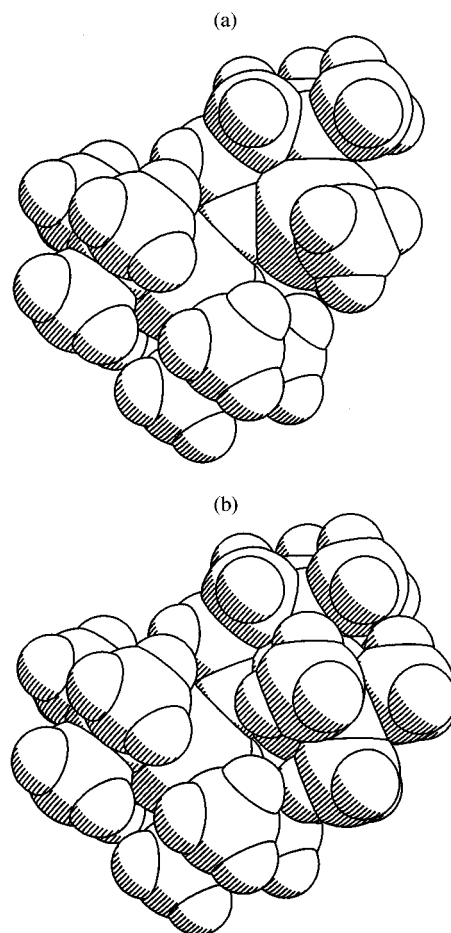


Fig. 3 Space filling representations of (a) $\text{Me}_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{NMe}_2)\text{Al}(\text{tBu})_3$ **2** and (b) a computer generated idealization of $(\text{tBu})_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{NMe}_2)\text{Al}(\text{tBu})_3$, showing the different steric interactions of the *tert*-butyl group on aluminium. Both views are perpendicular to the Al_2O plane.

$\text{Al}(\text{tBu})_3$ (0.4 g, 2.02 mmol). The solution was warmed to room temperature and stirred overnight. White solid precipitated which was isolated by filtration. Yield: 46%.

Method 2.—To a solution of $(\text{tBu})_3\text{Al}[\text{O}(\text{H})\text{CH}_2\text{CH}_2\text{CH}_2\text{NMe}_2]$ (0.39 g, 1.29 mmol) in hexane (40 mL), cooled to -78°C , was added $\text{Al}(\text{tBu})_3$ (0.5 g, 2.52 mmol). The solution was warmed to room temperature and stirred overnight. White solid precipitated which was isolated by filtration. Yield: 63%. MS (EI, %): m/z 429 [$2\text{M}^+ - \text{tBu} - 2\text{Al}(\text{tBu})_3$, 100], 186 [$\text{M}^+ - \text{tBu} - \text{Al}(\text{tBu})_3$, 26], 86 [$(\text{CH}_2)_3\text{NMe}_2$, 73], 57 (tBu , 82). IR (cm^{-1}): 1081m, 1038m (br), 1002m, 966m, 813m, 642s, 593m, 560s, 519m, 418s. ^1H NMR ($\text{C}_6\text{D}_5\text{CD}_3$): δ 3.83 [4 H, t, $J(\text{H-H}) = 8.2$, OCH_2], 2.89 [4 H, t, $J(\text{H-H}) = 8.1$ Hz, NCH_2], 2.11 [12 H, s, $\text{N}(\text{CH}_3)_2$], 1.87 (4 H, m, CH_2), 1.25 [54 H, s, $\text{C}(\text{CH}_3)_3$], 1.18 [36 H, s, $\text{C}(\text{CH}_3)_3$]. ^{13}C NMR ($\text{C}_6\text{D}_5\text{CD}_3$): δ 64.0 (OCH_2), 53.5 (NCH_2), 44.0 [$\text{N}(\text{CH}_3)_2$], 33.8 [$\text{C}(\text{CH}_3)_3$], 32.3 [$\text{C}(\text{CH}_3)_3$], 18.89 ($\text{CH}_2\text{CH}_2\text{CH}_2$). ^{27}Al NMR (CDCl_3): δ 126 ($w_2 = 4800$), 47 ($w_1 \approx 5000$ Hz).

$\text{Me}_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{NMe}_2)\text{Al}(\text{tBu})_3$ **2**. To a solution of $[\text{Me}_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{NMe}_2)]_2$ (0.5 g, 1.7 mmol) in hexane (40 mL), cooled to -78°C , was added $\text{Al}(\text{tBu})_3$ (0.68 g, 3.4 mmol). The reaction was warmed to room temperature and stirred overnight. After filtration the solution was placed in a freezer (-20°C). A white crystalline product precipitated and was isolated by filtration. Yield: 27%. MS (EI, %): m/z 286 ($\text{M}^+ - \text{tBu}$, 10), 230 ($\text{M}^+ - 2\text{tBu}$, 10), 130 [$\text{M}^+ - \text{Al}(\text{tBu})_3 - \text{Me}$, 60], 57 (tBu , 100). IR (cm^{-1}): 2690m, 1260m, 1202s, 1043s, 1009s, 950s, 878s, 808s. ^1H NMR (C_6D_6): δ 3.82 [2 H, t, $J(\text{H-H}) = 5.5$, OCH_2], 1.59 [2 H, t, $J(\text{H-H}) = 5.5$ Hz, NCH_2], 1.42 [27 H, s,

Table 2 Summary of X-ray diffraction data

Compound	Me ₂ Al(μ-OCH ₂ CH ₂ NMe ₂)Al(^t Bu) ₃ 2
Formula	C ₁₈ H ₄₃ Al ₂ NO
<i>M</i>	343.5
Crystal size/mm	0.21 × 0.23 × 0.26
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> /Å	10.2671(8)
<i>b</i> /Å	16.471(1)
<i>c</i> /Å	13.867(2)
β/°	99.407(8)
<i>U</i> /Å ³	2313.5(4)
<i>Z</i>	4
<i>D</i> _c /g cm ⁻³	0.986
μ/cm ⁻¹	1.25
<i>T</i> /K	298
2θ Range/°	3.0–44.0
No. reflections collected	3137
No. individual reflections	2955
No. observed reflections (<i>F</i> _o > 6.0σ <i>F</i> _o)	1265
Weighting scheme (<i>w</i> ⁻¹)	0.04 (<i>F</i> _o) ² + σ(<i>F</i> _o) ²
<i>R</i> ^a	0.0602
<i>R</i> _w ^b	0.0655
Largest difference peak/e Å ⁻³	0.41

^a $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. ^b $R_w = \Sigma(|F_o| - |F_c|)^2/\Sigma w|F_o|^2$.

C(CH₃)₃] 1.29 (6 H, s, NMe₂), -0.56 (6 H, s, AlCH₃). ¹³C NMR (C₆D₆): δ 61.7 (OCH₂), 58.8 (NCH₂), 45.0 [N(CH₃)₂], 33.8 [C(CH₃)₃]. ²⁷Al NMR (CDCl₃): δ 220 (*w*₂ ≈ 5000), 169 (*w*₂ = 3900 Hz).

Crystallographic studies

A crystal of compound **2** was sealed in a glass capillary under argon. Crystal and data collection and solution details are given in Table 2. Standard procedures in our laboratory have been described previously.¹⁴ Data were collected on an Enraf-Nonius CAD-4 diffractometer equipped with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) and corrected for Lorentz and polarization effects. The structures were solved by using direct methods (SHELXS 86¹⁵), and Fourier-difference synthesis and refined using full-matrix least squares.¹⁶ The side-chain exhibited a 1:1 static disorder of the β-carbon and methyl groups resulting from two different chain conformations. Such a chain disorder has been described as a molecular slinky (the so-called "slinky effect"¹⁰), in which the rigid ends of the molecule are fixed in space by molecular packing forces, leaving the interior link to adopt multiple orientations. In the

present case these are energetically degenerate. Except for the ligand backbone carbon atoms all non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were generally located from difference maps and included in the model in idealized positions [*d*_{C-H} = 0.95 Å, *U*(H) = 1.3 *U*_{eq} (attached atom)] and not refined. Scattering factors were taken from the usual source.¹⁷ No variation of *w*(|*F*_o| - |*F*_c|) versus |*F*_o| or (sin θ/λ) was observed.

CCDC reference number 186/1102.

Acknowledgements

Financial support for this work is provided by the Robert A. Welch Foundation.

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Paper 8/03414A