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FULL PAPER

Reaction of $\mathrm{Al(^tBu)_3}$ with $\mathrm{[R_2Al\{\mu\text{-}O(CH_2)_{\mathit{n}}NMe_2\}]_2}$: dependence on the extent of intra-molecular Al···N coordination

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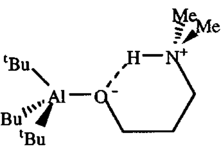
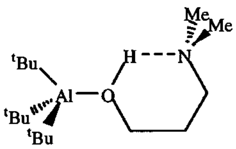
Reaction of $\mathrm{Al(^tBu)_3}$ with $\mathrm{(^tBu)_3Al[O(H)CH_2CH_2CH_2NMe_2]}$ yielded the Lewis acid–base complex $\mathrm{[(^tBu)_2Al\{\mu\text{-}OCH_2CH_2CH_2N(Me)_2Al(^tBu)_3\}]_2}$ **1**. Compound **1** is also formed directly when 2 equivalents of $\mathrm{Al(^tBu)_3}$ reacts with 1 equivalent of $\mathrm{[(^tBu)_2Al(\mu\text{-}OCH_2CH_2CH_2NMe_2)]_2}$. In contrast, the reaction of 2 equivalents of $\mathrm{Al(^tBu)_3}$ with 1 equivalent of $\mathrm{[Me_2Al(\mu\text{-}OCH_2CH_2NMe_2)]_2}$ yielded $\mathrm{Me_2Al(\mu\text{-}OCH_2CH_2NMe_2)Al(^tBu)_3}$ **2**. The molecular structure of compound **2** shows the $\mathrm{AlMe_2}$ moiety chelate bound to the anionic bidentate ligand, while the $\mathrm{Al(^tBu)_3}$ 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.*, $\mathrm{(^tBu)_2Al(\mu\text{-}OCH_2CH_2CH_2NMe_2)Al(^tBu)_3}$, which is unstable due to significant $\mathrm{^tBu\cdots{}^tBu}$ inter-ligand interactions. The implications of the differences in products is discussed with respect to the extent of intra-molecular Al···N coordination in compounds of the general formula $\mathrm{[R_2Al\{\mu\text{-}O(CH_2)_{\mathit{n}}NMe_2\}]_2}$.

Introduction

We have recently reported[1] that the reaction of $\mathrm{Al(^tBu)_3}$ with less than 2 equivalents of $\mathrm{HOCH_2CH_2CH_2NMe_2}$ allows for the isolation of the surprisingly stable Lewis acid–base complex, $\mathrm{(^tBu)_3Al[O(H)CH_2CH_2CH_2NMe_2]}$, in which a strong intra-ligand hydrogen bond and unusually short Al–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 $\mathrm{(^tBu)_3Al[O(H)CH_2CH_2CH_2NMe_2]}$ with additional Lewis acids, in particular trialkylaluminium compounds.



I

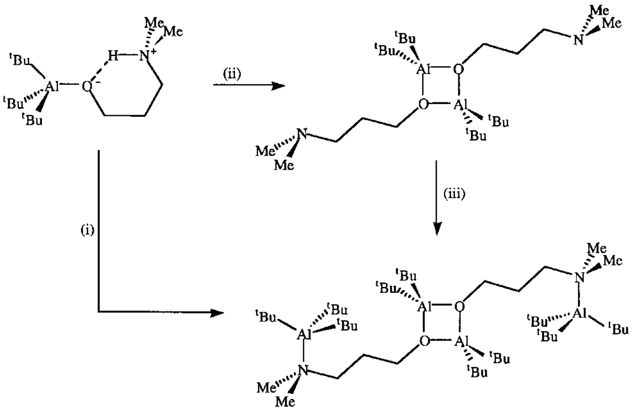


II

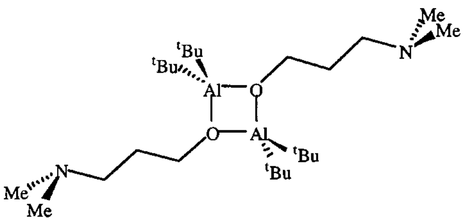
Results and discussion

Reaction of $\mathrm{(^tBu)_3Al[O(H)CH_2CH_2CH_2NMe_2]}$ with 2 equivalents of $\mathrm{Al(^tBu)_3}$ allows for the isolation of the Lewis acid–base complexes, $\mathrm{[(^tBu)_2Al\{\mu\text{-}OCH_2CH_2CH_2N(Me)_2Al(^tBu)_3\}]_2}$ **1** and the concomitant elimination of isobutane, see Scheme 1(i). Compound **1** has been characterized by NMR spectroscopy and mass spectrometry. The ^{27}Al 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 ^{27}Al NMR spectrum of $\mathrm{[(^tBu)_2Al(\mu\text{-}OCH_2CH_2CH_2NMe_2)]_2}$[1] **III** which shows a single resonance at δ 143 ($w_{\frac{1}{2}} = 4400$ Hz), we can assign the peak at δ 126 to the "$\mathrm{(^tBu)_2Al}$" moiety.

A comparison of the ^{1}H NMR spectrum of compound **1** with that of $\mathrm{[(^tBu)_2Al(\mu\text{-}OCH_2CH_2CH_2NMe_2)]_2}$ **III** shows that there is essentially no change in the chemical shifts for the $\mathrm{OCH_2CH_2}$ and *tert*-butyl resonances, but a significant downfield shift for the $\mathrm{CH_2N(CH_3)_2}$ 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 $\mathrm{Al(^tBu)_3}$ moiety to the amine nitrogen.[3] Furthermore, the ^{1}H NMR resonance of the *tert*-butyl groups of the $\mathrm{Al(^tBu)_3}$ unit in compound **1** (δ 1.18) is shifted downfield relative to that of uncomplexed $\mathrm{Al(^tBu)_3}$ (δ 1.07) in a similar manner to that observed for other Lewis acid–base complexes of $\mathrm{Al(^tBu)_3}$.[4]



Scheme 1 Synthetic routes to $\mathrm{[(^tBu)_2Al\{\mu\text{-}OCH_2CH_2CH_2N(Me)_2\text{-}Al(^tBu)_3\}]_2}$ **1**: (i) 2 equivalents $\mathrm{Al(^tBu)_3}$; (ii) heat, 45 °C in benzene; (iii) 2 equivalents $\mathrm{Al(^tBu)_3}$ in hexane.



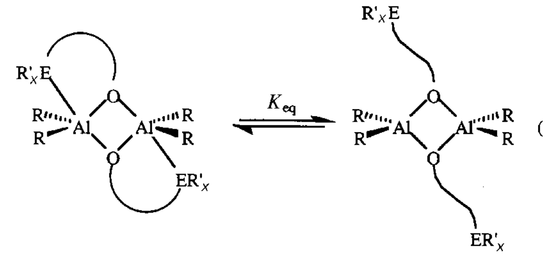
III

Clearly, compound **1** is best considered as the Lewis acid–base complex of $\mathrm{Al(^tBu)_3}$ with the previously reported alkoxide amine derivative, $\mathrm{[(^tBu)_2Al(\mu\text{-}OCH_2CH_2CH_2NMe_2)]_2}$, which is formed from the thermolysis of $\mathrm{(^tBu)_3Al[O(H)CH_2CH_2CH_2NMe_2]}$, see Scheme 1(ii). In fact, compound **1** is readily prepared by the direct reaction of 2 equivalents of $\mathrm{Al(^tBu)_3}$ with $\mathrm{[(^tBu)_2Al(\mu\text{-}OCH_2CH_2CH_2NMe_2)]_2}$, 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 $Me_2Al(\mu\text{-}OCH_2CH_2NMe_2)Al(^tBu)_3$ **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)		



(1)

$[O(CH_2)_nER'_x]^-$ (E = O, S or N; $n = 2$ or 3), $[(^tBu)_2Al(\mu\text{-}OCH_2CH_2CH_2NMe_2)]_2$ **III** exists as an equilibrium in solution between the dimeric five-coordinate and dimeric four-coordinate isomers, where K_{eq} = [4-coord]/[5-coord], eqn. (1).[5] Due to the steric bulk of the aluminium *tert*-butyl groups in $[(^tBu)_2Al(\mu\text{-}OCH_2CH_2CH_2NMe_2)]_2$ the amine is predominantly dissociated ($K_{eq} \approx 6.60$).[5] Thus, it is perhaps expected that the reaction of $[(^tBu)_2Al(\mu\text{-}OCH_2CH_2CH_2NMe_2)]_2$ with $Al(^tBu)_3$ yields compound **1**. In contrast, the amine in $[Me_2Al(\mu\text{-}OCH_2CH_2NMe_2)]_2$ is predominantly associated ($K_{eq} = 0.250$). Given this difference, can the reaction with a Lewis acid (*e.g.*, AlR_3) be used as a probe of the extent of coordination?

Reaction of $[Me_2Al(\mu\text{-}OCH_2CH_2NMe_2)]_2$ with 2 equivalents of $Al(^tBu)_3$ yields $Me_2Al(\mu\text{-}OCH_2CH_2NMe_2)Al(^tBu)_3$ **2** (see Experimental section), in which the $Al\text{–}N_{(amine)}$ intra-molecular interaction is retained but at the expense of the Al_2O_2 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 $Me_2Al(\mu\text{-}OCH_2CH_2NMe_2)Al(^tBu)_3$ **2** is shown in Fig. 1; selected bond lengths and angles are given in Table 1. The geometry of compound **2** is similar to $Me_2Al[\mu\text{-}OCH_2CH(CH_2Ph)NH_2]AlMe_3$,[6] $Me_2Al[\mu\text{-}OCMe_2C(H){=}N(^tBu)]AlMe_3$,[7] $Me_2Al[\mu\text{-}ON(Me)NO]AlMe_3$[8] and $Me_2Al[\mu\text{-}OC(H)(Me)N(Ph)C(Ph){=}O]AlMe_3$[9] in that the anionic bidentate ligand is chelate bound to the AlR_2 moiety, while the AlR_3 unit bonds to the anionic end of the ligand. The Al(2)–O(1) and Al(2)–N(4) bond lengths to the $AlMe_2$ units [1.837(4) and 2.013(6) Å, respectively] are significantly shorter than the analogous values in the dimeric compounds $[R_2Al(\mu\text{-}OCH_2CH_2NR'_2)]_2$ [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 AlR_3 units. The AlOCCN 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 $(^tBu)_3Al[O(H)CH_2CH_2CH_2NMe_2]$ **I** in which an $Al(^tBu)_3$ unit is complexed to a formally anionic oxygen in a heterocyclic ring.

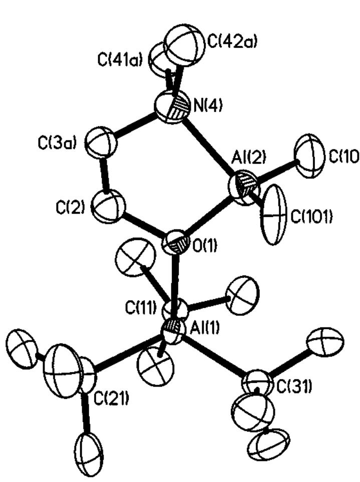


Fig. 1 Molecular structure of $Me_2Al(\mu\text{-}OCH_2CH_2NMe_2)Al(^tBu)_3$ **2**. Thermal ellipsoids shown at the 30% level, and hydrogen atoms are omitted for clarity. Only one confirmation of the cyclic ring is shown.

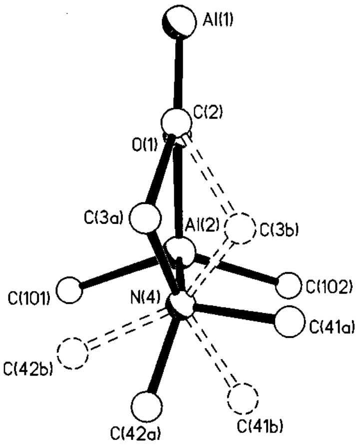
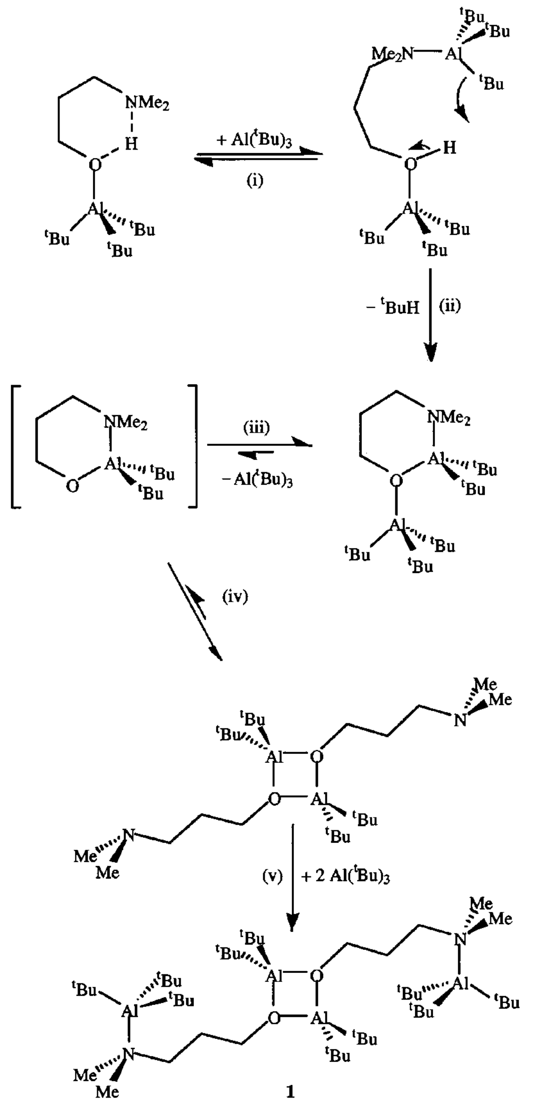


Fig. 2 Partial coordination sphere of $Me_2Al(\mu\text{-}OCH_2CH_2NMe_2)Al(^tBu)_3$ **2** showing the site disorder of the $OCH_2CH_2NMe_2$ group. Hydrogen atoms are omitted for clarity.

In each compound the oxygen is also bonded to a carbon and the formal cationic moiety (H^+ in $(^tBu)_3Al[O(H)CH_2CH_2CH_2NMe_2]$ and $[AlMe_2]^+$ in compound **2**). The analogy has some precedent since we have previously shown by ^{17}O NMR spectroscopy that aluminium and a proton have similar electronegatives with regard to oxygen.[11]

Although the differences in reactivity of $[Me_2Al(\mu\text{-}OCH_2CH_2NMe_2)]_2$ and $[(^tBu)_2Al(\mu\text{-}OCH_2CH_2CH_2NMe_2)]_2$ 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 $(^tBu)_3Al[O(H)CH_2CH_2CH_2NMe_2]$ 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.*, $(^tBu)_2Al(\mu\text{-}OCH_2CH_2CH_2NMe_2)Al(^tBu)_3$, 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 $(^tBu)_2Al(\mu\text{-}OCH_2CH_2NMe_2)Al(^tBu)_3$ (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 "$(^tBu)_2Al(OCH_2CH_2CH_2NMe_2)$" is formed it will dimerize [Scheme 2(iv)] to give the previously isolated $[(^tBu)_2Al(\mu\text{-}OCH_2CH_2CH_2NMe_2)]_2$, 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 (^{t}Bu)$_3$Al[O(H)CH$_2$CH$_2$CH$_2$NMe$_2$] with Al(^{t}Bu)$_3$ 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 (4000–400 cm^{-1}) were obtained using an 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$_6$D$_6$ solutions. Chemical shifts are reported relative to internal solvent resonances (^{1}H and ^{13}C), and external [Al(H$_2$O)$_6$]$^{3+}$ (^{27}Al). The synthesis of Al(^{t}Bu)$_3$ was performed according to modification of the literature methods.[12] [Me$_2$Al(μ-OCH$_2$CH$_2$NMe$_2$)]$_2$,[13] (^{t}Bu)$_3$Al[O(H)CH$_2$CH$_2$CH$_2$NMe$_2$][1] and [(^{t}Bu)$_2$Al(μ-OCH$_2$CH$_2$CH$_2$NMe$_2$)]$_2$[1] were prepared as previously reported.

Synthesis

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

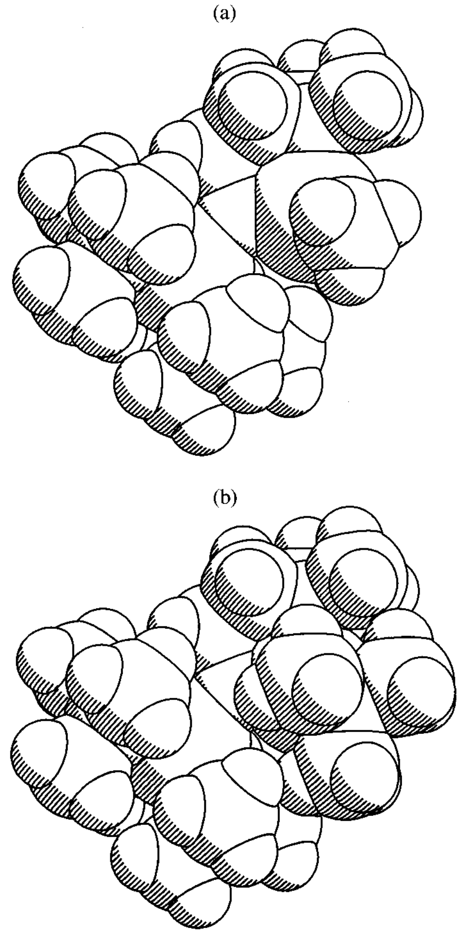


Fig. 3 Space filling representations of (a) Me$_2$Al(μ-OCH$_2$CH$_2$NMe$_2$)Al(^{t}Bu)$_3$ **2** and (b) a computer generated idealization of (^{t}Bu)$_2$Al(μ-OCH$_2$CH$_2$NMe$_2$)Al(^{t}Bu)$_3$, showing the different steric interactions of the *tert*-butyl group on aluminium. Both views are perpendicular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

Method 2.—To a solution of (^{t}Bu)$_3$Al[O(H)CH$_2$CH$_2$CH$_2$NMe$_2$] (0.39 g, 1.29 mmol) in hexane (40 mL), cooled to −78 °C, was added Al(^{t}Bu)$_3$ (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 [2M$^+$ − ^{t}Bu − 2 Al(^{t}Bu)$_3$, 100], 186 [M$^+$ − ^{t}Bu − Al(^{t}Bu)$_3$, 26], 86 [(CH$_2$)$_3$NMe$_2$, 73], 57 (^{t}Bu, 82). IR (cm^{-1}): 1081m, 1038m (br), 1002m, 966m, 813m, 642s, 593m, 560s, 519m, 418s. ^{1}H NMR (C$_6$D$_5$CD$_3$): δ 3.83 [4 H, t, *J*(H–H) = 8.2, OCH$_2$], 2.89 [4 H, t, *J*(H–H) = 8.1 Hz, NCH$_2$], 2.11 [12 H, s, N(CH$_3$)$_2$], 1.87 (4 H, m, CH$_2$), 1.25 [54 H, s, C(CH$_3$)$_3$], 1.18 [36 H, s, C(CH$_3$)$_3$]. ^{13}C NMR (C$_6$D$_5$CD$_3$): δ 64.0 (OCH$_2$), 53.5 (NCH$_2$), 44.0 [N(CH$_3$)$_2$], 33.8 [C(*C*H$_3$)$_3$], 32.3 [C(*C*H$_3$)$_3$], 18.89 (CH$_2$*C*H$_2$CH$_2$). ^{27}Al NMR (CDCl$_3$): δ 126 ($w_{\frac{1}{2}}$ = 4800), 47 ($w_{\frac{1}{2}}$ ≈ 5000 Hz).

Me$_2$Al(μ-OCH$_2$CH$_2$NMe$_2$)Al(^{t}Bu)$_3$ 2. To a solution of [Me$_2$Al(μ-OCH$_2$CH$_2$NMe$_2$)]$_2$ (0.5 g, 1.7 mmol) in hexane (40 mL), cooled to −78 °C, was added Al(^{t}Bu)$_3$ (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 (M$^+$ − ^{t}Bu, 10), 230 (M$^+$ − 2 ^{t}Bu, 10), 130 [M$^+$ − Al(^{t}Bu)$_3$ − Me, 60], 57 (^{t}Bu, 100). IR (cm^{-1}): 2690m, 1260m, 1202s, 1043s, 1009s, 950s, 878s, 808s. ^{1}H NMR (C$_6$D$_6$): δ 3.82 [2 H, t, *J*(H–H) = 5.5, OCH$_2$], 1.59 [2 H, t, *J*(H–H) = 5.5 Hz, NCH$_2$], 1.42 [27 H, s,

Table 2 Summary of X-ray diffraction data

Compound	$Me_2Al(\mu\text{-}OCH_2CH_2NMe_2)Al(^tBu)_3$ **2**
Formula	$C_{18}H_{43}Al_2NO$
M	343.5
Crystal size/mm	0.21 × 0.23 × 0.26
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	10.2671(8)
b/Å	16.471(1)
c/Å	13.867(2)
β/°	99.407(8)
U/Å^3	2313.5(4)
Z	4
D_c/g cm^{-3}	0.986
μ/cm^{-1}	1.25
T/K	298
2θ Range/°	3.0–44.0
No. reflections collected	3137
No. individual reflections	2955
No. observed reflections ($\lvert F_o\rvert > 6.0\sigma\lvert F_o\rvert$)	1265
Weighting scheme (w^{-1})	$0.04\,(\lvert F_o\rvert)^2 + \sigma(\lvert F_o\rvert)^2$
R^a	0.0602
$R_w{}^b$	0.0655
Largest difference peak/e Å^{-3}	0.41

^{a} $R = \Sigma(\lvert F_o\rvert - \lvert F_c\rvert)/\Sigma\lvert F_o\rvert$. ^{b} $R_w = \Sigma(\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert)^2/\Sigma w\lvert F_o\rvert^2$.

$C(CH_3)_3$] 1.29 (6 H, s, NMe_2), −0.56 (6 H, s, $AlCH_3$). ^{13}C NMR (C_6D_6): δ 61.7 (OCH_2), 58.8 (NCH_2), 45.0 [$N(CH_3)_2$], 33.8 [$C(CH_3)_3$]. ^{27}Al NMR ($CDCl_3$): δ 220 ($w_{\frac{1}{2}} \approx 5000$), 169 ($w_{\frac{1}{2}} = 3900$ 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 ($\lambda = 0.71073$ Å) and corrected for Lorentz and polarization effects. The structures were solved by using direct methods (SHELXS 86[15]), 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 $w(\lvert F_o\rvert - \lvert F_c\rvert)$ *versus* $\lvert F_o\rvert$ or (sin θ/λ) was observed.

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Acknowledgements

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References

1 C. N. McMahon, S. G. Bott and A. R. Barron, *J. Chem. Soc.*, *Dalton Trans.*, 1997, 3129.
2 A. R. Barron, *Polyhedron*, 1995, **14**, 3197.
3 A. R. Barron, *J. Chem. Soc.*, *Dalton Trans.*, 1988, 3047.
4 C. J. Harlan, S. G. Bott and A. R. Barron, *J. Am. Chem. Soc.*, 1995, **117**, 6465.
5 J. A. Francis, C. N. McMahon, S. G. Bott and A. R. Barron, *Organometallics*, submitted.
6 D. A. Atwood, F. P. Gabbai, J. Lu, M. P. Remington, D. Rutherford and M. P. Sibi, *Organometallics*, 1996, **15**, 2308.
7 M. R. P. van Vliet, G. van Koten, M. A. Rotteveel, M. Schrap, K. Vrieze, B. Kojic-Prodic, A. L. Spek and A. J. M. Duisenberg, *Organometallics*, 1986, **5**, 1389.
8 S. Amirkhalili, P. B. Hitchcock, J. D. Smith and J. G. Stamper, *J. Chem. Soc.*, *Dalton Trans.*, 1980, 2493.
9 Y. Kai, N. Yasuoka, N. Kassai and M. Kakudo, *Bull. Chem. Soc. Jpn.*, 1972, **45**, 3403.
10 C. L. Aitken and A. R. Barron, *J. Chem. Crystallogr.*, 1996, **26**, 297.
11 A. W. Apblett, A. C. Warren and A. R. Barron, *Can. J. Chem.*, 1992, **70**, 771.
12 W. Uhl, *Z. Anorg. Allg. Chem.*, 1989, **570**, 37; H. Lehmkuhl, O. Olbrysch and H. Nehl, *Liebigs Ann. Chem.*, 1973, 708; H. Lehmkuhl and O. Olbrysch, *Liebigs Ann. Chem.*, 1973, 715.
13 O. T. Beachley, jun. and K. C. Racette, *Inorg. Chem.*, 1976, **15**, 2110.
14 C. J. Harlan, S. G. Bott and A. R. Barron, *J. Am. Chem. Soc.*, 1995, **117**, 6465.
15 G. M. Sheldrick, *Acta Crystallogr.*, *Sect. A*, 1990, **46**, 467.
16 MOLEN, An interactive Structure Solution Procedure, Enraf-Nonius, Delft, Netherlands, 1990.
17 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.

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