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Synthesis of a base-stabilized alumoxane: preferential hydrolysis of an aluminium–amido over an aluminium–alkyl

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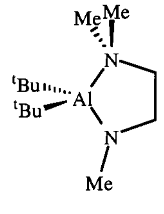
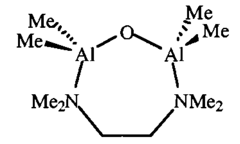
The preferential hydrolytic cleavage of an Al–N *versus* an Al–C bond allows for the isolation of the base stabilized alkylalumoxane, $[(^t\mathrm{Bu})_2\mathrm{Al}\{\mathrm{NH(Me)CH_2CH_2NMe_2}\}]_2(\mu\text{-O})$, from the hydrolysis of the intra-molecularly stabilized amino–amide compound, $(^t\mathrm{Bu})_2\mathrm{Al[N(Me)CH_2CH_2NMe_2]}$, providing a possible general route to alkylalumoxanes.

Conceptually, but not experimentally, the simplest route to alkylalumoxanes (compounds of the general formulae $[(\mathrm{R})\mathrm{Al(O)}]_n$ and $[\mathrm{R_2Al{-}O{-}AlR_2}]_n$) involves the reaction of water with a trialkylaluminium compound.[1] Reacting water (or ice)[2] with an aromatic or aliphatic hydrocarbon solution of a trialkylaluminium will yield an alkylalumoxane, however, it is important to control the temperature of this highly exothermic reaction both as a safety precaution[3] and in order to maximize the yield and ensure the solubility of the products.[4] In an effort to control the rate at which the water reacts with the trialkylaluminium, several researchers have employed hydrated salts, such as $\mathrm{Al_2(SO_4)_3{\cdot}14H_2O}$ or $\mathrm{CuSO_4{\cdot}5H_2O}$, as “indirect hydrolysis” sources,[5] since the water of crystallization in a hydrated salt reacts at a vastly decreased rate as compared to dissolved “free” water. While a number of alternative routes have also been investigated,[6] none is of generic application and the hydrolysis of trialkylaluminium compounds remains the method of preference. It would be desirable, however, to develop a more general approach to alkylalumoxanes in order to study their structure and reactivity. We have previously observed that in the presence of a heteroatom donor ligand (*e.g.*, alkoxide, aryloxide, amide, *etc.*) the basicity (reactivity) of an aluminium alkyl group is significantly reduced.[7] For example, reaction of $[\mathrm{Me_2Al}(\mu\text{-NH}_2)]_3$ with HOAr (Ar = $\mathrm{C_6H_2\text{-}Bu^t_2\text{-}2,6\text{-}Me\text{-}4}$) results in the formation of $\mathrm{Me_2Al(OAr)(NH_3)}$.[8] Based on these results it is reasonable to propose that alkylalumoxanes may be prepared through the hydrolysis of alkylaluminium amides, alkoxides, *etc.*

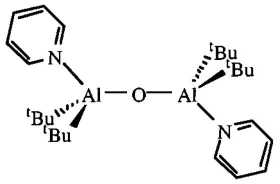
The intra-molecularly stabilized amino–amide compound $(^t\mathrm{Bu})_2\mathrm{Al[N(Me)CH_2CH_2NMe_2]}$ **I**[9] is a stable non-pyrophoric solid which undergoes slow hydrolysis resulting in the essentially stoichiometric formation of $[(^t\mathrm{Bu})_2\mathrm{Al}\{\mathrm{NH(Me)CH_2CH_2NMe_2}\}]_2(\mu\text{-O})$.† The molecular structure of $[(^t\mathrm{Bu})_2\mathrm{Al}\{\mathrm{NH(Me)CH_2CH_2NMe_2}\}]_2(\mu\text{-O})$ has been confirmed by X-ray crystallography,‡ and may be described as a base stabilized tetraalkylalumoxane. Pasynkiewicz and co-workers have reported that the partial hydrolysis of $\mathrm{AlMe_3}$ in the presence of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) gave a base stabilized tetramethylalumoxane **II** in low yield, however, no structural information was obtained.[10] Subsequently, we have reported a similar synthesis for the first example of a structurally characterized tetraalkylalumoxane, $[(^t\mathrm{Bu})_2\mathrm{Al(py)}]_2(\mu\text{-O})$ **III**.[11]



I



II



III

The molecular structure of $[(^t\mathrm{Bu})_2\mathrm{Al}\{\mathrm{NH(Me)CH_2CH_2NMe_2}\}]_2(\mu\text{-O})$ is shown in Fig. 1. The molecule exists as a dimer consisting of two $(^t\mathrm{Bu})_2\mathrm{Al}\{\mathrm{NH(Me)CH_2CH_2NMe_2}\}$ moieties linked by a single oxygen atom bridge, such that the amine ligands are in a staggered *anti* conformation, see Fig. 2. Although not constrained by crystal symmetry, as was observed for $[(^t\mathrm{Bu})_2\mathrm{Al(py)}]_2(\mu\text{-O})$,[11] the Al(1)–O(1)–Al(2) angle in $[(^t\mathrm{Bu})_2\mathrm{Al}\{\mathrm{NH(Me)CH_2CH_2NMe_2}\}]_2(\mu\text{-O})$ is close to linear [173.0(4)°], precluding its assignment as a bridging hydroxide or water. The Al–O distances [1.690(7) and 1.714(7) Å] are comparable to those found for $[(^t\mathrm{Bu})_2\mathrm{Al(py)}]_2(\mu\text{-O})$ [1.710(1) Å].[11] It is worth noting that these Al–O distances are within the range observed for oxo-bridged complexes that contain two five-coordinate aluminium atoms [1.679(2)–1.713(5) Å] in which the Al–O–Al angle varies between 152.0(3)° and 180°.[12] The infrared spectrum of $[(^t\mathrm{Bu})_2\mathrm{Al}\{\mathrm{NH(Me)CH_2CH_2NMe_2}\}]_2(\mu\text{-O})$ shows a strong asymmetric Al–O–Al stretch at 1035 $\mathrm{cm^{-1}}$. This is consistent with a linear $\mathrm{Al_2O}$ linkage by comparison to the stretches observed for structurally characterized compounds $[\mathrm{L_2Al}]_2(\mu\text{-O})$, L = 2-methyl-8-quinolinolato (997 $\mathrm{cm^{-1}}$), $\mathrm{L_2}$ = phthalocyanato (1051 $\mathrm{cm^{-1}}$), or *N*,*N*′-ethylenebis(salicylideneiminato) (1067 $\mathrm{cm^{-1}}$).[12]

The diamine ligands in $[(^t\mathrm{Bu})_2\mathrm{Al}\{\mathrm{NH(Me)CH_2CH_2NMe_2}\}]_2(\mu\text{-O})$ adopt a configuration that allow hydrogen bonding between the secondary amine’s hydrogen atom and the tertiary amine nitrogen. A similar configuration was observed in $(^t\mathrm{Bu})_3\mathrm{Al[NH(Me)CH_2CH_2NMe_2]}$ and $(^t\mathrm{Bu})_3\mathrm{Al[NH(Me)CH_2CH_2CH_2NMe_2]}$.[13] The N···N distances [2.87, 2.94 Å] and N–H···N angles [110, 114°] in $[(^t\mathrm{Bu})_2\mathrm{Al}\{\mathrm{NH(Me)CH_2CH_2NMe_2}\}]_2(\mu\text{-O})$ are similar to those in $(^t\mathrm{Bu})_3\mathrm{Al[NH(Me)CH_2CH_2NMe_2]}$ and $(^t\mathrm{Bu})_3\mathrm{Al[NH(Me)CH_2CH_2CH_2NMe_2]}$.[13]

The hydrolytic protonation of the amide nitrogen, rather than one of the *tert*-butyl groups, follows our previous observ-

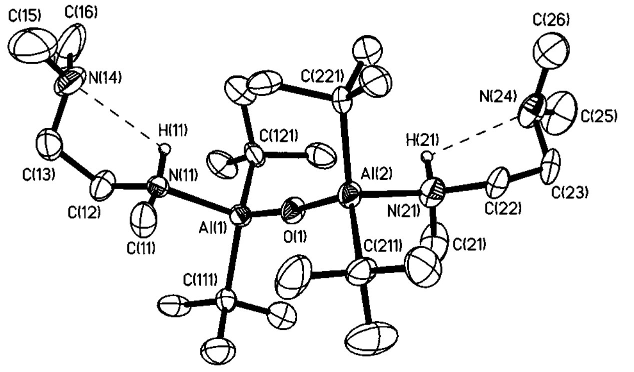


Fig. 1 Molecular structure of [(^{t}Bu)$_2$Al{NH(Me)CH$_2$CH$_2$NMe$_2$}]$_2$-(μ-O). Thermal ellipsoids shown at the 30% level, and only the amine hydrogens are shown for clarity. Selected bond lengths (Å) and angles (°): Al(1)–O(1) 1.690(7), Al(2)–O(1) 1.714(7), Al(1)–N(11) 2.053(8), Al(2)–N(21) 2.047(9), Al–C 2.00(1)–2.02(1); Al(1)–O(1)–Al(2) 173.0(4), O(1)–Al(1)–N(11) 100.8(3), O(1)–Al(2)–N(21) 101.6(4), O(1)–Al–C 112.6(4)–114.2(4).

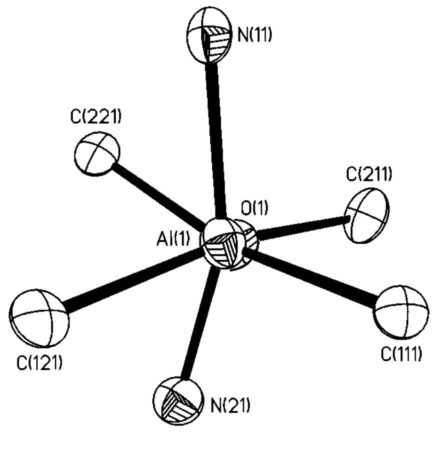


Fig. 2 The aluminium coordination sphere in [(^{t}Bu)$_2$Al{NH(Me)-CH$_2$CH$_2$NMe$_2$}]$_2$(μ-O) viewed along the Al(1)–Al(2) vector. The N(11)–Al(1)–Al(2)–N(21) torsion angle = 160°. Thermal ellipsoids shown at the 30% level, and hydrogen atoms are omitted for clarity.

ations that the presence of a heteroatom donor ligand (*e.g.*, alkoxide, aryloxide, amide, *etc.*) significantly reduces the basicity of the aluminium alkyl group.[14] Thus, the reaction of a Brönsted acid occurs *via* protonation of the hetero-atom [eqn. (1)] and not the alkyl group [eqn. (2)].[15]

$$[R_2Al(X)]_n + \tfrac{n}{2}\,H_2O \longrightarrow \tfrac{n}{2}\,[R_2Al\text{–}O\text{–}AlR_2]_n + n\,HX \tag{1}$$

$$[R_2Al(X)]_n + \tfrac{n}{2}\,H_2O \longrightarrow \tfrac{n}{2}\,[R(X)Al\text{–}O\text{–}Al(X)R]_n + n\,RH \tag{2}$$

Although alkylalumoxanes are ordinarily formed *via* the hydrolysis of trialkylaluminium compounds, with the concomitant liberation of the corresponding alkane, hydrolysis of readily prepared dialkylaluminium amides (and alkoxides) offers an alternative and milder synthesis to a variety of alkylalumoxane structures. We are presently using this method to obtain additional information into the structure of alkylalumoxanes.

Acknowledgements

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Notes and references

† A solution of (^{t}Bu)$_2$Al[N(Me)CH$_2$CH$_2$NMe$_2$] was dissolved in hexane and exposed to moist air. Colorless crystals (*ca.* 1.0 g) resulted upon cooling to −23 °C. Yield: ≈90%. IR (Nujol mull, KBr plates, cm^{-1}): 3329w, 2695m, 1613w, 1589w, 1570w, 1359s, 1383s, 1261s, 1188s, 1035s, 931m, 889m, 806m, 759m. ^{1}H NMR (Bruker AM-250, C$_6$D$_6$): δ 3.25 (4 H, m, NCH$_2$), 2.35 [6 H, d, *J*(H–H) = 6.2 Hz, N(CH$_3$)], 2.14 (4 H, m, NCH$_2$), 1.89 [12 H, s, N(CH$_3$)$_2$], 1.37 [18 H, s, C(CH$_3$)$_3$], 1.33 [18 H, s, C(CH$_3$)$_3$].

‡ Crystal data for [(^{t}Bu)$_2$Al{NH(Me)CH$_2$CH$_2$NMe$_2$}]$_2$(μ-O): C$_{26}$H$_{64}$-Al$_2$N$_4$O, $M = 502.8$, monoclinic, space group $P2_1/n$, $a = 15.096(3)$, $b = 14.919(3)$, $c = 15.337(3)$ Å, $\beta = 91.41(3)$°, $U = 3453(1)$ Å^3, $Z = 4$, $D_c = 0.967$ g cm^{-3}, $T = 298$ K, μ(Mo-Kα) = 13.29 cm^{-1}, $F(000) = 1128$, $R = 0.0489$, $R_w = 0.0504$ for 1177 independent observed reflections [$|F_o| > 6.0\sigma|F_o|$, $4.0 \le 2\theta \le 40.0$°] and 298 parameters, largest residual = 0.18 e Å^{-3}. CCDC reference number 186/1190.

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