

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

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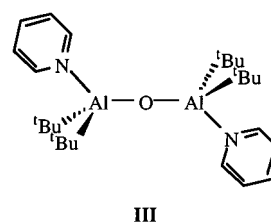
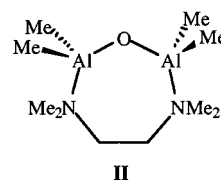
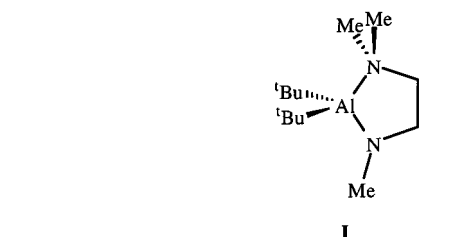
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The preferential hydrolytic cleavage of an Al–N *versus* an Al–C bond allows for the isolation of the base stabilized alkylalumoxane, [(^tBu)₂Al{NH(Me)CH₂CH₂NMe₂}]₂(μ-O), from the hydrolysis of the intra-molecularly stabilized amino–amide compound, (^tBu)₂Al[N(Me)CH₂CH₂NMe₂], providing a possible general route to alkylalumoxanes.

Conceptually, but not experimentally, the simplest route to alkylalumoxanes (compounds of the general formulae [(R)Al(O)]_n and [R₂Al–O–AlR₂]_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 precaution³ 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 Al₂(SO₄)₃·14H₂O or CuSO₄·5H₂O, 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, aryloxy, amide, *etc.*) the basicity (reactivity) of an aluminium alkyl group is significantly reduced.⁷ For example, reaction of [Me₂Al(μ-NH₂)₃] with HOAr (Ar = C₆H₂-Bu^t-2,6-Me-4) results in the formation of Me₂Al(OAr)(NH₃).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 (^tBu)₂Al[N(Me)CH₂CH₂NMe₂] **I**⁹ is a stable non-pyrophoric solid which undergoes slow hydrolysis resulting in the essentially stoichiometric formation of [(^tBu)₂Al{NH(Me)CH₂CH₂NMe₂}]₂(μ-O).[†] The molecular structure of [(^tBu)₂Al{NH(Me)CH₂CH₂NMe₂}]₂(μ-O) has been confirmed by X-ray crystallography,[‡] and may be described as a base stabilized tetraalkylalumoxane. Pasykiewicz and co-workers have reported that the partial hydrolysis of AlMe₃ 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, [(^tBu)₂Al(py)]₂(μ-O) **III**.¹¹

The molecular structure of [(^tBu)₂Al{NH(Me)CH₂CH₂NMe₂}]₂(μ-O) is shown in Fig. 1. The molecule exists as a dimer consisting of two (^tBu)₂Al{NH(Me)CH₂CH₂NMe₂} 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 [(^tBu)₂Al(py)]₂(μ-O),¹¹ the Al(1)–O(1)–Al(2) angle in [(^tBu)₂Al{NH(Me)CH₂CH₂NMe₂}]₂(μ-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 [(^tBu)₂Al(py)]₂(μ-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 [(^tBu)₂Al{NH(Me)CH₂CH₂NMe₂}]₂(μ-O) shows a strong asymmetric Al–O–Al stretch at 1035 cm⁻¹. This is consistent with a linear Al₂O linkage by comparison to the stretches observed for structurally characterized compounds [L₂Al]₂(μ-O), L = 2-methyl-8-quinolinolato (997 cm⁻¹), L₂ = phthalocyanato (1051 cm⁻¹), or *N,N'*-ethylenebis(salicylideneiminato) (1067 cm⁻¹).¹²



The diamine ligands in [(^tBu)₂Al{NH(Me)CH₂CH₂NMe₂}]₂(μ-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 (^tBu)₃Al[NH(Me)CH₂CH₂NMe₂] and (^tBu)₃Al[NH(Me)CH₂CH₂CH₂NMe₂].¹³ The N···N distances [2.87, 2.94 Å] and N–H···N angles [110, 114°] in [(^tBu)₂Al{NH(Me)CH₂CH₂NMe₂}]₂(μ-O) are similar to those in (^tBu)₃Al[NH(Me)CH₂CH₂CH₂NMe₂] and (^tBu)₃Al[NH(Me)CH₂CH₂CH₂NMe₂].¹³

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

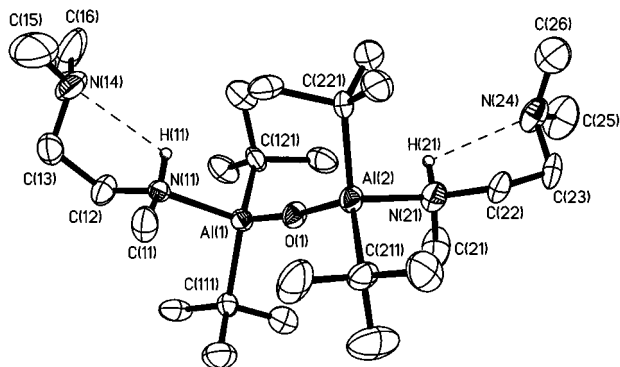


Fig. 1 Molecular structure of $[(t\text{Bu})_2\text{Al}\{\text{NH}(\text{Me})\text{CH}_2\text{CH}_2\text{NMe}_2\}]_2(\mu\text{-O})$. Thermal ellipsoids shown at the 30% level, and only the amine hydrogens are shown for clarity. Selected bond lengths (Å) and angles ($^\circ$): Al(1)–O(1) 1.690(7), Al(2)–O(1) 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).

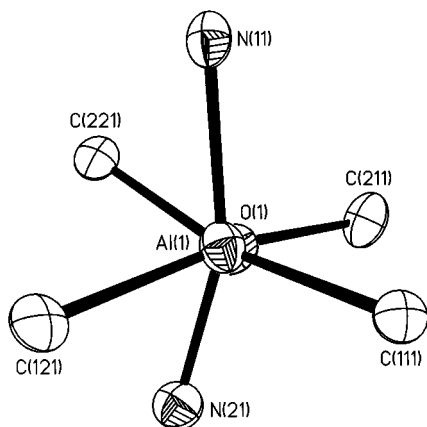
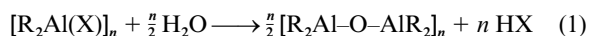


Fig. 2 The aluminium coordination sphere in $[(t\text{Bu})_2\text{Al}\{\text{NH}(\text{Me})\text{CH}_2\text{CH}_2\text{NMe}_2\}]_2(\mu\text{-O})$ viewed along the Al(1)–Al(2) vector. The N(11)–Al(1)–Al(2)–N(21) torsion angle = 160° . Thermal ellipsoids shown at the 30% level, and hydrogen atoms are omitted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

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



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

Acknowledgements

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Notes and references

† A solution of $(t\text{Bu})_2\text{Al}[\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{NMe}_2]$ was dissolved in hexane and exposed to moist air. Colorless crystals (*ca.* 1.0 g) resulted upon cooling to -23°C . Yield: $\approx 90\%$. IR (Nujol mull, KBr plates, cm^{-1}): 3329w, 2695m, 1613w, 1589w, 1570w, 1359s, 1383s, 1261s, 1188s, 1035s, 931m, 889m, 806m, 759m. ^1H NMR (Bruker AM-250, C_6D_6): δ 3.25 (4 H, m, NCH₂), 2.35 [6 H, d, $J(\text{H}-\text{H}) = 6.2$ Hz, N(CH₃)], 2.14 (4 H, m, NCH₂), 1.89 [12 H, s, N(CH₃)₂], 1.37 [18 H, s, C(CH₃)₃], 1.33 [18 H, s, C(CH₃)₃].

‡ Crystal data for $[(t\text{Bu})_2\text{Al}\{\text{NH}(\text{Me})\text{CH}_2\text{CH}_2\text{NMe}_2\}]_2(\mu\text{-O})$: $\text{C}_{26}\text{H}_{64}\text{Al}_2\text{N}_4\text{O}$, $M = 502.8$, monoclinic, space group $P2_1/n$, $a = 15.096(3)$, $b = 14.919(3)$, $c = 15.337(3)$ Å, $\beta = 91.41(3)^\circ$, $U = 3453(1)$ Å³, $Z = 4$, $D_c = 0.967$ g cm^{-3} , $T = 298$ K, $\mu(\text{Mo-K}\alpha) = 13.29$ cm^{-1} , $F(000) = 1128$, $R = 0.0489$, $R_w = 0.0504$ for 1177 independent observed reflections [$|F_o| > 6.0\sigma|F_o|$; $4.0 \leq 2\theta \leq 40.0^\circ$] and 298 parameters, largest residual = $0.18 \text{ e } \text{Å}^{-3}$. CCDC reference number 186/1190.

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