

An unprecedented coordination mode for hemilabile pendant-arm 1,4,7-triazacyclononanes and the synthesis of cationic organoaluminium complexes

David A. Robson,^a Leigh H. Rees,^a Philip Mountford^{*a} and Martin Schröder^{*b}

^a *Inorganic Chemistry Laboratory, South Parks Road, Oxford, UK OX1 3QR.*

E-mail: philip.mountford@chemistry.oxford.ac.uk

^b *School of Chemistry, University of Nottingham, University Park, Nottingham, UK NG7 2RD.*

E-mail: martin.schroder@nott.ac.uk

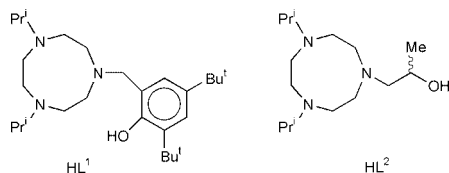
Received (in Cambridge, UK) 14th April 2000, Accepted 24th May 2000

Published on the Web 26th June 2000

Reaction of AlMe_3 or $[\text{AlMe}_3\text{-py}]$ with the pendant arm OH-functionalised 1,4,7-triazacyclononane proligands, HL^1 or HL^2 , affords the four- and five-coordinate derivatives $[\text{Al}(\text{L}^1)\text{Me}_2]$ **1** or $[\text{Al}_2(\text{L}^2)_2\text{Me}_4]$ **2** in which the pendant alkoxide O-donor and only *one* macrocycle N-donor is bound to Al; methyl anion abstraction from **1** yields cationic, pentacoordinate $[\text{Al}(\text{L}^1)\text{Me}]^+$ in which L^1 has a tetradentate coordination mode [$\text{L}^1 = 1$ -(2-hydroxy-3,5-di-*tert*-butylbenzyl)-4,7-diisopropyl-1,4,7-triazacyclononane; $\text{L}^2 = 1$ -(2-hydroxy-2-methylethyl)-4,7-diisopropyl-1,4,7-triazacyclononane].

Pendant-arm macrocycles offer the ability to modify and tune the electronic and stereochemical properties of a range of metal centres,¹ and may be regarded as potent protecting groups for catalytic reactions. We were therefore interested to explore the potential of pendant arm triazacyclononane ligands in neutral and cationic organoaluminium chemistry, for which there is no precedent in the literature, although several examples of compounds involving N-substituted 1,4,7-triazacyclononane ligands with the group 13 elements are known. Aluminium compounds in general are widely used as reagents or catalysts across a range of organic and inorganic chemistry, and cationic complexes, in particular, can lead to enhanced reactivity through more effective substrate coordination and activation.² We report herein preliminary results, including the first structurally authenticated examples of complexes having a triazacyclononane ligand coordinated through only *one* nitrogen, together with the first example of a cationic *p*-block organometallic complex of a triazacyclononane ligand.

Reaction of AlMe_3 or $\text{AlMe}_3\text{-py}$ with HL^1 or HL^2 causes elimination of methane and affords the mono- or bi-nuclear

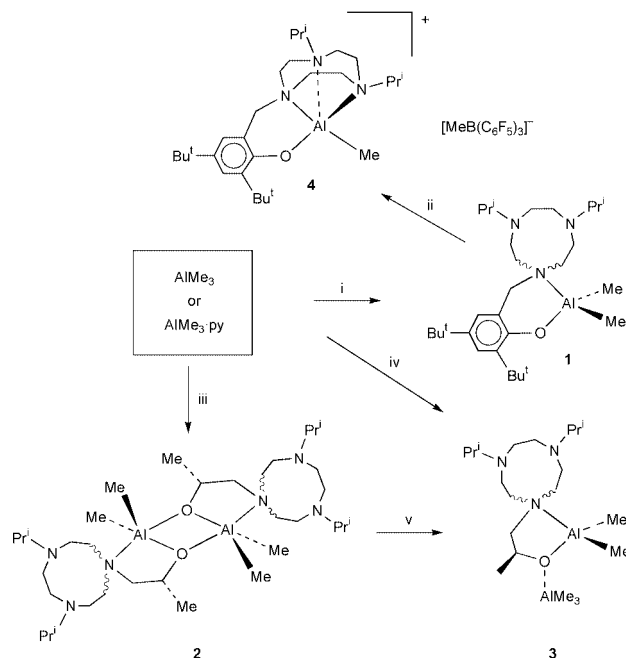


compounds $[\text{Al}(\text{L}^1)\text{Me}_2]$ **1** and $[\text{Al}_2(\text{L}^2)_2\text{Me}_4]$ **2** in good to fair yield (Scheme 1).^{†,3a} The molecular structures of **1** and **2** are shown in Figs. 1 and 2, respectively.[‡] The compound $[\text{Al}(\text{L}^1)\text{Me}_2]$ **1** possesses an approximately tetrahedral Al(III) centre [range of angles subtended at Al(1): 95.0(2)–119.8(2)°], the coordination sphere of which comprises two methyl groups, the oxygen atom of the pendant phenoxide group and only one N-donor of the triazacyclononane ligand. The compound $[\text{Al}_2(\text{L}^2)_2\text{Me}_4]$ **2** features two approximately trigonal bipyramidal Al(III) centres [e.g. N(1)–Al(1)–O(28) 151.0(2)°; sum of the angles subtended at Al(1) by O(13), C(14), C(15) = 360.1°] with the pendant oxygen donors bridging them. The most important and highly unusual feature of **1** and **2** is that only *one*

of the three macrocyclic N-donors binds to the Al(III) centre. That **2** forms a binuclear, μ -O-bridged complex is attributed to steric factors, the greater steric bulk of L^1 stabilising the mononuclear complex.

The low temperature, high-field NMR spectra of the highly fluxional compounds **1** and **2** are consistent with the solid state structures.[†] Of special note for both compounds is the presence of two low-field multiplets in the range δ 4–5 of the ^1H NMR spectra; these are assigned to two of the macrocyclic ring methylene hydrogens. These shifts appear to be particularly diagnostic of the mono-N-coordinated mode of ligation of the ligands L^1 and L^2 , as such features are absent from the ^1H NMR spectra of structurally authenticated tri-N-coordinated transition and main group metal complexes of pendant arm derivatives of triazacyclononanes.^{3a,4}

The reaction of HL_2 or $[\text{Al}_2(\text{L}^2)_2\text{Me}_4]$ **2** with 2 equiv. of AlMe_3 cleaves the dimer and gives binuclear $[\text{Al}(\text{L}^2\text{-AlMe}_3)\text{Me}_2]$ **3** (Scheme 1) in which AlMe_3 is bound to the pendant alkoxide oxygen,^{‡§} rather than forming a product with the AlMe_3 bound to a nitrogen lone pair of L^2 . As for **1** and **2**, the triazacyclononane ring in **3** binds through only one nitrogen, and the ^1H NMR spectrum shows a diagnostic pair of multiplets in the region δ 4–5. In contrast, $[\text{Al}(\text{L}^1)\text{Me}_2]$ **1** does not react at all with AlMe_3 , suggesting that neither the phenoxide oxygen nor the macrocycle nitrogen lone pairs are accessible.



Scheme 1 Reagents and conditions: i, HL^1 , hexane, r.t., 2 h, 57%; ii, $\text{B}(\text{C}_6\text{F}_5)_3$, CH_2Cl_2 , r.t., 30 min, quantitative; iii, HL^2 , hexane, r.t., 2 h, 30%; iv, 0.5 HL^2 , hexane, r.t., 2 h, 71%; v, 2 AlMe_3 , C_6D_6 , r.t., 5 min, quantitative.

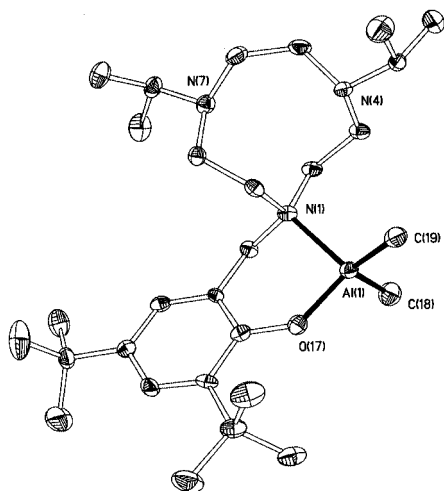


Fig. 1 Displacement ellipsoid plot of $[\text{Al}(\text{L}^1)\text{Me}_2]$ **1**. Hydrogen atoms are omitted for clarity and displacement ellipsoids are drawn at the 40% probability level. Selected bond lengths (Å): Al(1)–O(17) 1.759(4), Al(1)–N(1) 2.011(4), Al(1)–C(18) 1.965(5), Al(1)–C(19) 1.953(5).

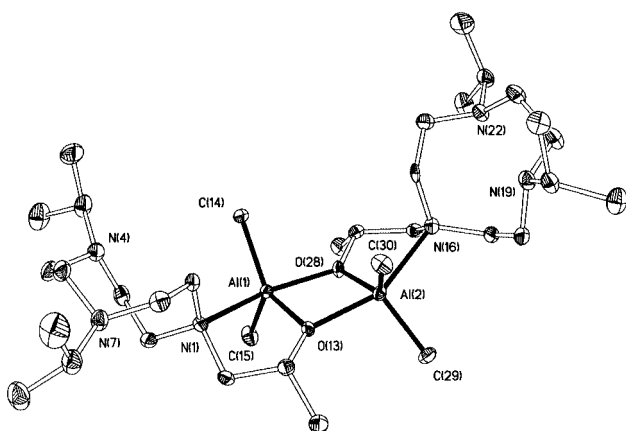


Fig. 2 Displacement ellipsoid plot of $[\text{Al}_2(\text{L}^2)_2\text{Me}_4]$ **2**. Hydrogen atoms are omitted for clarity and displacement ellipsoids are drawn at the 40% probability level. Selected bond lengths (Å): Al(1)–O(13) 1.849(3), Al(1)–N(1) 2.245(4), Al(1)–C(14) 1.977(5), Al(1)–C(15) 1.972, Al(1)–O(28) 1.935(3), Al(2)–O(28) 1.845(3), Al(2)–N(16) 2.265(4), Al(2)–C(29) 1.966(5), Al(2)–C(30) 1.983(5), Al(2)–O(13) 1.946(3).

The mono-N-coordination modes for L^1 and L^2 in compounds **1–3** are unique in the now very extensive and important field of triazacyclononane ligand coordination (transition and main group metal) chemistry.^{1,3} While there are a few examples of triazacyclononane ligands bonding through only two nitrogen ligands, these are found only for later transition metals where ligand field effects (*e.g.* those associated with d^8 square planar complexes) are particularly dominant.⁵ Only one triazacyclononane complex of aluminium has been previously structurally characterised, namely six-coordinate $[\text{Al}(\text{L})]$ where L is the tris(pendant arm) ligand 1,4,7-(O_2CCH_2)₃[9]aneN₃.⁶

As mentioned above, there is considerable current interest in well defined, cationic organoaluminium compounds.^{2c–g} Reaction of $[\text{Al}(\text{L}^1)\text{Me}_2]$ **1** with $\text{B}(\text{C}_6\text{F}_5)_3$ gives $[\text{Al}(\text{L}^1)\text{Me}][\text{MeB}(\text{C}_6\text{F}_5)_3]$ **4** (Scheme 1). We have not yet obtained diffraction-quality crystals of **4** and so this complex has been characterised by non-crystallographic techniques.[†] The ^1H and ^{19}F NMR data for the $[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ anion show that there is no interaction with the $[\text{Al}(\text{L}^1)\text{Me}]^+$ cation in which L^1 now bonds to Al through *all three* macrocyclic nitrogens.⁷ This coordination mode is suggested by the *ca.* 0.3–0.9 ppm downfield ^1H NMR shifts of the NPr^i group resonances

compared to those in **1–3** (consistent with bonding to a cationic metal centre) and the absence of any macrocyclic ring methylene resonances in the region δ 4–5 which would be expected for a mono-N-coordinated L^1 . Analogous trigonal bipyramidal coordination modes have been reported for $[\text{Zn}(\text{L}^1)\text{Cl}]$ and its homologues.^{3a}

Compound **4** is the first example of a cationic *p*-block organometallic complex of any triazacyclononane ligand. Moreover, the interconversion of coordination modes (mono-N-bound in **1** to tri-N-bound in **4**) has never before been observed for triazacyclononane complexes, and the current work suggests that the hemilability of functionalised [9]ane₃ ligands can be used to control and tune the reactivity of the Al centre. Preliminary studies of the reactions of other complexes $[\text{Al}(\text{L})\text{Me}_2]$ (L = monopendant arm functionalised triazacyclononane) with $\text{B}(\text{C}_6\text{F}_5)_3$ show that other examples of organoaluminium cations related to **4** can be prepared, and reactivity studies of these cations towards organic substrates are in progress.

This work was supported by the EPSRC and Royal Society. We thank Dr N. A. H. Male for helpful discussions.

Notes and references

[†] Full spectroscopic data and elemental analyses have been obtained for all the new compounds which were prepared under dry, anaerobic conditions.

[‡] *Crystal data* for **1**: $\text{C}_{29}\text{H}_{54}\text{AlN}_3\text{O}$, $M = 487.73$, orthorhombic, $P2_12_12_1$, $a = 10.3380(4)$, $b = 13.9560(7)$, $c = 20.8520(11)$ Å, $U = 3008.5(2)$ Å³, $Z = 4$, $T = 150(2)$ K, $\mu = 0.091$ mm⁻¹, 7450 reflections measured, 3926 ($R_{\text{int}} = 0.0338$) used in refinement, final R indices: $R_1 = 0.0715$ [data with $I > 2\sigma(I)$], $wR_2(F^2) = 0.1466$ (all data). For **2**: $\text{C}_{34}\text{H}_{76}\text{Al}_2\text{N}_6\text{O}_2$, $M = 654.97$, monoclinic, $P2_1$, $a = 12.2690(5)$, $b = 13.4100(6)$, $c = 12.4290(4)$ Å, $\beta = 95.998(2)^\circ$, $U = 203.71(14)$ Å³, $Z = 2$, $T = 150(2)$ K, $\mu = 0.106$ mm⁻¹, 4232 independent reflections measured and used in refinement, final R indices: $R_1 = 0.0691$ [data with $I > 2\sigma(I)$], $wR_2(F^2) = 0.174$ (all data).

CCDC 182/1658. See [http://www.rsc.org/supp data/cc/b0/b003019h/](http://www.rsc.org/supp/data/cc/b0/b003019h/) for crystallographic files in .cif format.

[§] The X-ray structure of $[\text{Al}(\text{L}^2)\text{AlMe}_3]\text{Me}_2$ **3** has been determined and will be reported in full elsewhere.⁴

- For leading references, see: P. V. Bernhardt and G. A. Lawrence, *Coord. Chem. Rev.*, 1990, **104**, 297; J. P. Danks, N. R. Chapman and M. Schröder, *Coord. Chem. Rev.*, 1998, **174**, 417; P. Chaudhuri and K. Wieghardt, *Prog. Inorg. Chem.*, 1987, **25**, 329.
- For leading references in neutral and cationic aluminium chemistry, see: (a) J. J. Eisch, in *Comprehensive Organometallic Chemistry II*, ed. E. W. Abel, F. G. A. Stone and G. Wilkinson, 1995, vol. 11, ch. 6; (b) K. B. Starowieyski, in *Chemistry of Aluminium, Gallium, Indium and Thallium*, ed. A. J. Downs, Chapman & Hall, London, UK, 1993, pp. 322–371; (c) S. Dagorne, I. A. Guzei, M. P. Coles and R. F. Jordan, *J. Am. Chem. Soc.*, 2000, **122**, 274; (d) P. A. Cameron, V. C. Gibson, C. Redshaw, J. A. Segal, M. D. Bruce, A. J. P. White and D. J. Williams, *Chem. Commun.*, 1999, 1883; (e) J. P. Corden, W. Errington, P. Moore and M. G. H. Wallbridge, *Chem. Commun.*, 1999, 323; (f) J. A. Jegier and D. A. Atwood, *Inorg. Chem.*, 1997, **36**, 2034; (g) M. Bochmann and D. M. Dawson, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 2226.
- (a) J. A. Halfen, B. A. Jazdzewski, S. Mahapatra, L. M. Berreau, E. C. Wilkinson, L. Que and W. B. Tolman, *J. Am. Chem. Soc.*, 1997, **119**, 8217; (b) S. Mahapatra, J. A. Halfen, E. C. Wilkinson, G. Pan, X. Wang, V. G. Young, C. J. Cramer, L. Que and W. B. Tolman, *J. Am. Chem. Soc.*, 1996, **118**, 11 555.
- S. Y. Bylikin, N. A. H. Male, L. H. Rees, D. A. Robson, P. Mountford and M. Schröder, unpublished results.
- For examples, see: A. J. Blake, I. A. Fallis, S. Parsons, S. A. Ross and M. Schröder, *J. Chem. Soc., Dalton Trans.*, 1996, 525; G. Schlager, K. Weighardt and B. Nuber, *Inorg. Chem.*, 1995, **34**, 6449 and references therein.
- U. Bossek, D. Hanke, K. Weighardt and B. Nuber, *Polyhedron*, 1993, **12**, 1.
- D. J. Gillis, M. J. Turodet and M. C. Baird, *J. Am. Chem. Soc.*, 1993, **115**, 2543; A. D. Horton, J. d. With, J. v. d. Linden and H. v. d. Weg, *Organometallics*, 1996, **15**, 2672.