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Neutral and cationic organometallic aluminium and indium complexes of mono-pendant arm triazacyclononane ligands

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Organometallic monomeric and dimeric, neutral and cationic, κ^2- and κ^4-coordinated mono-pendant arm triazacyclononane complexes of aluminium and indium have been prepared, along with three new mono-pendant arm triazacyclononane ligand precursors HL^4, HL^5 and HL^6 (HL^4 = 1-(2-hydroxy-2-methylethyl)-4,7-diisopropyl-1,4,7-triazacyclononane; HL^5 = 1-(2-hydroxy-2-methylethyl)-4,7-dimethyl-1,4,7-triazacyclononane; HL^6 = 1-(2-hydroxy-2,2-diphenylethyl)-4,7-diisopropyl-1,4,7-triazacyclononane). Reaction of HL^4 or HL^5 with $AlMe_3$ or $AlMe_3$·py gives the μ-alkoxide bridged dimeric complexes $[Al_2(\kappa^2\text{-}L^4)_2Me_4]$ and $[Al_2(\kappa^2\text{-}L^5)_2Me_4]$. Reaction of HL^4 with two equivalents of $AlMe_3$ gives the monomeric compound $[Al(\kappa^2\text{-}L^4\cdot AlMe_3)Me_2]$ which can also be prepared by treating $[Al_2(\kappa^2\text{-}L^4)_2Me_4]$ with two equivalents of $AlMe_3$. Reaction of HL^2 with $AlMe_3$·py gives $[Al(\kappa^2\text{-}L^2)Me_2]$, whereas $AlMe_3$ reacts with one or two equivalents of HL^1 to give exclusively $[Al(\kappa^2\text{-}L^1)_2Me]$ which contains two κ^2-L^1 ligands (HL^1 = 1-(2-hydroxy-3,5-dimethylbenzyl)-4,7-diisopropyl-1,4,7-triazacyclononane; L^2 = 1-(3,5-di-*tert*-butyl-2-hydroxybenzyl)-4,7-diisopropyl-1,4,7-triazacyclononane). Reaction of $AlMe_3$ with HL^6 gives low yields of the monomeric derivative $[Al(\kappa^2\text{-}L^6)Me_2]$. The κ^2-coordination mode of the triazacyclononane ligands in all these compounds is unique in the chemisty of these ligands. The crystal structures of four of them are discussed. Methyl group abstraction from $[Al(\kappa^2\text{-}L^4\cdot AlMe_3)Me_2]$ or $[Al(\kappa^2\text{-}L^2)Me_2]$ using $B(C_6F_5)_3$ gives the κ^4-coordinated cationic derivatives $[Al(\kappa^4\text{-}L^2)Me][MeB(C_6F_5)_3]$ and $[Al(\kappa^4\text{-}L^4\cdot AlMe_3)Me][MeB(C_6F_5)_3]$, and the latter undergoes reaction with pyridine or MeCN to form $[Al(\kappa^4\text{-}L^4)Me][MeB(C_6F_5)_3]$. The cationic centres in the last three compounds are unreactive to unsaturated substrates and aprotic Lewis bases. Reaction of $In(CH_2Ph)_3$ with HL^1 or HL^2 affords the four-coordinate complexes $[In(\kappa^2\text{-}L^1)(CH_2Ph)_2]$ and $[In(\kappa^2\text{-}L^2)(CH_2Ph)_2]$ in which the $L^{1,2}$ ligand is κ^2 bound to In. With the sterically less demanding HL^3 [1-(3,5-di-*tert*-butyl-2-hydroxybenzyl)-4,7-dimethyl-1,4,7-triazacyclononane], however, the six-coordinate complex $[In(\kappa^4\text{-}L^3)(CH_2Ph)_2]$ is formed. The compound $[In(\kappa^2\text{-}L^2)(CH_2Ph)_2]$ reacts with $B(C_6F_5)_3$ to form $[In(\kappa^4\text{-}L^2)(CH_2Ph)][(PhCH_2)B(C_6F_5)_3]$.

Introduction

The 1,4,7-triazacyclononane ligands $R_3[9]aneN_3$ (R typically = H or alkyl) and their N-functionalised derivatives with one, two or three pendant arms (terminated with neutral or anionic donor groups) are well established, effective and important ligands in metal coordination chemistry, and there is an extensive literature associated with them.[1–3] This interest stems from the well defined environments that these face-capping ligands and their functionalised derivatives can provide and the subsequent opportunities for complex synthesis and reactivity studies that this presents. However, apart from our own recent work on aluminium systems,[4] there has been only one other report (without structural authentication) of a *mono-pendant arm* triazacyclononane complex of a Group 13 metal.[5] A number of derivatives with tris-pendant arm homologues have, however, been described.[6–9] We report herein novel neutral and cationic organo-aluminium and -indium complexes of mono-pendant arm triazacyclononanes, including the first structurally authenticated examples of complexes having a triazacyclononane ligand coordinated through only one nitrogen. Part of work has been communicated.[4]

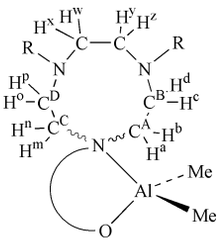
Experimental

General methods and instrumentation

All manipulations of air- and/or moisture-sensitive compounds were carried out under an atmosphere of dinitrogen using Schlenk-line or dry-box techniques. All protio-solvents and commercially available reagents were pre-dried over activated molecular sieves and refluxed over an appropriate drying agent under an atmosphere of dinitrogen and collected by distillation. NMR solvents for air- and/or moisture-sensitive compounds were dried over freshly ground calcium hydride at rt (CD_2Cl_2), molten potassium (C_6D_6) or molten sodium ($C_6D_5CD_3$), distilled under reduced pressure and stored under N_2 in J. Young ampoules. NMR samples of air- and moisture-sensitive compounds were prepared in the dry-box in 5 mm Wilmad tubes, equipped with a Young's Teflon valve.

^1H and ^{13}C NMR spectra were recorded on Varian Unity Plus 500 or Varian Mercury Vx300 spectrometers and referenced internally to residual protio-solvent (^1H) or solvent (^{13}C) resonances. Chemical shifts are reported relative to tetramethylsilane (δ 0) in δ (ppm) and coupling constants in Hertz. ^{19}F NMR Spectra were recorded on a Varian Mercury Vx300 spectrometer and referenced to external CF_3Cl. Assignments were supported by DEPT-135 and DEPT-90, homo- and hetero-nuclear, one- and two-dimensional experiments as appropriate. Mass spectra were recorded on an AEI MS902, Micromass LC Tof ESI or Micromass Autospec 500 mass spectrometer. Elemental analyses were carried out by the analysis laboratory of this department.

Where appropriate, NMR assignments are quoted with reference to the general labelling scheme illustrated below.



Preparations

$HPr^i_2[9]aneN_3$,[10] $HMe_2[9]aneN_3$,[11] HL[1] **1**,[12] HL[2] **2**,[12] HL[3] **3**,[13] 2,2-diphenyloxirane,[14] $In(CH_2Ph)_3$,[15] and $AlMe_3$·MeCN[16] were prepared according to literature methods. Propylene oxide was purchased from Sigma-Aldrich and dried over freshly ground calcium hydride under an atmosphere of dinitrogen and collected by distillation. $AlMe_3$ was purchased from Sigma-Aldrich and used as received. $AlMe_3$·py[17] was prepared by dropwise addition of a pentane solution of pyridine to $AlMe_3$ also diluted in pentane.

1-(2-Hydroxy-2-methylethyl)-4,7-diisopropyl-1,4,7-triazacyclononane (HL[4], 4). $HPr^i_2[9]aneN_3$ (2.0 g, 9.4 mmol) was diluted in EtOH (30 cm^3) and an EtOH (10 cm^3) solution of propylene oxide (1.3 cm^3, 18.7 mmol) added dropwise at 0 °C. The resulting solution was allowed to stir for 4 d at rt before all volatiles were removed *in vacuo* affording a pale yellow oil. The product was purified by distillation using Kügelröhr apparatus (90 °C, 0.04 Torr) to afford a colourless oil. Yield: 2.1 g (93%). ^{1}H NMR (C_6D_6, 500.0 MHz, 298 K): δ 5.54 (br s, 1 H, OH), 3.86 (m, 1 H, $NCH_2C(H)$MeOH), 2.63 (sept, $J = 6.0$, 2 H, $NCHMe_2$), 2.60–2.40 (m, 12 H, NCH_2CH_2N), 2.32 (m, 2 H, $NCH_2C(H)$MeOH), 1.19 (d, $J = 6.0$, 3 H, $NCH_2C(H)$-*Me*OH) and 0.90 (apparent triplet, apparent $J = 7.0$ Hz, 12 H, $CHMe_2$). ^{13}C-{^{1}H} NMR (C_6D_6, 125.7 MHz, 298 K): δ 66.5 ($NCH_2C(H)$MeOH), 65.5 ($NCH_2C(H)$MeOH), 58.6, 54.6 (NCH_2CH_2N), 54.5 ($CHMe_2$), 52.3 (NCH_2CH_2N), 20.3 ($NCH_2C(H)$*Me*OH), 18.5 and 18.2 ($2 \times CHMe_2$). APCI-MS (Atmospheric Pressure Chemical Ionisation-Mass Spectroscopy): $m/z = 272$, $[M + H]^+$. Found (calculated for $C_{15}H_{33}N_3O$): C, 66.0 (66.3); H, 12.6 (12.3); N, 15.4 (15.5)%.

1-(2-Hydroxy-2-methylethyl)-4,7-dimethyl-1,4,7-triazacyclononane (HL[5], 5). $HMe_2[9]aneN_3$ (0.75 g, 4.8 mmol) was diluted in EtOH (20 cm^3) and an EtOH (20 cm^3) solution of propylene oxide (0.67 cm^3, 9.5 mmol) added dropwise at 0 °C. The colourless solution was allowed to warm to rt and stirred for 20 h before all volatiles were removed under reduced pressure. The resulting pale yellow oil was purified by distillation using a Kügelröhr apparatus (73–77 °C, 0.1 Torr) to give a colourless oil. Yield: 0.69 g (67%). ^{1}H NMR (C_6D_6, 300 MHz, 298 K): δ 5.47 (br s, 1H, OH), 3.82 (m, 1H, $NCH_2C(H)$MeOH), 2.58–2.45 (m, 12 H, NCH_2CH_2N), 2.33–2.25 (m, 2 H, $NCH_2C(H)$MeOH), 2.19 (s, 6 H, NMe) and 1.17 (d, 3H, $J = 6.3$ Hz, $NCH_2C(H)$*Me*OH). ^{13}C-{^{1}H} NMR (C_6D_6, 75.5 MHz, 298 K): δ 66.4 ($NCH_2C(H)$MeOH), 65.6 ($NCH_2C(H)$MeOH), 59.1, 58.4 and 56.8 ($3 \times NCH_2CH_2N$), 46.3 (NMe) and 20.3 ($NCH_2C(H)$*Me*OH). HRMS: Found $m/z = 216.206$, calculated for $C_{11}H_{26}N_3O$ 216.207.

1-(2-Hydroxy-2,2-diphenylethyl)-4,7-diisopropyl-1,4,7-triazacyclononane (HL[6], 6). $HPr^i_2[9]aneN_3$ (2.00 g, 9.37 mmol) was diluted in EtOH (30 cm^3) and an EtOH (20 cm^3) solution of 2,2-diphenyloxirane (3.68 g, 18.7 mmol) added dropwise. The colourless solution was allowed to stir at rt for 10 d before the solvent was removed under reduced pressure. The product was isolated by fractional distillation using Kügelröhr apparatus. The second fraction, a thick colourless oil, was collected (228–232 °C, 0.05 Torr) and subsequently crystallised on standing to yield a white solid. Yield: 2.76 g (72%). ^{1}H NMR (C_6D_6, 500 MHz, 298 K): δ 7.76 (m, 4H, *o*-H of C_6H_5), 7.18 (m, 4H, *m*-H of C_6H_5, 7.03 (m, 2H, *p*-H of C_6H_5), 6.79 (s, 1H, OH), 3.38 (s, 2H, $NCH_2C(Ph)_2OH$), 2.65 (sept, $J = 6.5$, 2 H, $NCHMe_2$), 2.60 (m, 4 H, NCH_2), 2.32 (s, 4 H, NCH_2), 2.24 (m, 4 H, NCH_2) and 0.85 (d, 12 H, $J = 6.5$ Hz, $CHMe_2$). ^{13}C -{^{1}H} NMR (C_6D_6, 125.7 MHz, 298 K): δ 148.8 (1-C of C_6H_5), 128.1, 126.7 and 126.4 (2-, 3-, and 4-C of C_6H_5), 77.1 ($NCH_2C(Ph)_2OH$), 70.4 ($NCH_2C(Ph)_2OH$), 60.8 (NCH_2CH_2N), 54.4 ($CHMe_2$), 54.0, 53.2 ($2 \times NCH_2CH_2N$) and 18.4 ($CHMe_2$). APCI-MS: $m/z = 410$, $[M + H]^+$. Found (calculated for $C_{26}H_{39}N_3O$): C, 75.85 (76.22); H, 9.29 (9.61); N, 10.27 (10.26)%.

[$Al_2(\kappa^2\text{-}L^4)_2Me_4$] 7. The ligand precursor HL[4] (0.57 g, 2.09 mmol) was diluted in hexanes (25 cm^3) and a hexane (15 cm^3) solution of $AlMe_3$ (0.15 g, 2.1 mmol) added dropwise. The resulting colourless solution was allowed to stir at rt for 2 h before all volatiles were removed under reduced pressure affording a white solid. The solid was dissolved in pentane, the solution concentrated and placed at −30 °C overnight. White crystalline needles of the product were collected. Yield: 0.21 g (30%). ^{1}H NMR ($C_6D_5CD_3$, 500.0 MHz, 223 K): δ 4.66 (app. t, $J = 14$, 2H, $CH_aH_bCH_2N$), 4.00 (m, 4H, $NCH_2C(H)$Me and $NCH_mH_nCH_2N$), 3.28 (app. t, $J = 14$, 1H, $NCH_2CH_oH_pN$), 3.09 (m, 2H, $CHMe_2$), 2.60–2.20 (m, 18H, $NCH_aH_bCH_2N$, $NCH_wH_xCH_2N$, $NCH_2CH_cH_dN$, $NCH_2CH_oH_pN$, NCH_mH_n-CH_2N, $CHMe_2$ and $NCH_2C(H)$Me), 1.79 (d, $J = 12$, 2H, $NCH_2CH_cH_dN$), 1.64 (m, 4H, $NCH_2CH_yH_zN$), 1.32 (d, $J = 5.5$, 6H, $NCH_2C(H)Me$), 0.98 (d, $J = 6.5$ Hz, 6H, $CHMe_2$), 0.79 and 0.66 ($2 \times$ overlapping d, 12H, $4 \times CHMe_2$), −0.28, −0.35 ($2 \times$ s, 4×3H, $4 \times$ AlMe). ^{13}C-{^{1}H} NMR ($C_6D_5CD_3$, 125.7 MHz, 223 K): δ 62.1 ($NCH_2C(H)$Me), 59.8 ($NCH_2C(H)$Me), 56.2 ($CHMe_2$), 55.4 ($NC_CH_2C_DH_2N$), 55.2 ($CHMe_2$), 54.0 (NCH_2CH_2N), 53.8 ($NC_CH_2C_DH_2N$), 49.9 ($NC_AH_2C_BH_2N$), 48.8 (NCH_2CH_2N), 46.1 ($NC_AH_2C_BH_2N$), 22.9 ($CHMe_2$), 22.5 ($NCH_2C(H)Me$), 15.8, 12.9 ($4 \times CHMe_2$), −6.4, −6.8 ($4 \times$ AlMe). EI-MS: $m/z = 327$, $[½M]^+$; and 312, $[(½M) - Me]^+$. Found (calculated for $C_{17}H_{38}AlN_3O$): C, 60.3 (62.3); H, 11.9 (11.7); N, 12.6 (12.8)%. Despite repeated attempts, a satisfactory %C analysis could not be obtained for this compound.

[$Al_2(\kappa^2\text{-}L^5)_2Me_4$] 8. The ligand precursor HL[5] (0.50 g, 2.3 mmol) was diluted in hexanes (20 cm^3) and a hexane (20 cm^3) solution of $AlMe_3$·py (0.35 g, 2.3 mmol) added dropwise. The colourless solution was allowed to stir at rt for 2 h before all volatiles were removed under reduced pressure. The resulting white solid was dissolved in the minimum volume of pentane and placed at 4 °C for 2 d. White crystals of the product were collected. Yield: 0.38 g (61%). ^{1}H NMR ($C_6D_5CD_3$, 500.0 MHz, 203 K): δ 4.64 (app. t, $J = 14$, 2H, $NCH_aH_bCH_2N$), 3.91 (app t, $J = 14$, 2H, $NCH_mH_nCH_2N$), 3.90 (m, 2H, $NCH_2C(H)$Me), 3.39 (app t, $J = 14$, 2H, $NCH_2CH_oH_pN$), 2.49 (d, $J = 14$, 2H, $NCH_aH_bCH_2N$), 2.43–2.31 (m, 8H, $NCH_mH_nCH_2N$, NCH_2-CH_cH_dN and $NCH_wH_xCH_2N$), 2.30 (d, 2H, $NCH_2C(H)$Me), 2.28 (s, 6H, NMe), 2.27–2.05 (m, 8H, $NCH_2C(H)$Me and $NCH_wH_xCH_2N$), 2.0 (m, 6H, $NCH_2CH_oH_pN$ and NCH_2-CH_yH_zN), 1.94 (s, 6H, N*Me*), 1.5 (d, $J = 14$, 2H, NCH_2CH_c-H_dN), 1.24 (d, $J = 5.5$ Hz, 6H, $NCH_2C(H)Me$), −0.25, −0.35 ($2 \times$ s, 4×3 H, $4 \times$ AlMe). ^{13}C-{^{1}H} NMR ($C_6D_5CD_3$, 125.7 MHz, 203 K): δ 61.9 ($NCH_2C(H)$Me), 60.8 (NCH_2CH_2N), 59.1 (NCH_2CH_2N), 58.3 ($NCH_2C(H)$Me), 58.2 ($NCH_2C_DH_2N$), 54.6 ($NCH_2C_BH_2N$), 53.4 ($NC_CH_2CH_2N$), 49.0 (NMe), 48.4 (NMe), 45.8 ($NC_AH_2CH_2N$), 22.1 ($NCH_2C(H)Me$), −6.6, −6.7 ($4 \times$ AlMe). EI-MS: $m/z = 256$, $[(½M) - Me]^+$. Found (calculated for $C_{13}H_{30}AlN_3O$): C, 55.0 (57.5); H, 11.1 (11.2); N, 15.2 (15.5)%. Despite repeated attempts, a satisfactory %C analysis could not be obtained for this compound.

[$Al(\kappa^2\text{-}L^4\cdot AlMe_3)Me_2$] 9. The ligand precursor HL[4] (1.35 g, 5.0 mmol) was diluted in hexanes (30 cm^3) and a hexane (20 cm^3) solution of $AlMe_3$ (0.72 g, 10.0 mmol) added dropwise.

The resulting cloudy white solution was allowed to stir for 2 h before all volatiles were removed under reduced pressure. The resulting white solid was recrystallised from a saturated pentane solution at −30 °C. Colourless crystals of the product were collected. Yield: 1.4 g (71%). ^{1}H NMR (CD_2Cl_2, 500.0 MHz, 213 K): δ 4.81 (app t, J = 13, 1 H, NC$H_aH_bCH_2$N), 4.57 (app t, J = 13, 1 H, NC$H_mH_nCH_2$N)), 4.16 (m, 1 H, NCH$_2$C(H)Me), 3.10 (m, 1 H, NCH_2C(H)Me), 3.00–2.83 (m, 3 H, NCH_2CH_2N and CHMe$_2$), 2.83–2.79 (m, 2 H, NCH$_2$CH_cH_dN and NCH$_2$-CH_oH_pN), 2.71 (app. t, J = 13, NCH$_2$CH$_c$$H_d$N and NC$H_2$-CH$_2$N), 2.55 (d, J = 13, 1H, NCH_2C(H)Me), 2.51 (d, J = 13, 1 H, NCH$_a$$H_bCH_2$N), 2.43 (app. t, J = 14, 2 H, NCH$_m$$H_nCH_2$N), 1.90 (app. quin, J = 14, 2 H, NCH$_2$CH$_o$$H_p$N and NCH$_2CH_2$N), 1.30 (d, J = 6.5, 3 H, NCH$_2$C(H)Me), 0.97, 0.95, 0.93, 0.87, 0.79 (overlapping 4 × d and m, J = 6.5 Hz, 13 H, 4 × CHMe_2 and NCH$_2$CH$_c$$H_d$N), −0.73, −0.85 (2 × s, 2 × 3 H, 2 × AlMe) and −1.07 (s, 9H, AlMe$_3$). ^{13}C-{^{1}H} NMR (CD_2Cl_2, 125.7 MHz, 213 K): δ 66.3 (NCH$_2$$C$(H)Me), 58.3 (N$CH_2$C(H)Me), 56.1, 55.1 (2 × CHMe$_2$), 54.6 (NCH$_2$$C_BH_2$N), 53.6 (NCH$_2$$C_DH_2$N), 53.3 (N$C_CH_2CH_2$N), 48.9 (N$CH_2$$CH_2$N), 46.1 (N$C_AH_2CH_2$N), 21.7, 20.0, 15.6, 13.2 (4 × CHMe_2), 20.9 (NCH$_2$C(H)Me), −6.8 (AlMe$_3$), −8.5, −10.8 (2 × AlMe). Found (calculated for $C_{20}H_{47}Al_2N_3O$): C, 59.7 (60.1); H, 11.9 (11.9); N, 10.3 (10.5)%.

NMR tube scale synthesis of [Al(κ^2-L^4·AlMe$_3$)Me$_2$] 9 from [Al$_2$(κ^2-L^4)$_2$Me$_4$] 7. Compound **7** (0.01 g, 0.052 mmol) was dissolved in C_6D_6 (500 μl) and placed in an NMR tube equipped with a Young's Teflon valve. Trimethylaluminium (3 μl, 0.104 mmol) was added *via* microsyringe and the resulting colourless solution shaken. ^{1}H NMR analysis showed quantitative formation of **9**.

NMR tube scale synthesis of [Al$_2$(κ^2-L^4)$_2$Me$_4$] 7 from [Al(κ^2-L^4·AlMe$_3$)Me$_2$] 9. Compound **9** (0.01 g, 0.027 mmol) was dissolved in C_6D_6 (500 μl) and placed in an NMR tube equipped with a Young's Teflon valve. Pyridine (2.2 μl, 0.027 mmol) was added *via* a microsyringe and the resulting colourless solution shaken. ^{1}H NMR analysis revealed quantitative formation of **7** and AlMe$_3$·py.

[Al(κ^2-L^2)Me$_2$] 10. The ligand precursor HL^2 (0.5 g, 1.2 mmol) was dissolved in hexanes (30 cm^3) and a hexane (20 cm^3) solution of AlMe$_3$·py (0.086 g, 1.2 mmol) added dropwise. The resulting colourless solution was allowed to stir at rt for 2 h then concentrated and placed at −30 °C for 3 d affording the product as colourless crystals. Yield: 0.34 g (57%). ^{1}H NMR ($C_6D_5CD_3$, 500.0 MHz, 213 K): δ 7.57 and 6.99 (s, 2H, C_6H_2Bu$^t_2$), 4.40 (app. t, J = 13, 1 H, NC$H_aH_bCH_2$N), 4.05 (app. t, J = 13, 1 H, NCH$_2$CH_mH_nN), 3.86, 3.23 (2 × d, J = 13, 2 × 1 H, ArCH_2), 3.02 (app. t, J = 13, 1 H, NCH$_2$CH_oH_pN), 2.87 (m, 1 H, CHMe$_2$), 2.85 (app. t, J = 13, 1 H, NCH$_2$CH_cH_dN), 2.68 (m, 1 H, CHMe$_2$), 2.35 (d, J = 13, 1 H, NCH$_a$$H_bCH_2$N), 2.26 (d, J = 13, 1 H, NCH$_2$CH$_o$$H_p$N), 2.20 (m, 3 H, NC$H_2CH_2$N and NCH$_m$$H_nCH_2$N), 1.78 and 1.47 (s, 18 H, Bu^t), 1.45 (m, 2 H, NCH$_2$CH_2N), 1.36 (d, J = 13, 1 H, NCH$_2$CH$_c$$H_d$N), 0.93 (d, J = 7, 3H, CHMe_2), 0.81 (overlapping 2 × d, 6 H, CHMe_2), 0.61 (d, J = 7 Hz, 3 H, CHMe_2), −0.23, −0.26 (2 × s, 2 × 3 H, 2 × AlMe). ^{13}C-{^{1}H} NMR ($C_6D_5CD_3$, 125.7 MHz, 213 K): δ 157.5, 138.2 and 137.5 (C_q of Ar), 124.9 and 124.3 (CH of Ar), 120.3 (C_q of Ar), 58.3 (ArCH$_2$), 56.8, 55.5 (2 × CHMe$_2$), 55.4 (NCH$_2$CH$_2$N), 55.0 (NCH$_2$$C_DH_2$N), 53.6 (N$C_CH_2CH_2$N), 49.0 (NCH$_2$$CH_2$N), 48.6 (NCH$_2$$C_BH_2$N), 46.1 (N$C_AH_2CH_2$N), 35.6, 34.5 (2 × CMe$_3$), 32.2, 29.9 (2 × CMe_3), 22.4, 19.2, 17.7, 13.2 (4 × CHMe_2) and −9.4 (AlMe). Found (calculated for $C_{29}H_{54}AlN_3O$): C, 71.1 (71.4); H, 11.1 (11.2); N, 8.4 (8.6)%.

[Al(κ^2-L^1)$_2$Me] 11. AlMe$_3$ (0.23 g, 3.1 mmol) was diluted in hexanes (20 cm^3) and was added to HL^1 (2.17 g, 6.2 mmol) in hexanes (35 cm^3). The resulting cloudy solution was allowed to stir for 2 h at rt. All volatiles were then removed under reduced pressure affording an off-white solid which was washed with cold hexanes (2 × 20 cm^3). Further crops of product were obtained from placing the washings at −30 °C. Yield: 0.90 g (35%). ^{1}H NMR ($C_6D_5CD_3$, 500.0 MHz, 213 K): δ 7.00 and 6.72 (s, 4 H, C_6H_2Me$_2$), 4.65 (app. t, J = 13, 2 H, NCH_aH_b-CH$_2$N), 4.36 (d, J = 13, 2 H, ArCH_2), 4.30 (app. t, J = 13, 2 H, NCH_mH_nCH$_2$N), 3.65 (m, 4 H, NCH$_2$CH_oH$_p$N and NCH$_m$$H_n$-CH$_2$N), 3.32 (d, J = 13, 2 H, ArCH_2), 3.20 (m, 2 H, CHMe$_2$), 2.95 (t, J = 13, 2 H, NCH$_2$CH_cH$_d$N), 2.82 (m, 2 H, CHMe$_2$), 2.67 (d, J = 13, 2 H, CH$_2$CH$_o$$H_p$N), 2.55 (d, J = 13, 2 H, NCH$_a$$H_bCH_2$N), 2.44, 2.31 (2 × s, 12 H, $C_6H_2Me_2$), 2.30 (m, 4 H, NCH_2CH$_2$N), 1.83 (d, J = 13, 2 H, NCH$_2$CH$_c$$H_d$N), 1.65 (m, 4 H, NCH$_2CH_2$N), 0.93, 0.86, 0.76, 0.69 (4 × d, J = 6 Hz, 24 H, 4 × CHMe_2) and −0.05 (s, 3 H, AlMe). ^{13}C-{^{1}H} NMR ($C_6D_5CD_3$, 125.7 MHz, 213 K): δ 157.0 , 137.5 and 131.6 (C_q of Ar), 128.4 and 126.2 (CH of Ar), 122.4 (C_q of Ar), 58.7 (ArCH$_2$), 56.5 (NCH$_2$$C_DH_2$N), 56.4 ($CHMe_2$), 55.0 (overlapping CHMe$_2$ and NC_CH$_2$CH$_2$N), 54.3 (NCH$_2$CH$_2$N), 51.3 (NCH$_2$$C_BH_2$N), 49.5 (NCH$_2$$CH_2$N), 46.4 (N$C_AH_2CH_2$N), 23.2 (CH$Me_2$), 21.0, 19.2 (2 × $C_6H_2Me_2$), 16.4 , 12.5 (2 × CHMe_2) and −7.9 (AlMe). EI-MS: m/z = 388, [M − L^1 − Me]$^+$. Found (calculated for $C_{43}H_{75}AlN_6O_2$): C, 70.0 (70.2); H, 10.5 (10.3); N, 11.4 (11.4)%.

[Al(κ^2-L^6)Me$_2$] 12. The ligand precursor HL^6 (1.0 g, 2.45 mmol) was dissolved in hexanes (30 cm^3) and to this stirring solution AlMe$_3$ (0.17 g, 2.45 mmol) in hexanes (20 cm^3) added dropwise. The solution was allowed to stir for 3 h before all volatiles were removed under reduced pressure. The solution was concentrated and placed at −30 °C affording a white crystalline solid. This was filtered off and the mother liquors evaporated to dryness. A further crop of compound **12** was obtained by high vacuum tube sublimation (180 °C, 6 × 10^{-6} mbar). Combined yield: 0.16 g (15%). ^{1}H NMR (CD_2Cl_2, 500.0 MHz, 213 K): δ 7.66, 7.50, 7.26, 7.11 (4 × m, 10 H, C_6H_5), 4.62 (app. t, J = 13, 1 H, NC$H_aH_bCH_2$N), 4.42 (app. t, J = 13, 1 H, NC$H_mH_nCH_2$N), 4.18 and 3.20 (d, J = 13, 2 H, NCH_2CPh$_2$), 2.87 (overlapping 3 × m, 3 H, 2 × CHMe$_2$ and NCH$_2$CH_cH$_d$N), 2.65 (overlapping m, 3 H, NCH_2CH$_2$N and NCH$_2$CH$_c$$H_d$N), 2.56 (app. t, J = 13 Hz, 1 H, NCH$_2$CH_oH$_p$N), 2.39 (d, J = 13, 1 H, NCH$_a$$H_bCH_2$N), 2.13 (d, J = 13, 1 H, NCH$_m$$H_nCH_2$N), 1.82 and 1.75 (2 × app. t, J = 13, 2 H, NCH$_2$CH_2N), 1.57 (d, J = 13, 1 H, NCH$_2$CH$_o$$H_p$N), 0.88 (overlapping 3 × d, 9 H, 3 × CHMe_2), 0.75 (d, J = 6.5 Hz, 3 H, CHMe_2), −0.8, −1.02 (2 × s, 2 × 3 H, AlMe). ^{13}C-{^{1}H} NMR (CD_2Cl_2, 125.7 MHz, 213 K): δ 151.5 and 149.3 (1-C of C_6H_5), 127.9, 127.7 (2 × 2-C of C_6H_5), 125.9, 125.8 (2 × 4-C of C_6H_5), 124.7 and 124.4 (2 × 3-C of C_6H_5), 76.2 (NCH$_2$$CPh_2$), 63.3 (N$CH_2CPh_2$), 56.2 and 55.1 (2 × C$HMe_2$), 55.0 (NCH$_2$$C_BH_2$N), 54.4 (NCH$_2$-$C_DH_2$N), 53.4 (N$C_CH_2CH_2$N), 49.3 and 48.0 (N$CH_2$$CH_2$N), 47.0, (N$C_AH_2CH_2$N), 21.4, 19.1, 16.6 and 13.6 (4 × CHMe_2) and −10.7 (AlMe). EI-MS: m/z = 450 [M − Me]$^+$. Found (calculated for $C_{28}H_{44}AlN_3O$): C, 72.2 (71.3); H, 9.6 (9.5); N, 9.0 (9.0)%.

[Al(κ^4-L^2)Me][MeB(C$_6$F$_5$)$_3$] 13. [Al(κ^2-L^2)Me$_2$] **10** (0.34 g, 0.71 mmol) was dissolved in CH_2Cl_2 (20 cm^3) and a CH_2Cl_2 (15 cm^3) solution of B(C$_6$F$_5$)$_3$ (0.36 g, 0.71 mmol) added dropwise. The colourless solution was stirred for 30 min at rt before the solvent was removed under reduced pressure. The product was collected as a white solid. Yield: 0.67 g (96%). ^{1}H NMR (CD_2Cl_2, 500.0 MHz, 298 K): δ 7.35, 6.91 (2 × d, J = 2.5, 2 × 1 H, C_6H_2Bu$^t_2$), 4.00 (s, 2H, ArCH_2), 3.64 (m, 2 H, CHMe$_2$), 3.05, 2.96, 2.82 and 2.74 (m, 12 H, NCH_2CH_2N), 1.37, 1.23 (2 × s, 2 × 9 H, 2 × Bu^t), 1.25, 1.19 (2 × d, J = 6.5 Hz, 2 × CHMe_2), 0.44 (br s, 3H, MeB(C$_6$F$_5$)) and −0.28 (s, 3H, AlMe). ^{13}C -{^{1}H} NMR (CD_2Cl_2, 125.7 MHz, 298 K): δ 156.4 (C_q of Ar), 148.6 (d, $^1J_{CF}$ = 233, o-C of C_6F_5), 140.6 (C_q of Ar), 137.9 (d,

$^1J_{CF}$ = 238, *p*-C of C_6F_5), 137.6 (C_q of Ar), 136.7 (d, $^1J_{CF}$ = 233, *m*-C of C_6F_5), 126.0 and 124.6 (CH of Ar), 118.5 (C_q of Ar), 64.2 (CH_2Ar), 57.8 ($CHMe_2$), 43.8, 49.5 and 47.3 (NCH_2CH_2N), 35.1 and 34.4 (CMe_3), 31.6 and 30.5 (CMe_3), 19.7 and 16.9 ($CHMe_2$), 10.3 (BMe) and −4.3 (AlMe). ^{19}F NMR (CD_2Cl_2, 282 MHz, 298 K): δ −133.6 (d, $^1J_{CF}$ = 20, *o*-F of C_6F_5), −165.2 (t, $^1J_{CF}$ = 20, *p*-F of C_6F_5) and −167.9 (m, $^1J_{CF}$ = 20 Hz, *m*-F of C_6F_5). Found (calculated for $C_{47}H_{54}AlBF_{15}N_3O$): C 55.7 (56.4), H 5.1 (5.4), B 0.9 (1.1), N 4.2 (4.0)%.

[Al(κ^4-L^4·AlMe$_3$)Me][MeB(C$_6$F$_5$)$_3$] 14. [Al(κ^2-L^4·AlMe$_3$)Me$_2$] **9** (0.5 g, 1.25 mmol) was dissolved in CH_2Cl_2 (25 cm^3) and a CH_2Cl_2 (15 cm^3) solution of $B(C_6F_5)_3$ (0.36 g, 0.71 mmol) added dropwise. The resulting solution was allowed to stir at rt for 30 min before the solvent was removed under reduced pressure. The product was collected as a white solid. Yield: 0.96 g (84%). ^{1}H NMR (CD_2Cl_2, 300.0 MHz, 298 K): δ 4.12 (m, 1H, NCH_2CH(Me)), 3.76 and 3.40 (sept, *J* = 11, 1H, $CHMe_2$), 3.4–2.6 (m, 15 H, NCH_2CH_2N and NCH_2CH(Me)), 1.38 (d, *J* = 9, 3H, $NCH_2CH(Me)$), 1.31 (overlapping 3 × d, 3 × 3 H, 3 × $CHMe_2$), 1.18 (d, *J* = 11 Hz, 3 H, $CHMe_2$), 0.47 (br s, 3 H, $MeB(C_6F_5)_3$), −0.32 (s, 3 H, AlMe) and −0.84 (s, 9 H, $AlMe_3$). ^{13}C-{^{1}H} NMR (CD_2Cl_2, 75.5 MHz, 298 K): δ 148.4 (d, $^1J_{CF}$ = 240, *o*-C of C_6F_5), 137.8 (d, $^1J_{CF}$ = 243, *p*-C of C_6F_5), 136.6 (d, $^1J_{CF}$ = 246 Hz, *m*-C of C_6F_5), 66.6 ($NCH_2C(H)CH_3$), 66.0 ($NCH_2C(H)CH_3$), 58.6, 57.8, 52.6, 52.0, 46.3 and 41.7 (NCH_2CH_2N), 22.5 ($NCH_2C(H)CH_3$), 19.7, 17.0 and 14.6 ($CHMe_2$), 10.6 (BMe), −4.0 ($AlMe_3$) and −4.7 (AlMe). ^{19}F NMR (CD_2Cl_2, 282 MHz, 298 K): δ −133.4 (d, $^1J_{CF}$ = 20, *o*-F of C_6F_5), −164.9 (t, $^1J_{CF}$ = 20, *p*-F of C_6F_5) and −167.6 (m, $^1J_{CF}$ = 20 Hz, *m*-F of C_6F_5). Found (calculated for $C_{38}H_{47}Al_2BF_{15}N_3O$) C 49.4 (50.0), H 5.0 (5.2), B 0.7 (1.2), N 4.6 (4.6)%.

NMR tube scale synthesis of [Al(κ^4-L^4)Me][MeB(C$_6$F$_5$)$_3$] 15. Compound **14** (0.01 g, 0.011 mmol) was dissolved in CH_2Cl_2 (500 μl) and added to an NMR tube equipped with a Young's Teflon tap. Pyridine (1.8 μl, 0.022 mmol) was added *via* microsyringe and the resulting colourless solution shaken. All volatiles were removed under reduced pressure overnight and the residue was dissolved in CD_2Cl_2 (500 μl). ^{1}H and ^{19}F NMR analysis was conducted on the product. Attempts to prepare analytically pure samples of **15** on a preparative scale were unsuccessful. ^{1}H NMR (CD_2Cl_2, 300.0 MHz, 298 K): δ 3.81 (m, 1H, NCH_2CH(Me)), 3.41 (m, 2H, 2 × $CHMe_2$), 3.30–3.10 (m, 4H, NCH_2CH_2N), 3.09–3.02 (m, 2H, NCH_2CH_2N), 3.00 (dd, 1H, NCH_2CH(Me)), 2.98–2.80 (m, 4H, NCH_2CH_2N), 2.78–2.45 (m, 6H, NCH_2CH_2N), 2.12 (dd, 1H, NCH_2CH(Me)), 1.39, 1.33, 1.20 and 1.15 (d, *J* = 7, 12H, 4 × $CHMe$), 1.09 (d, *J* = 6 Hz, 3H, $NCH_2CH(Me)$), 0.47 (br s, 3H, BMe) and −0.72 (s, 3H, AlMe). ^{19}F NMR (CD_2Cl_2, 282 MHz, 298 K): δ −133.6 (d, $^1J_{CF}$ = 20, *o*-F of C_6F_5), −165.6 (t, $^1J_{CF}$ = 20, *p*-F of C_6F_5) and −168.2 (m, $^1J_{CF}$ = 20 Hz, *m*-F of C_6F_5).

[In(κ^2-L^1)(CH$_2$Ph)$_2$] 16. $In(CH_2Ph)_3$ (0.39 g, 1 mmol) was dissolved in benzene (25 cm^3) and a solution of HL^1 (0.35 g, 1 mmol) in benzene (25 cm^3) added dropwise over 20 min. The mixture was stirred at rt for 24 h. The volatiles were removed under reduced pressure. The residue was washed with pentane (2 × 20 cm^3) and dried *in vacuo* for 24 h to give the product as a white solid. Yield: 0.47 g (73%). ^{1}H NMR (toluene-d^8, 300 MHz, 248 K): δ 6.7–7.5 (m, 12H, C_6H_5 and C_6H_2), 4.14 (broad m, 1H, $N(CH_2)_2N$), 3.91 (broad d, *J* = 12.4, 1H, $NCH_2C_6H_2$), 3.39 (broad d, *J* = 12.4, 1H, $NCH_2C_6H_2$), 2.98 (broad m, 2H, $N(CH_2)_2N$), 2.71 (s, 3H, $Me_2C_6H_2$), 2.39 (s, 3H, $Me_2C_6H_2$), 1.9–2.7 (broad m, 11H, $N(CH_2)_2N$ + CH_2Ph + Me_2CH), 1.69 (broad d, 2H, $N(CH_2)_2N$), 1.39 (broad d, 2H, $N(CH_2)_2N$), 0.65–0.85 (broad m, 9H, Me_2CH) and 0.60 (broad d, *J* = 6.1 Hz, 3H, Me_2CH). EI-MS: *m*/*z* = 552, $[M - CH_2Ph]^+$; and 461, $[M - 2(CH_2Ph)]^+$. Found (calculated for $C_{35}H_{50}InN_3O$): C, 65.0 (65.3); H, 7.9 (7.8); N, 6.1 (6.5)%.

[In(κ^2-L^2)(CH$_2$Ph)$_2$] 17. $In(CH_2Ph)_3$ (0.39 g, 1 mmol) was dissolved in benzene (15 cm^3) and a solution of HL^2 (0.43 g, 1 mmol) in benzene (15 cm^3) added dropwise over 2 h. The mixture was stirred at rt for 24 h. The volatiles were removed under reduced pressure and the residue dried *in vacuo* for 24 h to give the product as a white solid. Yield: 0.52 g (71%). ^{1}H NMR ($CDCl_3$, 300.1 MHz, 248 K): δ 7.71 (s, 1H, C_6H_2), 6.9–7.3 (m, 11H, C_6H_5 + C_6H_2), 4.12 (broad m, 1H, $N(CH_2)_2N$), 3.95 (broad d, *J* = 12.6, 1H, $NCH_2C_6H_2$), 3.41 (broad d, *J* = 12.6, 1H, $NCH_2C_6H_2$), 3.12 (broad m, 2H, $N(CH_2)_2N$), 1.94 (s, 9H, $Me_3CC_6H_2$), 1.55 (s, 9H, $Me_3CC_6H_2$), 1.5–2.8 (broad m, 15H, $N(CH_2)_2N$ + CH_2Ph + Me_2CH), 0.91 (broad d, *J* = 6.0, 3H, Me_2CH), 0.81 (broad m, 6H, Me_2CH) and 0.60 (broad d, *J* = 6.0 Hz, 3H, Me_2CH). EI-MS: *m*/*z* = 636, $[M - (CH_2Ph)]^+$; and 545, $[M - 2(CH_2Ph)]^+$. Found (calculated for $C_{41}H_{62}InN_3O$): C, 67.1 (67.7); H, 8.3 (8.6); N, 5.5 (5.8)%.

[In(κ^4-L^3)(CH$_2$Ph)$_2$] 18. $In(CH_2Ph)_3$ (0.76 g, 2 mmol) was dissolved in benzene (30 cm^3) and a solution of HL^3 (0.75 g, 2 mmol) in benzene (15 cm^3) added dropwise over 3 h. The mixture was stirred at rt for 16 h. The solution was filtered and all volatiles were removed under reduced pressure. The resulting white solid was washed with pentane (2 × 20 cm^3) and dried *in vacuo*. Yield: 1.06 g (78%). ^{1}H NMR (C_6D_6, 500 MHz, 298 K): δ 7.62 (d, *J* = 2.5, 1H, $C_6H_2Bu^t_2$), 7.22–7.00 (m, 7H, $InCH_2C_6H_5$), 6.93 (m, 2H, $InCH_2C_6H_5$), 6.87 (d, *J* = 2.5, 1H, $C_6H_2Bu^t_2$), 6.81 (m, 1H, $InCH_2C_6H_5$), 4.40 (d, *J* = 12, 1H, CH_2Ar), 2.75 (d, *J* = 12, 1H, CH_2Ar), 2.69 (d, *J* = 10, 1H, $InCH_2Ph$), 2.43 (m, 1H, NCH_2CH_2N), 2.31 (m, 5H, NCH_2CH_2N), 2.25 (d, *J* = 10, 1H, $InCH_2Ph$), 2.20 (d, *J* = 10 Hz, 1H, $InCH_2Ph$), 2.08 (s, 3H, NMe), 1.84 (s, 9H, $C(Me_3)$, 1.78 (m, 4H, NMe and $InCH_2Ph$), 1.62 (m, 2H, 0.48, NCH_2CH_2N), 1.44 (s, 9H, CMe_3), 1.35–1.20 (m, 2H, NCH_2CH_2N), 1.15 (m, 1H, NCH_2CH_2N) and 1.05 (m, 1H, NCH_2CH_2N). ^{13}C -{^{1}H} NMR (C_6D_6, 75.5 MHz, 298 K): δ 165.1 (2-C of $C_6H_2Bu^t_2$), 149.8 (1-C of $C_6H_2Bu^t_2$), 138.0 (3-C of $C_6H_2Bu^t_2$), 133.5 (1-C of C_6H_5), 128.5, 128.4, 128.3, 128.2, 127.8, 127.6, 126.7, 125.9 and 124.0 (C_6H_5), 121.1 and 120.9 (4,6-C of $C_6H_2Bu^t_2$), 120.6 (C_6H_5), 120.0 (5-C of $C_6H_2Bu^t_2$), 64.9 (CH_2Ar), 55.9, 55.7, 54.2, 50.3 and 50.2 (NCH_2CH_2N), 48.2 (NMe), 47.8 (NCH_2CH_2N), 47.6 (NMe), 35.8 and 34.0 (CMe_3), 32.3 and 30.3 (CMe_3), 28.5 and 27.5 (CH_2Ph). Found (calculated for $C_{37}H_{58}InN_3O$): C, 66.4 (66.2); H, 8.1 (8.2); N, 5.5 (6.2)%.

[In(κ^4-L^2)(CH$_2$Ph)][(PhCH$_2$)B(C$_6$F$_5$)$_3$] 19. [In(κ^2-L^2)$(CH_2Ph)_2$] **17** (0.14 g, 0.192 mmol) was dissolved in benzene (8 cm^3) and a solution of $B(C_6F_5)_3$ (0.099 g, 0.192 mmol) in benzene (8 cm^3) added dropwise over 20 min. The mixture was stirred at rt for 3 h. The volatiles were removed under reduced pressure, the residue was washed with pentane (10 cm^3) and dried *in vacuo* for 24 h to afford the product as a white solid. Yield 0.19 g (78%). ^{1}H NMR (C_6D_6, 300.1 MHz, 298 K): δ 7.61 (s, 1 H, $C_6H_2Bu^t_2$), 7.05–7.25 (m, 6 H, $InCH_2C_6H_5$ and $BCH_2C_6H_5$), 6.9–7.0 (m, 4 H, $InCH_2C_6H_5$, $BCH_2C_6H_5$ and $C_6H_2Bu^t_2$), 6.81 (m, 1 H, $InCH_2C_6H_5$ or $BCH_2C_6H_5$), 3.35 (br. s, 2 H, $BCH_2C_6H_5$), 3.24 (broad s, 2 H, $ArCH_2$), 2.64 (m, 2 H, CH-Me_2), 2.38 (s, 2 H, $InCH_2Ph$), 2.1–2.3 (m, 2 H, NCH_2CH_2N), 2.03 (m, 4 H, NCH_2CH_2N), 1.89 (overlapping m, 4 H, NCH_2-CH_2N), 1.6–1.8 (overlapping m, 2 H, NCH_2CH_2N), 1.57, 1.39 (2 × s, 2 × 9 H, 2 × Bu^t), 0.48, 0.24 (2 × d, *J* = 6.5, 2 × 6 H, 2 × $CHMe_2$). ^{19}F NMR (C_6D_6, 300 MHz, 298 K): δ −136.0 (d, *J* = 23.6, *o*-F of C_6F_5), −168.7 (t, *J* = 21.3, *p*-F of C_6F_5) and −171.8 (t, *J* = 21.3 Hz, *m*-F of C_6F_5). ES-MS: *m*/*z* = 636

Table 1 X-Ray data collection and processing parameters for $[Al_2(\kappa^2\text{-}L^5)_2Me_4]$ **8** and $[Al(\kappa^2\text{-}L^4\cdot AlMe_3)Me_2]$ **9**

	8	**9**
Formula	$C_{26}H_{60}Al_2N_6O_2$	$C_{20}H_{47}Al_2N_3O$
Formula weight	542.76	399.57
Crystal system	Orthorhombic	Triclinic
Space group	*Pbcn*	$P\bar{1}$
a/Å	22.345(1)	7.6670(6)
b/Å	139720(4)	11.4630(15)
c/Å	10.6340(3)	15.1650(13)
α/°	—	70.965(5)
β/°	—	88.397(5)
γ/°	—	78.458(6)
V/Å^3	3319.9	1233.4
Z	4	2
μ(Mo-Kα)/mm^{-1}	0.110	0.131
Total reflections	18308	3762
Observed reflections	1731 ($I > 3\sigma(I)$)	3296 ($I > 2\sigma(I)$)
Final R, R_w ($I > 3\sigma(I)$)	0.054, 0.066	—
Final R, wR_2 (all data)	—	0.0485, 0.131
Final R, wR_2 ($I > 2\sigma(I)$)	—	0.0409, 0.118

$[M]^+$. Found (calculated for $C_{59}H_{62}BF_{15}InN_3O$): C, 56.9 (57.2); H, 5.3 (5.0); N, 3.3 (3.4)%.

Crystal structure determinations of $[Al_2(\kappa^2\text{-}L^5)_2Me_4]$ 8 and $[Al(\kappa^2\text{-}L^4\cdot AlMe_3)Me_2]$ 9

Structure determinations of compounds **7** and **10** have been communicated previously.[4] Crystal data collection and processing parameters for **8** and **9** are given in Table 1. Crystals were immersed in a film of perfluoropolyether oil on a glass fibre and transferred to an Enraf-Nonius DIP2000 image plate diffractometer equipped with an Oxford Cryosystems low-temperature device.[18] Data were collected at 150 K using Mo-Kα radiation; equivalent reflections were merged and the images processed with the DENZO and SCALEPACK programs.[19] Corrections for Lorentz-polarisation effects and absorption were performed and the structures solved by direct methods. Subsequent Fourier difference syntheses revealed the positions of all other non-hydrogen atoms, and hydrogen atoms were included in calculated positions. Examination of the refined extinction parameters and agreement analyses suggested that no extinction correction was required. Crystallographic calculations were performed using SIR 92,[20] CRYSTALS-PC,[21] SHELXS 96,[22] and SHELXL 93.[23]

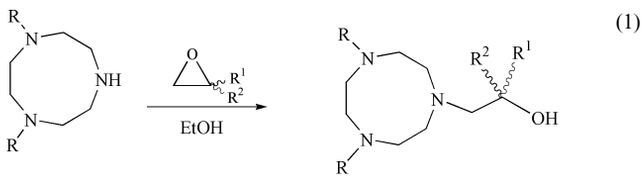
CCDC reference number 186/2230.

See http://www.rsc.org/suppdata/dt/b0/b007323g/ for crystallographic files in .cif format.

Results and discussion

Ligand precursors

The ligand precursors used in this work are shown below. The 2-hydroxybenzyl derivatives HL^1 **1**, HL^2 **2** and HL^3 **3** were prepared according to literature procedures.[12,13] The 2-hydroxyethyl N-substituted compounds HL^4 **4**, HL^5 **5** and HL^6 **6** have not been described previously. They were prepared from either $HMe_2[9]aneN_3$[10] or $HPr^i_2[9]aneN_3$[11] and the appropriate mono- or di-substituted oxirane in good yield as shown in eqn (1). Analogous ring-opening procedures have been used previously to attach one or more 2-hydroxyalkyl side chains to triazacyclononane rings.[24,25] The 2-hydroxypropyl derivatives **4** and **5** are colourless oils whereas the diphenyl substituted analogue **6** forms a white, semi-crystalline solid on standing.



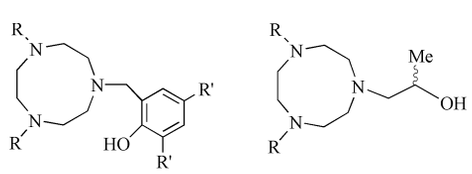
(1)

$HR_2[9]aneN_3$

(R = Me or Pr^i)

R^1 = Me, R^2 = H, R = Pr^i **4** (HL^4) or Me **5** (HL^5)

$R^1 = R^2$ = Ph, R = Pr^i **6** (HL^6)

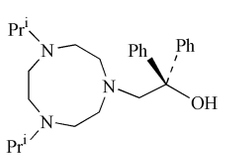


R = Pr^i, R' = Me (HL^1 **1**)

R = Pr^i, R' = Bu^t (HL^2 **2**)

R = Me, R' = Bu^t (HL^3 **3**)

R = Pr^i (HL^4 **4**) or Me (HL^5 **5**)



HL^6 **6**

There is considerable literature precedent for the synthesis of hydroxy- or phenoxy-aluminium compounds from the corresponding alcohol or phenol and an aluminium trialkyl derivative.[26–28] The compounds $HL^{1–6}$ **1–6** were therefore selected as starting materials and the reactions between them and either $AlMe_3$ or $AlMe_3$·py[17] are summarised in Scheme 1. Full characterising data for these, and all the new compounds, are given in the Experimental section.

Dimeric complexes of aluminium

Reaction between $AlMe_3$ or $AlMe_3$·py and one equivalent of the 2-hydroxypropyl functionalised triazacyclononanes HL^4 **4** or HL^5 **5** in hexanes at room temperature afforded the white, crystalline products $[Al_2(\kappa^2\text{-}L^4)_2Me_4]$ **7** and $[Al_2(\kappa^2\text{-}L^5)_2Me_4]$ **8** in 30 and 61% isolated yield, respectively. The single crystal structures of both compounds have been determined and views of the molecular structures are given in Figs. 1 and 2. Data collection parameters for **8** are listed in Table 1 and selected bond lengths and angles for **7** and **8** are summarised in Tables 2 and 3. Both compounds exist as binuclear μ-alkoxy-bridged compounds in the solid state. Crystals of **7** contain one complete molecule in each asymmetric unit whereas molecules of **8** lie across crystallographic two-fold

Table 2 Selected bond distances (Å) and angles (°) for $[Al_2(\kappa^2\text{-}L^4)_2Me_4]$ **7**[4]

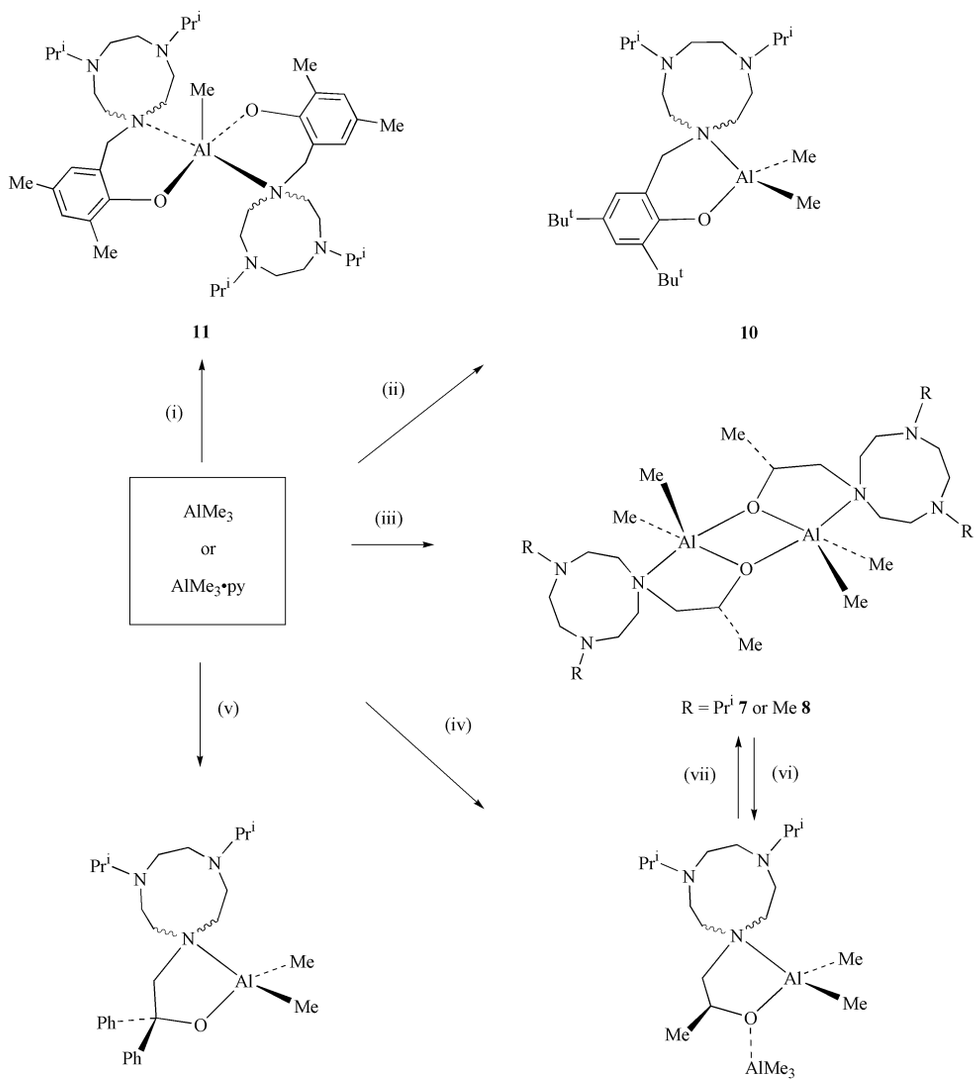
Al(1)–O(13)	1.849(3)	Al(2)–O(28)	1.845(3)
Al(1)–O(28)	1.935(3)	Al(2)–O(13)	1.946(3)
Al(1)–C(15)	1.972(5)	Al(2)–C(29)	1.966(5)
Al(1)–C(14)	1.977(5)	Al(2)–C(30)	1.983(5)
Al(1)–N(1)	2.245(4)	Al(2)–N(16)	2.265(4)
O(13)–Al(1)–O(28)	74.56(14)	O(28)–Al(2)–O(13)	74.36(14)
O(13)–Al(1)–C(15)	112.2(2)	O(28)–Al(2)–C(29)	113.7(2)
O(28)–Al(1)–C(15)	104.5(2)	O(13)–Al(2)–C(29)	103.2(2)
O(13)–Al(1)–C(14)	127.9(2)	O(28)–Al(2)–C(30)	128.4(2)
O(28)–Al(1)–C(14)	92.1(2)	O(13)–Al(2)–C(30)	93.5(2)
C(15)–Al(1)–C(14)	120.0(2)	C(29)–Al(2)–C(30)	117.9(2)
O(13)–Al(1)–N(1)	79.05(15)	O(28)–Al(2)–N(16)	79.12(15)
O(28)–Al(1)–N(1)	151.0(2)	O(13)–Al(2)–N(16)	151.33(15)
C(15)–Al(1)–N(1)	96.5(2)	C(29)–Al(2)–N(16)	97.2(2)
C(14)–Al(1)–N(1)	94.7(2)	C(30)–Al(2)–N(16)	94.5(2)
C(10)–N(1)–Al(1)	100.3(3)	C(25)–N(16)–Al(2)	99.5(3)
C(9)–N(1)–Al(1)	106.2(3)	C(24)–N(16)–Al(2)	107.5(3)
C(2)–N(1)–Al(1)	116.9(3)	C(17)–N(16)–Al(2)	117.0(3)
Al(1)–O(13)–Al(2)	104.1(2)	Al(1)–O(28)–Al(2)	104.7(2)
C(11)–O(13)–Al(1)	123.9(3)	C(26)–O(28)–Al(1)	129.7(3)
C(11)–O(13)–Al(2)	130.6(3)	C(26)–O(28)–Al(2)	123.3(3)

rotation axes and only one half of each moleule is crystallographically independent.

Each of the aluminium centres in $[Al_2(\kappa^2\text{-}L^4)_2Me_4]$ **7** and $[Al_2(\kappa^2\text{-}L^5)_2Me_4]$ **8** possesses an approximately trigonal bipyramidal coordination environment. In each case the two methyl groups and one of the bridging oxygens form the equatorial donors; the axial sites are occupied by a single nitrogen of the κ^2 coordinated triazacyclic ligand and the second bridging oxygen atom. The Al–O distances to the bridging alkoxide moieties are inequivalent, the oxygen binding most tightly to the aluminium to which the N of the same $L^{4,5}$ ligand is bonded. The Al–Me, Al–N and Al–μ-O distances in **7** and **8** are comparable to previously reported values in related binuclear systems.[29] The compounds contain two chiral centres (not resolved in the racemic ligand precursors HL^4 and HL^5), namely the $CH_2C(H)MeO$ carbons of the pendant arms. As

Table 3 Selected bond distances (Å) and angles (°) for $[Al_2(\kappa^2\text{-}L^5)_2Me_4]$ **8**. Atoms carrying the suffix "B" are related to their counterparts by the symmetry operator $[2 - x, y, \frac{1}{2} - z]$

Al(1)–O(1)	1.851(2)	Al(1)–C(11)	1.993(4)
Al(1)–O(1B)	1.944(3)	Al(1)–C(12)	1.984(4)
Al(1)–N(3)	2.306(3)		
N(3)–Al(1)–O(1)	78.6(1)	O(1)–Al(1)–C(12)	112.2(1)
N(3)–Al(1)–O(1B)	151.0(1)	O(1B)–Al(1)–C(12)	103.7(1)
O(1)–Al(1)–O(1B)	74.8(1)	C(11)–Al(1)–C(12)	118.9(2)
N(3)–Al(1)–C(11)	94.0(1)	Al(1)–N(3)–C(2)	106.6(2)
O(1)–Al(1)–C(11)	128.9(1)	Al(1)–N(3)–C(4)	118.0(2)
O(1B)–Al(1)–C(11)	93.8(1)	Al(1)–N(3)–C(31)	99.3(2)
N(3)–Al(1)–C(12)	96.9(1)	Al(1)–O(1)–Al(1B)	104.7(1)
C(32)–O(1)–Al(1)	123.9(2)	C(32)–O(1)–Al(1B)	129.7(2)



Scheme 1 Reagents and conditions: (i) HL^1 (2 equivalents), hexane, rt, 2 h, 35%; (ii) HL^2, hexane, rt, 2 h, 57%; (iii) HL^4 or HL^5, hexane, rt, 2 h, 30 (**7**) or 61% (**8**); (iv) 0.5 HL^4, hexane, rt, 2 h, 71%; (v) HL^6, hexane, rt, 3 h, 15%; (vi) 2 $AlMe_3$, C_6D_6, rt, 5 min, > 95%; (vii) py, C_6D_6, rt, 5 min, > 95%.

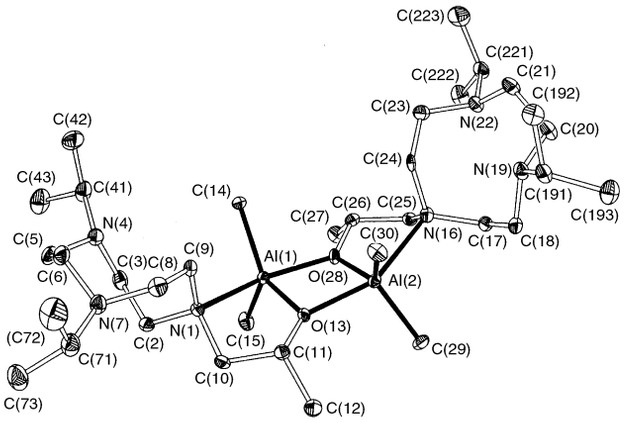


Fig. 1 Displacement ellipsoid (35%) plot of $[Al_2(\kappa^2\text{-}L^4)_2Me_4]$ **7** with H atoms omitted.

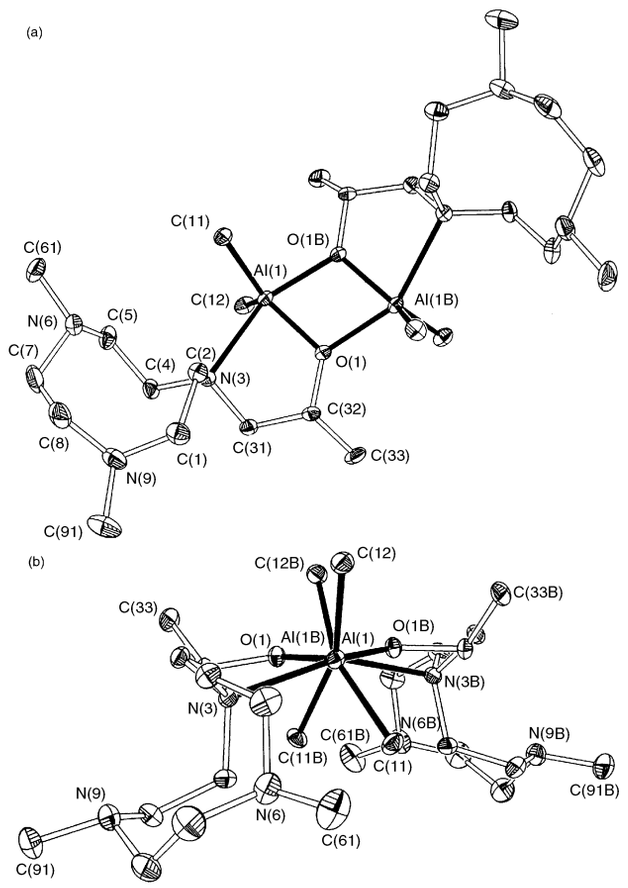


Fig. 2 Displacement ellipsoid (20%) plot of $[Al_2(\kappa^2\text{-}L^5)_2Me_4]$ **8** with H atoms omitted. Atoms carrying the suffix "B" are related to their counterparts by the symmetry operator $[2 - x, y, \frac{1}{2} - z]$. (a) Viewed approximately perpendicular to the Al_2O_2 planes. (b) Viewed along the Al(1)···Al(1B) vector.

the axial view of **8** in Fig. 2(b) illustrates, the $CH_2C(H)MeO$ methyl groups (C(33) and C(33B)) are both oriented "up" towards the AlMe carbons C(12) and C(12B) and away from the two triazacyclononane rings. As is apparent from the structures of **7** and **8**, the molecules form exclusively *R*,*R* (and *S*,*S*) enantiomers and there is no evidence in the solid state or solution (see below) for a second distinguishable product corresponding to the *R*,*S* or *S*,*R* diastereoisomers. Presumably this arises from the need to minimise steric interactions in the binuclear products. The axial view in Fig. 2(b) also emphasises the different Me–Al···Al–Me torsion angles: C(12)–Al(1)···Al(1B)–C(12B) 16.7° and C(11)–Al(1)···Al(1B)–C(11B) 60.1°; the corresponding values for **7** are C(15)–

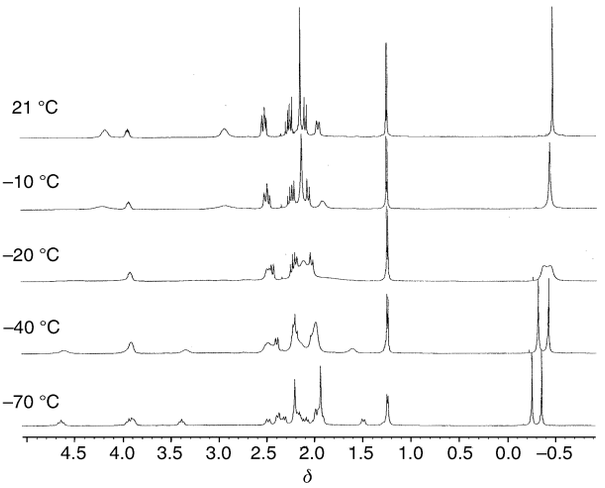


Fig. 3 Variable temperature 500.0 MHz ^{1}H NMR spectra of $[Al_2(\kappa^2\text{-}L^5)_2Me_4]$ **8** in $C_6D_5CD_3$.

Al(1)···Al(2)–C(29) 18.3° and C(14)–Al(1)···Al(2)–C(30) 59.8°. These differences are attributed to the greater steric crowding around C(11), C(11B) *versus* that for C(12), C(12B) in **8** (and around the corresponding carbons in **7**).

While the kind of binuclear, five-coordinate motif found for compounds **7** and **8** is structurally well established in aluminium chemistry,[29] the unique feature of these compounds is the κ^2 coordination mode of the L^4 and L^5 ligands that bind through only one of the triazacyclononane nitrogens. There is no structural precedent for any pendant arm functionalised triazacyclononane ligand binding through fewer than all three ring nitrogens. Triazacyclononanes without pendant arms have been observed to bind in a κ^2 mode (*i.e.* through two ring nitrogens) to transition metals with a d^8 electronic configuration.[30,31] This is presumed to arise from strong ligand field effects in these square planar complexes. Aluminium complexes of triazacyclononanes with three pendant anionic donor arms have been described.[8,32] These possess κ^6-bound ligands in which all three triazacyclic nitrogens are bound to the metal centre. The κ^2 coordination of the mono pendant arm macrocycles described here is presumably a function of the small radius of aluminium and the good σ-donor ability of the metal-bound methyl groups.

A solution molecular weight measurement for compound **7** (found: 657, calculated for dimeric **7**: 655 g mol^{-1}) confirms that the dimeric structures are maintained in the solution phase. The ^{1}H and ^{13}C NMR data for **7** and **8** are temperature-dependent and show that these compounds are fluxional in solution. The data for the ring N-methylated homologue **8** are the easiest to interpret and we will discuss in detail only these. Those for **7** are analogous but, for example, the ^{1}H spectra feature additional doublets and septets for the four methyl groups and two methine hydrogens of the inequivalent, diastereotopic ring N-isopropyl groups. Selected 500 MHz ^{1}H spectra of $[Al_2(\kappa^2\text{-}L^5)_2Me_4]$ **8** in toluene-d_8 between −70 and 21 °C are shown in Fig. 3.

The slow exchange limit is reached at −70 °C and the spectrum is consistent with the solid state structure (Fig. 2a and 2b). The two singlets between δ *ca.* 0 and −0.5 are attributed to the inequivalent AlMe groups, the doublet at δ 1.24 is assigned to the $CH_2C(H)MeO$ methyl group of the pendant arm and couples to the $CH_2C(H)MeO$ methine hydrogen that appears at δ *ca.* 3.9 (overlapping with a triazacyclononane ring CH_2 signal). The two singlets at δ 1.94 and 2.28 are assigned to the two inequivalent macrocycle NMe groups. The remaining multiplets all arise from the macrocycle ring and arm diastereotopic methylene hydrogens, all of which are inequivalent. The ^{13}C NMR spectrum of compound **8** at this temperature shows the expected 13 different carbon atom

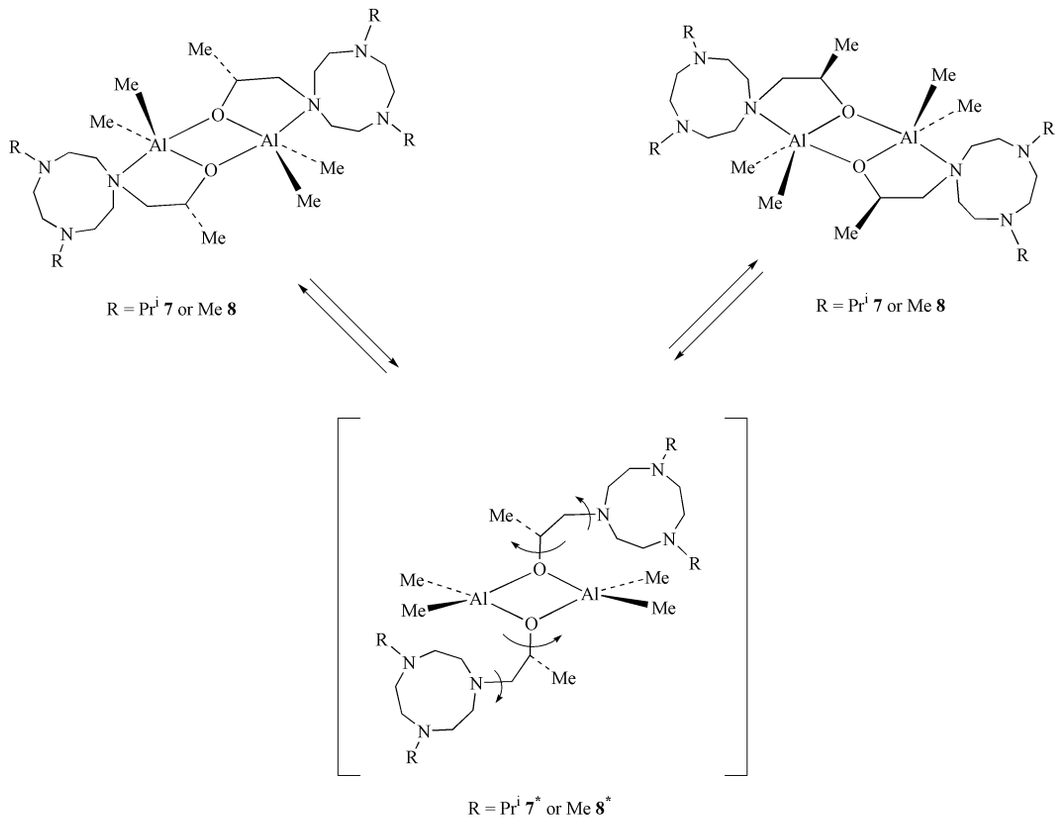


Fig. 4 Proposed mechanism for the fluxional process in $[Al_2(\kappa^2\text{-}L^4)_2Me_4]$ **7** and $[Al_2(\kappa^2\text{-}L^5)_2Me_4]$ **8**.

environments. It has been possible through the use of 1- and 2-dimensional shift correlation and NOE (Nuclear Overhauser Effect) NMR spectroscopy to make a partial assignment of the macrocycle ring methylene hydrogens. Details are given in the Experimental section. Of particular interest are the apparent triplets (each of intensity 2 H per dimer) at δ 4.64 and 3.91 (overlapping with the signal from $CH_2C(H)MeO$ mentioned above). These are not mutually coupled and each is assigned to one of the two methylene hydrogens either side of the Al-bound N atom (*i.e.* one is attached to C(2) and one to C(4) in Fig. 2). Such low-field shifts of triazacyclononane methylene resonances are not encountered in the κ^4-coordinated ligands (the typical shift range being δ *ca.* 2 to < 4) and appear to be characteristic of all the κ^2-bound pendant arm macrocycles described herein.

The ^{1}H NMR spectra in Fig. 3 clearly change with increasing temperature. The macrocycle NMe groups and pairs of methylene H atoms undergo mutual site exchange. Thus at 21 °C the NMe groups appear as a singlet at δ 2.14 (intensity 12 H per dimer) while the unusually shifted apparent triplets at δ 4.64 and 3.91 at −70 °C give rise to an averaged apparent triplet at δ 4.17 (intensity 4 H per dimer) at 21 °C. The $CH_2C(H)MeO$ (δ 3.93) and $CH_2C(H)MeO$ (doublet, δ 1.24) resonances of the pendant arm do not significantly change with temperature. The two AlMe signals at −70 °C coalesce to a singlet at δ −0.47 (intensity 12 H per dimer). These ^{1}H NMR spectral changes are paralleled in the ^{13}C spectra. For example, at 21 °C there are three macrocyclic ring CH_2 carbon signals (instead of the six observed at −70 °C) and one NMe and AlMe signal. The ^{1}H and ^{13}C NMR spectra of compound **7** show analogous features.

We have estimated $\Delta G_{Tc}^{\ddagger}$ values (Gibbs free energy of activation at the coalescence temperature, T_c) for the AlMe group exchange processes in compounds **7** and **8** from the ^{1}H NMR coalescence points (T_c = 261 and 255 K, respectively).[33] For **7** $\Delta G^{\ddagger}_{261K}$ is 54.0 ± 1 kJ mol^{-1} and for **8** the corresponding $\Delta G^{\ddagger}_{255K}$ is 52.1 ± 1 kJ mol^{-1}. The values are comparable within experimental error. Unfortunately we cannot reliably extract kinetic data from the NMe resonances in either the ^{1}H or ^{13}C spectra of **7** (or the NPr^i signals of **8**) due to overlapping resonances, and so the following discussion of the exchange mechanisms in **7** and **8** is only a qualitative one based on the general appearance of the spectra. However, the interpretation is underpinned by detailed and quantitative NMR studies by Oliver and co-workers of a series of related fluxional systems $[Al_2(\mu\text{-}\text{“O-N”})_2Me_4]$ where “O-N” denotes an optically active amino-alkoxide ligand.[34]

The spectra in Fig. 3 can be interpreted with the aid of Fig. 4. The overall dynamic processes probably proceed *via* the binuclear species denoted **7*** or **8*** which possess four-coordinate aluminium centres and κ^1-coordinated $L^{4,5}$ ligands. Oliver and co-workers have eliminated the possibility of mononuclear intermediates (favouring binuclear intermediates analogous to **7*** or **8***) in their related systems on the basis of detailed kinetic data. Furthermore, binuclear, four-coordinate complexes related to **7*** and **8*** (*i.e.* with a pendant donor group) have often been proposed to be in equilibrium with their binuclear, five-coordinate counterparts.[34–37] As shown in Fig. 4, for exchange of the two inequivalent AlMe groups to occur the macrocycle nitrogen must detach from one Al atom and (*via* a rotation about the O–C(H)Me single bond) then coordinate to the other. Thus the AlMe groups that were originally closest to the macrocyclic moiety (*e.g.* C(11), C(11B) in Fig. 2a) are now furthest away, and *vice versa*. The estimated $\Delta G^{\ddagger}_{Tc}$ values of 52.1–54.0 ± 1 kJ mol^{-1} for AlMe group exchanges in **7** and **8** are consistent with the values reported by Oliver and co-workers for the exchange processes in their $[Al_2(\mu\text{-}\text{“O-N”})_2Me_4]$ systems. However, careful examination of molecular models and the solid state structures in Figs. 1 and 2 shows that this simple decoordination–rotation–recoordination process cannot alone account for the observed mutual exchange of the macrocyclic NR (R = Me or Pr^i) groups. To exchange these two groups (and to account for all the pairwise ring methylene proton and carbon exchange processes in **7** and **8**) requires a rotation about the $N_{macrocycle}$–$CH_2C(H)MeO$ (*i.e.* C(31)–N(3) in Fig. 2) bond *and* subsequent inversion at the $N_{macrocycle}$ atom.

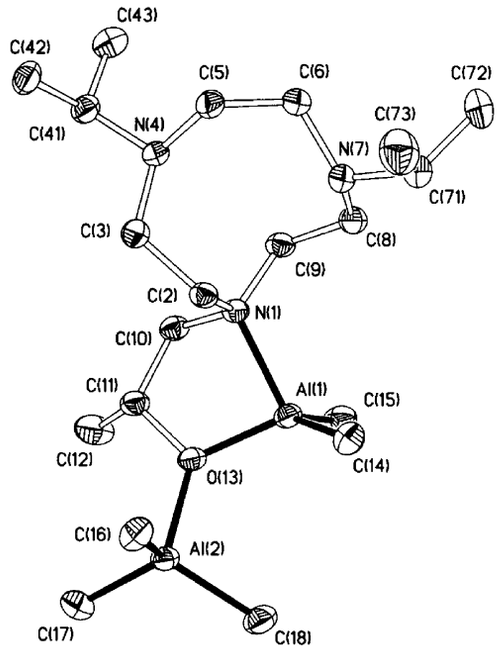


Fig. 5 Displacement ellipsoid (40%) plot of [Al(κ²-L⁴·AlMe₃)Me₂] **9** with H atoms omitted.

Only this process can account for the apparent C_2 symmetry of the R_2[9]aneN_3 moiety sub-spectra of **7** and **8** at ambient temperatures.

It is apparent (at least qualititatively) from Fig. 3 that the AlMe group exchange in compounds **7** and **8** and the exchange processes for the macrocyclic CH_2 and NMe groups are not kinetically degenerate. Thus the initial rates of broadening of the AlMe and NMe signals (which are directly related to the exchange rate constants[33,38]) are evidently different, with the NMe signals broadening more quickly. This suggests that the macrocycles in the intermediates **7*** and **8*** can undergo the pairwise methylene and methyl group exchange processes described above and then recoordinate at the *same* aluminium centre to reform **7** and **8** without AlMe group exchange.

Monomeric four- and five-coordinate complexes of aluminium

The syntheses of monomeric aluminium complexes are also summarised in Scheme 1. NMR tube scale reactions of [Al_2-(κ²-$L^{4,5}$)$_2$$Me_4$] **7**,**8** in benzene with $AlMe_3$ gave a clean reaction to form [Al(κ²-L^4·$AlMe_3$)Me_2] **9** in the case of **8**, but no clean product could be obtained from **7**. Barron and co-workers have recently reported the analogous reaction of dimeric [Al_2-(μ-$OCH_2CH_2NMe_2$)$_2$$Me_4$] with $Al(Bu^t)_3$ to form the monomeric derivative [Al{$OCH_2CH_2NMe_2$·$Al(Bu^t)_3$}Me_2] which has the $Al(Bu^t)_3$ bound to the anionic oxygen donor.[35a] The new compound **9** was synthesized on a preparative scale by the reaction of HL^4 **4** with two equivalents of $AlMe_3$ in hexanes. Recrystallisation from pentane afforded diffraction-quality crystals in 71% isolated yield. The structure of **9** has been determined; the molecular structure is shown in Fig. 5 and selected bond lengths and angles are listed in Table 4.

[Al(κ²-L^4·$AlMe_3$)Me_2] **9** possesses an L^4 ligand that is κ²-coordinated to a $AlMe_2$ unit displaying approximately tetrahedral coordination. The anionic O-donor of L^4 is datively bonded to an $AlMe_3$ molecule that also has approximately tetrahedral geometry. The Al(1)–O(13) bond length is somewhat shorter than Al(2)–O(13) in keeping with this description. The Al(1)–C_{methyl} distances in **9** are only slightly shorter (av. 1.924 Å) than the Al(2)–C_{methyl} values (av. 1.942 Å), but are considerably contracted in comparison to those in the dimeric, five-coordinate compound [Al_2(κ²-L^4)$_2$$Me_4$] **7** (av. 1.975 Å).

Table 4 Selected bond distances (Å) and angles (°) for [Al(κ²-L^4·$AlMe_3$)Me_2] **9**

Al(1)–O(13)	1.7959(11)	Al(2)–O(13)	1.8671(12)
Al(1)–C(15)	1.917(2)	Al(2)–C(18)	1.932(2)
Al(1)–C(14)	1.931(2)	Al(2)–C(17)	1.940(2)
Al(1)–N(1)	1.9819(14)	Al(2)–C(16)	1.953(2)
O(13)–Al(1)–C(15)	111.25(8)	O(13)–Al(2)–C(18)	101.56(7)
O(13)–Al(1)–C(14)	116.15(7)	O(13)–Al(2)–C(17)	111.46(7)
C(15)–Al(1)–C(14)	118.83(9)	C(18)–Al(2)–C(17)	109.64(10)
O(13)–Al(1)–N(1)	87.76(5)	O(13)–Al(2)–C(16)	103.58(7)
C(15)–Al(1)–N(1)	108.78(8)	C(18)–Al(2)–C(16)	118.06(9)
C(14)–Al(1)–N(1)	109.43(8)	C(17)–Al(2)–C(16)	111.84(9)
C(10)–N(1)–Al(1)	97.58(10)	C(11)–O(13)–Al(1)	113.03(10)
C(9)–N(1)–Al(1)	116.03(10)	C(11)–O(13)–Al(2)	121.71(10)
C(2)–N(1)–Al(1)	108.87(10)	Al(1)–O(13)–Al(2)	121.72(6)

These variations in Al–C distances reflect the different coordination numbers in **7** and **9**. The Al–$N_{macrocycle}$ distance of 1.9819(14) Å in **9** is considerably shorter than those found in five-coordinate **7** and **8** (2.245(4)–2.306(3) Å), again presumably because of the different coordination numbers. The geometry of compound **9** is similar to that of Barron's [Al{OCH_2CH_2-NMe_2·$Al(Bu^t)_3$}Me_2].[35a] A number of other related compounds with an $AlMe_3$ unit bound to the anionic donor of a chelating, bidentate ligand have crystallographically been characterised.[35b–d] There is no evidence from NMR tube scale reactions for the coordination of $AlMe_3$ to either of the "free" triazacyclonane nitrogens. A solution molecular weight measurement for **9** (found 430; calculated for monomeric **9** 400 g mol^{-1}) confirms that the monomeric structure is maintained in solution. Reaction of **9** with pyridine in C_6D_6 showed quantitative formation of **7** and $AlMe_3$·py.[17]

The room temperature ^{1}H and ^{13}C NMR data for compound **9** are consistent with the solid state structure, although some of the ^{1}H ring methylene resonances are slightly broad, possibly due to conformational flexing of the macrocyclic moiety. At −60 °C all of the ^{1}H resonances are very sharp. Three singlets at δ −0.73 (intensity 3 H), −0.85 (3 H) and −1.07 (9 H) are assigned to the two inequivalent $AlMe_2$ and the three $AlMe_3$ methyl groups, respectively. Rotation around the O(13)–Al(2) bond is apparently rapid even at −60 °C. In addition to signals for two inequivalent, diastereotopic N-isopropyl groups, macrocyclic ring methylene and pendant arm resonances in the δ *ca.* 0.8 to 4.2 region, there are also two apparent triplets (intensity 1 H each) at δ 4.81 and 4.57. These are each assigned to one of the two ring methylene hydrogens either side of the coordinated N donor and, as for **7**, appear to be characteristic of the κ² coordination of L^4. There is neither evidence in the NMR spectra for $AlMe_2$ methyl group exchange, nor for exchange between macrocycle NPr^i groups.

The formation of monomeric [Al(κ²-L^4·$AlMe_3$)Me_2] **9** on coordination of $AlMe_3$ to the aryl oxide oxygen is attributable to increased steric demands at the metal centre. Another potential way to achieve this is by use of the phenolic ligand precursors HL^1 **1**, HL^2 **2** or HL^3 **3** that feature methyl or *tert*-butyl substituents, respectively, *ortho* to the oxygen donor. The reactions of **1** and **2** with $AlMe_3$·py or $AlMe_3$ are summarised in Scheme 1; reactions with HL^3 **3** gave complex mixtures.

Reaction of HL^2 with $AlMe_3$·py in hexanes followed by cooling to −30 °C afforded diffraction quality crystals of colourless [Al(κ²-L^2)Me_2] **10** in 57% isolated yield. The structure has been determined; selected bond lengths and angles are listed in Table 5 and a view of the molecular structure is given in Fig. 6. Molecules of [Al(κ²-L^2)Me_2] **10** are mononuclear in the solid state and feature an approximately tetrahedral aluminium with a κ²-coordinated L^2 ligand and two methyl groups. The Al–O distance of 1.759(4) Å is slightly shorter than that of 1.7959(11) Å in four-coordinate **9** while the Al–N and Al–Me distances are somewhat longer. The distances and angles

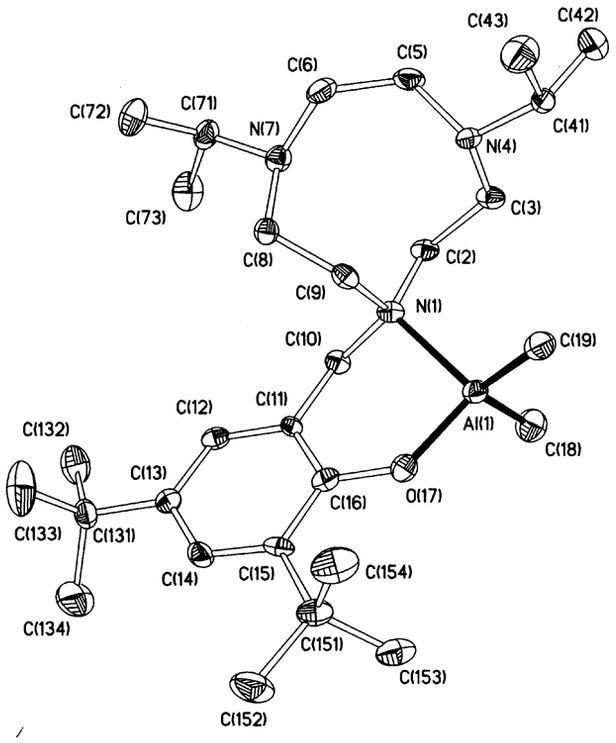


Fig. 6 Displacement ellipsoid (40%) plot of $[Al(\kappa^2\text{-}L^2)Me_2]$ **10** with H atoms omitted.

within the Pr^i_2[9]aneN_3 moiety are comparable to those in **7**–**9** and the Pr^i_2[9]aneN_3 ring is folded somewhat to one side of the complex. A solution molecular weight measurement for **10** (found 524, calculated for monomeric **10** 575 g mol^{-1}) confirms that the monomeric structure is maintained in solution.

At room temperature the ^{1}H and ^{13}C NMR spectra of compound **10** are very broad and clearly indicative of one or more fluxional processes. At low temperature the spectra are fully consistent with the solid state structure. On warming the sample, the two individual AlMe resonances coalesce ($\Delta G^{\ddagger}_{256K} = 54.7 \pm 1.2$ kJ mol^{-1}), and signals of the $CH_2Pr^i_2$-[9]aneN_3 moiety (but not those of the $C_6H_2Bu^t$ ring) broaden and undergo pairwise exchange of the type described above for **7** and **8**. To account for all of these processes, a mechanism involving the decoordination of N(1) (see Fig. 6), inversion at N(1) as well as rotation around the N(1)–C(10) *and* Al(1)–O(17) bonds is required. Finally, recoordination of N(1) effectively gives inversion of configuration at Al(1) and exchanges the relative positions of C(18) and C(19). These processes are analogous to those proposed in Fig. 4 for **7** and **8** and are in line with the $\Delta G^{\ddagger}_{256K}$ value of 54.7 ± 1.2 kJ mol^{-1}. It is not entirely clear, however, why the compounds $[Al(\kappa^2\text{-}L^4\cdot AlMe_3)Me_2]$ **9** and $[Al(\kappa^2\text{-}L^2)Me_2]$ **10** differ so much with regard to their degrees of fluxionality on the NMR timescale. Possibly the 3,5-di-*tert*-butylphenoxy derived ligand of **10** is a more sterically demanding than $L^4\cdot AlMe_3$ in **9**, thus aiding decoordination of the triazacyclic nitrogen.

Reaction of the less sterically demanding ligand HL^1 **1** with $AlMe_3$ in a 1:1 molar ratio gave very poor yields of the bis-(pendant arm ligand) complex $[Al(\kappa^2\text{-}L^1)_2Me]$ **11** (Scheme 1). It was not possible to prepare monosubstituted products analogous to $[Al(\kappa^2\text{-}L^2)Me_2]$ **10**. Better yields of **11** were obtained by reaction of two equivalents of HL^1 with one of $AlMe_3$. We were not able to obtain diffraction-quality crystals of **11** but a monomeric, five-coordinate structure is assigned on the basis of a solution molecular weight measurement (found 701, calculated for monomeric **11** 736 g mol^{-1}). The NMR spectra of **11** show only one L^1 ligand environment at all accessible temperatures (overall ratio of L^1:Me signals being 2:1). Resonances at δ 4.65 and 4.30 in the 500.0 MHz, 213 K

Table 5 Selected bond distances (Å) and angles (°) for $[Al(\kappa^2\text{-}L^2)Me_2]$ **10**

Al(1)–O(17)	1.759(4)	Al(1)–C(18)	1.965(5)
Al(1)–C(19)	1.953(5)	Al(1)–N(1)	2.011(4)
O(17)–Al(1)–C(19)	110.7(2)	C(19)–Al(1)–N(1)	110.0(2)
O(17)–Al(1)–C(18)	111.4(2)	C(18)–Al(1)–N(1)	107.0(2)
C(19)–Al(1)–C(18)	119.8(2)	O(17)–Al(1)–N(1)	95.0(2)
C(16)–O(17)–Al(1)	131.2(3)	C(9)–N(1)–Al(1)	108.4(3)
C(2)–N(1)–Al(1)	112.7(3)	C(10)–N(1)–Al(1)	103.8(3)

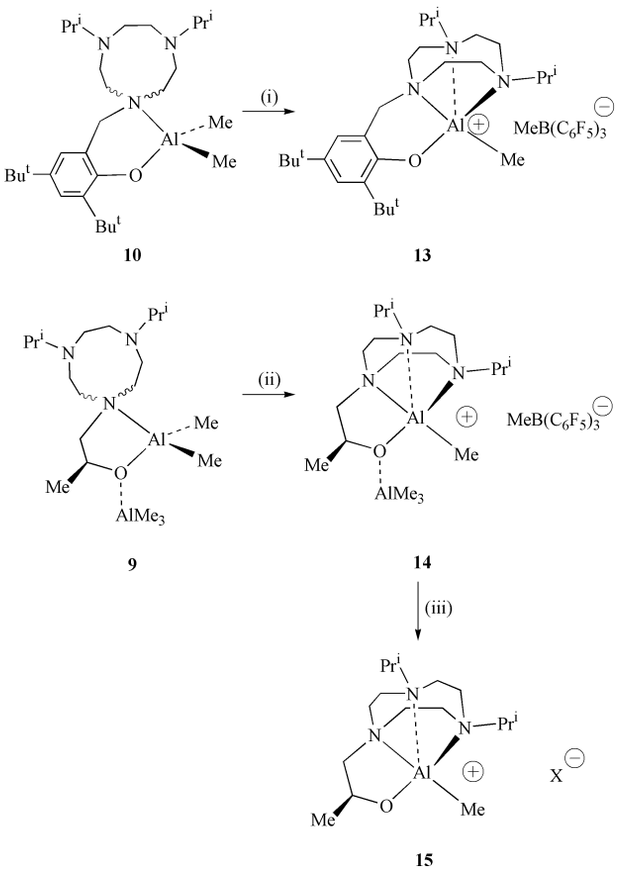
^{1}H NMR spectrum are diagnostic of a κ^2 coordination mode for the L^1 ligand. The most likely structure based on the NMR data has the square based pyramidal geometry (C_2 symmetry) shown in Scheme 1. The proposed structure and aluminium coordination sphere of **11** is reminiscent of that previously reported for N_2O_2-donor Schiff base complexes $[Al(N_2O_2$ donor)Me].[39–41] The formation of only $[Al(\kappa^2\text{-}L^1)_2Me]$ **11** in the 1:1 reaction of HL^1 with $AlMe_3$ (as opposed to the target $[Al(\kappa^2\text{-}L^1)Me_2]$ complex) suggests that the expected intermediate $[Al(\kappa^2\text{-}L^1)Me_2]$ (*i.e.* analogous to the isolated compound **10**) can either react rapidly with further HL^1 forming **11** and CH_4, or disproportionate to form **11** and $AlMe_3$. Either way, it is likely that it is the diminished steric demands of the L^1 ligand (in comparison with those of the *tert*-butyl substituted homologue L^2) that facilitate formation of **11**.

The results obtained so far show the importance of the steric demands of the pendant arm in the ligands L^1–L^5. We were therefore interested to examine the reaction of the 2,2-diphenylethyl substituted ligand precursor HL^6 with $AlMe_3$. It was expected that the presence of the two bulky phenyl substituents in the pendant arm of L^6 would lead to monomeric products analogous to **9** and **10**. Reaction of HL^6 **6** with $AlMe_3$ in hexanes afforded a mixture of products from which $[Al(\kappa^2\text{-}L^6)Me_2]$ **12** could be isolated in 15% yield by a combination of fractional crystallisation and high vacuum sublimation. The NMR spectra of **12** at 213 K show signals two inequivalent AlMe groups; these coalesce on warming of the sample ($T_c = 255$ K, $\Delta G^{\ddagger}_{255} = 52.6 \pm 1.2$ kJ mol^{-1}). The remainder of the ^{1}H NMR spectra are consistent with the κ^2 coordination proposed for **12** in Scheme 1. Attempts to obtain reproducible or reliable solution molecular weight measurements of **12** were unsuccessful. The highest observed fragment in the electron impact mass spectrum showed an envelope at $m/z = 450$, corresponding to the monomeric fragment $\{[Al(\kappa^2\text{-}L^6)Me_2] - Me\}^+$. However, this observation could equally be consistent with a dimeric ground state structure that has undergone symmetrical cleavage prior to loss of a methyl radical. Nevertheless, on balance, we favour the formulation of **12** as a monomer analogous to **9** and **10** on the basis of the steric crowding imposed by the two phenyl substituents adjacent to the alkoxide donor atom.

Cationic complexes of aluminium

There is considerable current interest in well defined, cationic organoaluminium compounds.[39,42–52] We were interested to make cationic derivatives of the new compounds in Scheme 1 in order to explore their structures and reactivity. Jordan, Gibson and Lappert have shown that the Lewis acid $B(C_6F_5)_3$ (along with related reagents) can be used to generate alkyl aluminium cations from dialkyl precursors.[52,43–47,50] The reactions of $[Al(\kappa^2\text{-}L^2)Me_2]$ **10** and $[Al(\kappa^2\text{-}L^4\cdot AlMe_3)Me_2]$ **9** with $B(C_6F_5)_3$ are summarised in Scheme 2. Reactions of **7**, **8** or **11** with either $B(C_6F_5)_3$ or $[Ph_3C][B(C_6F_5)_4]$ produced intractable mixtures.

Reaction of $[Al(\kappa^2\text{-}L^2)Me_2]$ **10** with $B(C_6F_5)_3$ in CH_2Cl_2 afforded $[Al(\kappa^4\text{-}L^2)Me][MeB(C_6F_5)_3]$ **13** as a white solid in 96% yield. The ^{1}H NMR spectrum of the $[Al(\kappa^4\text{-}L^2)Me]^+$ cation in **13** is substantially different from that of **10**. A broad singlet (intensity 3 H) at δ 0.44 is attributed to the free $[MeB(C_6F_5)_3]^-$



10 **13** **9** **14** **15**

Scheme 2 Reagents and conditions: (i) $B(C_6F_5)_3$, CH_2Cl_2, rt, 30 min, >95%; (ii) $B(C_6F_5)_3$, CH_2Cl_2, rt, 30 min, 84%; (iii) py (2 equivalents), CH_2Cl_2, rt, 5 min, >95%.

anion,[53] there being no evidence for significant Al···MeB-$(C_6F_5)_3$ interactions of the kind recently reported by Coles and Jordan.[43] The AlMe resonance for $[Al(\kappa^4\text{-}L^2)Me]^+$ appears at δ −0.28, but the most significant features are those associated with the macrocyclic ligand itself. The ^{1}H resonances for L^2 are consistent with C_s symmetry such that there is only a singlet for the two ArCH_2N methylene protons of the pendant arm, and only one set of resonances (one multiplet and two doublets) for the diastereotopic isopropyl groups. Most significantly, all of the triazacyclic NCH_2CH_2N resonances appear in the δ 3.05 to 2.74 range (*i.e.* not at $\delta >$ *ca.* 4 that would indicate a κ^2-coordinated L^2 ligand). We propose that the cation in **13** therefore possesses a *fac*-coordinated triazacyclonane ring.

These data are consistent with the trigonal bipyramidal, five-coordinate $[Al(\kappa^4\text{-}L^2)Me]^+$ cation shown in Scheme 2. The NMR spectra for the cation broaden on cooling to −80 °C, but no slow exchange limiting spectrum could be obtained. We propose that the implied low activation energy, fluxional process involves conformational flexing of the pendant arm that would be expected to lie either side of the molecular plane containing the Al, Me and aryl oxide O atoms. We have not been able to obtain crystals of **13**, but Tolman and co-workers have reported the crystal structures of trigonal bipyramidal complexes $[M(L^2)X]$ and $[M(L^1)X]^+$ (M = Cu or Zn; X = Cl or MeCN) that have the same geometry as that proposed here (with the pendant arm folded to one side of the approximate molecular mirror plane). Moreover, the diamagnetic complexes give ^{1}H NMR spectra that are consistent with C_s symmetrical structures on the NMR timescale.[12]

Reaction of $[Al(\kappa^2\text{-}L^4\cdot AlMe_3)Me_2]$ **9** with $B(C_6F_5)_3$ in CH_2Cl_2 gives $[Al(\kappa^4\text{-}L^4\cdot AlMe_3)Me][MeB(C_6F_5)_3]$ **14** as a white solid in 84% yield. The ^{1}H NMR spectrum shows a broad singlet at δ *ca.* 0.47 again consistent with a free $[MeB(C_6F_5)_3]^-$ anion. In addition, there are two aluminium methyl resonances at δ −0.32 (intensity 3 H) and −0.84 (intensity 9 H) and these are assigned to single AlMe and $AlMe_3$ groups of a $[Al(\kappa^4\text{-}L^4\cdot AlMe_3)Me]^+$ cation (Scheme 2). The remaining signals are attributed to a non-C_s symmetrical κ^4-L^4 ligand (to which the $AlMe_3$ is coordinated) on the NMR timescale. This is indicated by, for example, the presence of two septets and four independent doublets for the chemically distinct ring isopropyl methine and methyl groups, respectively. The lower NMR symmetry of the pendant arm ligand in $[Al(\kappa^4\text{-}L^4\cdot AlMe_3)Me]^+$ is consistent with the proposed structure in Scheme 2, since flexing of the $CH_2CH(Me)O(AlMe_3)$ pendant arm would not, in this case, be expected to exchange the ring H and C atoms.

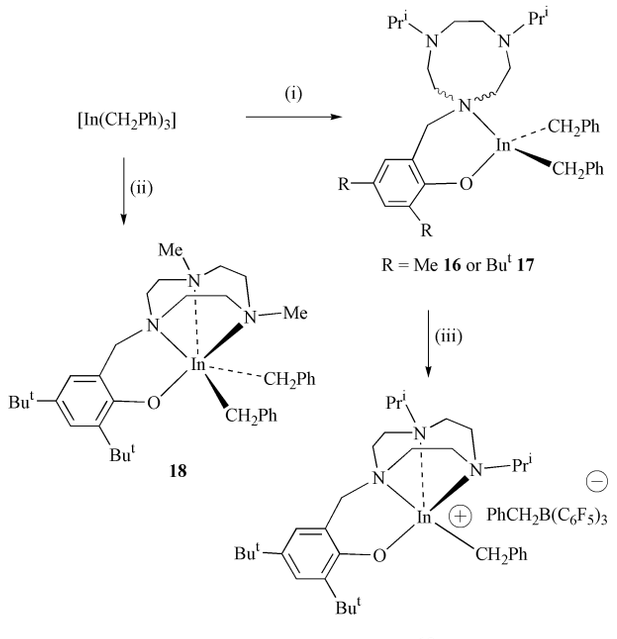
We have investigated the NMR tube scale reactions of $[Al(\kappa^4\text{-}L^2)Me][MeB(C_6F_5)_3]$ **13** and $[Al(\kappa^4\text{-}L^4\cdot AlMe_3)Me][MeB(C_6F_5)_3]$ **14** towards the following representative range of substrates: benzophenone, acetone, propylene oxide, ethene, $Me_3SiC{\equiv}CH$, $PhC{\equiv}CH$, pyridine and MeCN. Compound **13** is unreactive towards any of them, and **14** does not react with benzophenone or $RC{\equiv}CH$. Reaction of **14** with pyridine and MeCN affords $AlMe_3\cdot L$ (L = py or MeCN)[16,17] and a new complex tentatively identified as $\{[Al(\kappa^4\text{-}L^4)Me][MeB(C_6F_5)_3]\}$ **15**. Repeated attempts to isolate analytically pure samples of **15** on a preparative scale were unsuccessful and it has been characterised by ^{1}H NMR spectroscopy only. The B*Me* resonance of the $[MeB(C_6F_5)_3]^-$ appears at δ 0.47 indicating that the anion does not interact significantly with $[Al(\kappa^4\text{-}L^4)Me]^+$ in solution. The cation shows a single Al*Me* resonance (intensity 3 H) at δ −0.72 which is shifted somewhat upfield from the corresponding signal (δ −0.32) of $[Al(\kappa^4\text{-}L^4\cdot AlMe_3)Me]^+$. The κ^4-L^4 resonances are sharp at room temperature and reveal a non-C_s symmetrical environment. Thus the two isopropyl groups give rise to two septets (overlapping) and four distinct doublets for the methine and methyl groups, respectively. There are no macrocyclic ring methylene resonances at shifts higher than δ 3.3 consistent with the κ^4-coordination mode illustrated in Scheme 2. Addition of pyridine or MeCN to samples of **15** gives no adduct formation (*i.e.* only signals for free pyridine or MeCN and $[Al(\kappa^4\text{-}L^4)Me]^+$ are observed). This behaviour is analogous to that of **13**.

Apart from the reactions with pyridine and MeCN, compound **14** also undergoes reactions with acetone and propylene oxide. However, in both instances the disappearance of signals for the $[Al(\kappa^4\text{-}L^4\cdot AlMe_3)Me]^+$ cation of **14** is accompanied by the appearance of signals for the $[Al(\kappa^4\text{-}L^4)Me]^+$ cation of **15**. These do not change further with time or excess reagent. It is proposed that only the $AlMe_3$ fragment of the $[Al(\kappa^4\text{-}L^4\cdot AlMe_3)Me]^+$ cation undergoes reactions with added substrates, while the "core" $[Al(\kappa^4\text{-}L^4)Me]^+$ cation (like its aryl oxide analogue, $[Al(\kappa^4\text{-}L^2)Me]^+$) is unreactive. The absence of any reactivity associated with the cationic centres in **13** to **15** demonstrates the very effective shielding provided by the κ^4-$L^{2,4}$ ligands.

Neutral and cationic complexes of indium

A number of indium complexes of non-pendant arm or tris(pendant arm) triazacyclononanes have been reported previously,[6,8,9,54] but no organometallic derivatives of these ligands have been described. In very recent work,[55] we have prepared and structurally characterised the mono-pendant arm triazacyclononane complex $[In(\kappa^4\text{-}L^2)Cl_2]$. Reactions of this with alkylating reagents are unsuccessful and so we sought other routes to dialkyl complexes with a view to preparing the corresponding cations. Organoindium cations are comparatively rare.[42,56] The syntheses and proposed structures of the new neutral and cationic indium complexes are shown in Scheme 3.

Reaction of HL^1 **1** or HL^2 **2** with $In(CH_2Ph)_3$ in benzene at room temperature for 24 h affords the four-coordinate



Scheme 3 Reagents and conditions: (i) HL^1 or HL^2, benzene, rt, 24 h, 73 (**16**) or 71% (**17**); (ii) HL^3, benzene, 16 h, 78%; (iii) $B(C_6F_5)_3$, benzene, rt, 3 h, 78%.

compounds $[In(\kappa^2\text{-}L^1)(CH_2Ph)_2]$ **16** and $[In(\kappa^2\text{-}L^2)(CH_2Ph)_2]$ **17** as white, semi-crystalline solids in *ca*. 70% yield. These compounds are fluxional in solution at room temperature. On cooling the samples to 248 K in toluene-d_8 the spectra sharpen to resemble those of the crystallographically characterised, four-coordinate aluminium homologue $[Al(\kappa^2\text{-}L^2)Me_2]$ **10** (Scheme 1). When the reaction between HL^1 and $In(CH_2Ph)_3$ was monitored by ^{1}H NMR in benzene-d_6 there was no evidence of formation of a di-substituted complex of the type $[In(\kappa^2\text{-}L^1)_2(CH_2Ph)]$ analogous to $[Al(\kappa^2\text{-}L^1)_2Me]$ **11**. Possibly the larger benzyl substituent in **16** prevents formation of a five-coordinate complex $[In(\kappa^2\text{-}L^1)_2(CH_2Ph)]$.

Although reaction of $AlMe_3$ with HL^3 gave a complex mixture of products (see above), the corresponding reaction with $In(CH_2Ph)_3$ afforded the six-coordinate derivative $[In(\kappa^4\text{-}L^3)(CH_2Ph)_2]$ **18** in 78% yield. The κ^4-coordination mode proposed for L^3 in **18** is supported by the NMR spectra which are sharp at room temperature. The ^{1}H NMR spectra show two inequivalent triazacyclononane ring NMe resonances, and no ring methylene signals are observed at δ values greater than *ca*. 2.4. The low temperature ^{1}H NMR spectra of the fluxional four-coordinate homologues **16** and **17** both show ring methylene signals at δ values greater than 4.0 (as is the case for the aluminium complexes **7**–**12**). In addition, the NMR spectra of **18** are very similar to those of the crystallographically characterised, six-coordinate dichloride complex $[In(\kappa^4\text{-}L^2)Cl_2]$.[55] That the ring NPr^i substituted homologues **16** and **17** possess κ^2-bound ligands whereas **18** possesses a κ^4-bound one can be attributed to the reduced steric crowding achieved on changing from L^1 or L^2 to L^3.

Organoindium cations are comparatively rare,[42,56] and it was of interest to see whether one of the compounds **16**–**18** could be used to generate a new example. Thus reaction of $[In(\kappa^2\text{-}L^2)(CH_2Ph)_2]$ **17** with $B(C_6F_5)_3$ in benzene gave $[In(\kappa^4\text{-}L^2)(CH_2Ph)][(PhCH_2)B(C_6F_5)_3]$ **19** as a white solid in 78% yield. There is no NMR evidence for any interaction between the $[(PhCH_2)B(C_6F_5)_3]^-$ anion[57,58] and the cation $[In(\kappa^4\text{-}L^2)(CH_2Ph)]^+$ which is proposed to possess a κ^4 coordinated L^2 ligand on the basis of its NMR data and by analogy with the aluminium derivatives **13**–**15** (Scheme 2). As for the compounds **13**–**15** the cation $[In(\kappa^4\text{-}L^2)(CH_2Ph)]^+$ is unreactive to all potential nucleophiles and reagents examined.

Conclusion

We have described the first neutral and organometallic monopendant arm triazacyclononane complexes of aluminium and indium. All of the neutral aluminium complexes, and two of the indium derivatives, feature an unprecedented κ^2 coordination mode for the ligands, with the macrocycle being bound to the metal through one nitrogen only. Reaction of certain aluminium and indium dialkyl complexes with $B(C_6F_5)_3$ gives monoalkyl, cationic derivatives, all of which possess κ^4-coordinated L^1 or L^2 ligands. These complexes are unreactive at the cationic metal centres.

Acknowledgements

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