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FULL PAPER

# New main-group and early transition-metal complexes of mono-pendant arm triazacyclononane ligands

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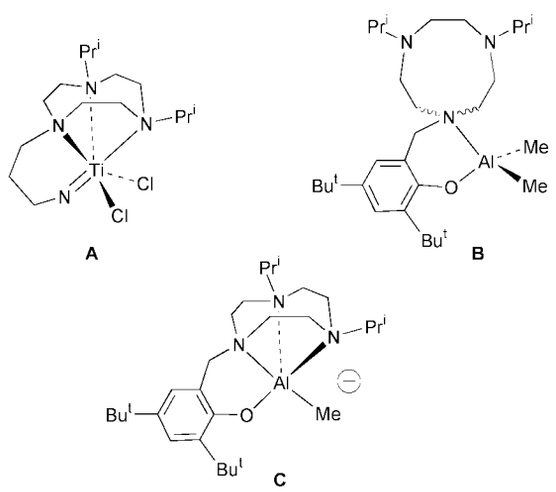
A family of new Group 3, Group 13 and early transition metal complexes of the previously described monoanionic, pendant arm macrocyclic ligands $L^a$, $L^b$ and $L^c$ are described where $HL^a$ = (3,5-dimethyl-2-hydroxybenzyl)-4,7-diisopropyl-1,4,7-triazacyclononane **1a**, $HL^b$ = (3,5-di-*tert*-butyl-2-hydroxybenzyl)-4,7-diisopropyl-1,4,7-triazacyclononane **1b**, and $HL^c$ = (3,5-di-*tert*-butyl-2-hydroxybenzyl)-4,7-dimethyl-1,4,7-triazacyclononane **1c**. The ligand precusors **1a**–**c** are quantitatively converted to the corresponding new potassium salts $KL^a$, $KL^b$ and $KL^c$ **2a**–**c** by reaction with potassium hydride in tetrahydrofuran (THF). An improved synthesis of $HL^c$ **1c** is also reported. Reaction of $KL^{a–c}$ with Group 13 metal salts $MCl_3$ (M = Al, Ga or In) gives monomeric derivatives $[M(\kappa^4\text{-}L^{a–c})Cl_2]$ **3**–**5** in good yields. The crystal structure of $[In(\kappa^4\text{-}L^b)Cl_2]$ **5b** has been determined and confirms the six-coordinate, *cis*-dichloride structures proposed for these complexes. Reaction of $KL^{a–c}$ with $TlCl_3$ gives the asymmetric, binuclear analogues $[Tl(\kappa^4\text{-}L^{a–c})Cl_2]_2$ **6a**–**c**. Reaction of $[Al(\kappa^4\text{-}L^c)Cl_2]$ **3c** with $AlCl_3$ gives the unstable, five-coordinate cation $[Al(\kappa^4\text{-}L^c)Cl]^+$ as its $AlCl_4^-$ salt **8c**. Reaction of $KL^{a–c}$ with $MCl_3$ (M = Sc or Y) or $[MCl_3(THF)_3]$ (M = Ti, V, Cr) in THF gives generally good yields of the Group 3 *cis*-dichloride derivatives $[M(\kappa^4\text{-}L^{1a–c})Cl_2]$ (M = Sc **8a**–**c** or Y **9b**,**c**) and the early transition metal analogues $[M(\kappa^4\text{-}L^{b,c})Cl_2]$ (M = Ti **10b**,**c**, V **11b**,**c** or Cr **12b**,**c**). Reaction of $HL^{1a–c}$ with TlOEt yields the monomeric, four-coordinate thallium(I) derivatives $[Tl(\kappa^4\text{-}L^{1a–c})]$ **13a**–**c** as confirmed by the X-ray crystal structures of **13b** and **13c**.

## Introduction

The 1,4,7-triazacyclononane ligands $R_3[9]aneN_3$ (R typically = H, 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 that this presents in, for example the synthesis of models of biologically relevant molecules or the design of ligands with high metal ion selectivity. The majority of work to date has focussed on symmetrically tri-N-functionalised triazacyclononanes (with or without pendant donor arms). Studies of triazacyclononanes functionalised with only one pendant arm have not been as extensive and have mostly concentrated on the mid- to late-transition metals, for example in the context of the modelling of metalla-enzymes.[1,4]

In recent reports,[5,6] we have started to exploit mono-pendant arm functionalised triazacyclononane ligands for the development of new main group and early transition metal catalytic and organometallic chemistry. These potentially tetradentate ligand sets provide a well defined steric and electronic environment at the metal centre around which new chemistry can be built up. Thus the titanium imido–triazacyclononane derivative **A** is a novel isolobal analogue of the Group 4 bis(cyclopentadienyl) complexes $[M(\eta\text{-}C_5R_5)_2X_2]$.[5] These, in turn, comprise an important class of polymerisation catalyst and stoichiometric reagent.[7] The aluminium complex **B** provided the first example of a triazacyclononane ring binding through only one N atom;[6] abstraction of a $CH_3^-$ anion from **B** gave the first cationic organometallic Group 13 triazacyclononane complex **C**.




The compounds **A**–**C** suggest that there exists an extensive range of chemistry to be accessed through such ligand sets. We have therefore set out to establish a class of main group and representative early transition metal complexes of the type **D** that incorporate monoanionic phenolato pendant arm macrocycles. The target complexes are electronic and structural relatives of the side-chain functionalised cyclopentadienyl ligands shown in **E** which are well established for the main group, lanthanide and transition metals, and support a rich and diverse chemistry.[8] The compounds **D** are ideal starting points because chloride ligands can generally be substituted by a range of other groups depending on the desired application. To date, however, only one structurally authenticated report of any compound of the type $[M(L)Cl_2]$ (L = anionic mono-pendant

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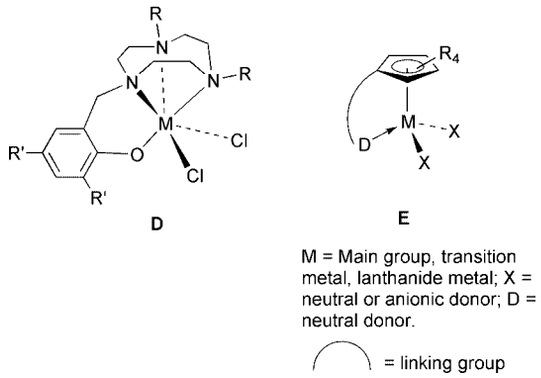



arm triazacyclononane) has appeared, namely [Fe{1-OC(O)-$CH_2$–[9]ane$N_3$}$Cl_2$].[9]

## Experimental

### General methods and instrumentation

All manipulations of air- and/or moisture-sensitive compounds were carried out under an atmosphere of dinitrogen or argon using standard 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 room temp. ($CD_2Cl_2$) or molten potassium ($C_6D_6$), 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.

$^1$H and $^{13}$C NMR spectra were recorded on Varian Unity Plus 500 or Varian Mercury Vx300 spectrometers and referenced internally to residual protio-solvent ($^1$H) or solvent ($^{13}$C) resonances. Chemical shifts are reported relative to tetramethylsilane ($\delta = 0$) in $\delta$ (ppm) and coupling constants in Hz. 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.

### Literature preparations

The compounds 1,4-dimethyl-1,4,7-triazacyclononane,[10] 1-(3,5-dimethyl-2-hydroxybenzyl)-4,7-diisopropyl-1,4,7-triazacyclononane (HL$^a$) **1a**,[11] 1-(3,5-di-*tert*-butyl-2-hydroxybenzyl)-4,7-diisopropyl-1,4,7-triazacyclononane (HL$^b$) **1b**[11] and [$MCl_3$-$(THF)_3$][12] (M = Ti, V, Cr) were prepared according to literature methods. $TlCl_3$ was purchased from Sigma–Aldrich and dried *in vacuo* for 4 d prior to use. All other reagents were purchased commercially and used as received. The synthesis of 1-(3,5-*di*-*tert*-butyl-2-hydroxybenzyl)-4,7-dimethyl-1,4,7-triazacyclononane HL$^c$ **1c** has been previously reported.[13] However analytical data were not obtained on the compound which was isolated as a yellow–brown oil. We report here an alternative, high-yielding synthesis.

### 1-(3,5-Di-*tert*-butyl-2-hydroxybenzyl)-4,7-dimethyl-1,4,7-triazacyclononane (HL$^c$, 1c)

1,4-Dimethyl-1,4,7-triazacyclononane (1.2 g, 7.6 mmol) was transferred into a two-necked flask equipped with a reflux condenser and dissolved in methanol (20 cm$^3$). Formaldehyde (0.75 g, 40% w/v solution) was added and the solution brought to reflux with stirring for 2 h. The reaction was then allowed to cool slightly and a methanol (10 cm$^3$) solution of 1,4-di-*tert*-butylphenol (1.73 g, 8.4 mmol) was added. The resulting mixture was brought to reflux and stirred for 14 h. The reaction was cooled to room temp. and distilled water (5 cm$^3$) was added resulting in the formation of an oily precipitate. The solution was decanted and the oil was dissolved in diethyl ether (15 cm$^3$). This solution was washed with aqueous NaOH (3 M, 30 cm$^3$) and dried over anhydrous magnesium sulfate. The product was isolated by filtration and evaporated to dryness under reduced pressure affording a cloudy white oil. The oil crystallised on standing to give a white solid. Yield: 2.29 g, 80%.

**Data for 1c**. $^1$H NMR ($C_6C_6$, 300 MHz, 298 K): $\delta$ 11.62 (br s, 1H, *H*O$C_6H_2$), 7.53 (s, 1H, $C_6H_2Bu^t_2$), 6.94 (s, 1H, $C_6H_2Bu^t_2$), 3.61 (s, 2H, NC$H_2$Ar), 2.72 (m, 4H, $NCH_2CH_2N$), 2.47 (m, 4H, $N(CH_2CH_2N)$, 2.28 (s, 4H, $NCH_2CH_2N$), 2.17 (s, 6H, NMe), 1.73 (s, 9H, $C_6H_2Bu^t_2$), 1.38 (s, 9H, $C_6H_2Bu^t_2$). $^{13}$C-{$^1$H} NMR ($C_6D_6$, 300 MHz, 298 K): $\delta$ 155.6 (2-$C_6H_2Bu^t_2$), 140.2 and 136.0 (1-$C_6H_2Bu^t_2$ and 3-$C_6H_2Bu^t_2$), 123.4 and 122.7 (4-$C_6H_2Bu^t_2$ and 6-$C_6H_2Bu^t_2$), 122.4 (5-$C_6H_2Bu^t_2$), 62.2 (N$C$H$_2$Ar), 58.8, 58.6 and 53.5 ($NCH_2CH_2N$), 46.4 (NMe), 35.3 and 34.2 ($C$Me$_3$), 31.9 and 30.0 (C$Me_3$). CI-MS: *m*/*z* 376 [M + H]$^+$. Anal. Found (calc. for $C_{23}H_{41}N_3O$): C, 72.8 (73.5); H, 10.5 (11.0); N, 10.6 (11.2)%.

### Preparation of the potassium salts KL$^a$ (2a), KL$^b$ (2b) and KL$^c$ (2c)

A typical preparation is as follows. A solution of HL$^c$ **1c** (0.94 g, 2.5 mmol) in THF (40 cm$^3$) was added to potassium hydride (0.41 g, 10 mmol) in THF (30 cm$^3$) at −30 °C and allowed to warm to room temp. overnight. Once filtered and evaporated to dryness the product was collected as an off-white solid and used without further purification. Yield of **2c**: 0.90 g (87%). The compounds KL$^a$ **2a** (yield: 93%) and KL$^b$ **2b** (yield: 98%) were prepared similarly.

**$^1$H NMR data.** For **2a** ($C_6D_6$, 300 MHz, 298 K): $\delta$ 7.25 (s, 1H, $C_6H_2$), 7.07 (s, 1H, $C_6H_2$), 4.8–4.0 (br m, 2H, N$CH_2C_6H_2$), 3.0–1.8 (br m, 20H, $N(CH_2)_2N$, *Me*$C_6H_2$ and $Me_2CH$), 0.72 (br s, 12H, $Me_2$CH).

For **2b** ($C_6D_6$, 500 MHz, 298 K): $\delta$ 7.52 (s, 1H, $C_6H_2$), 7.28 (s, 1H, $C_6H_2$), 4.51 (br s, 2H, N$CH_2C_6H_2$), 3.09 (br s, 2H, $Me_2CH$), 2.9–1.8 (br m, 12H, $N(CH_2)_2N$), 1.74 (s, 9H, Bu$^t$), 1.49 (s, 9H, Bu$^t$), 1.0–0.4 (s, 12H, $Me_2$CH).

For **2c** ($C_6D_6$, 300 MHz, 298 K): $\delta$ 7.53 (s, 1H, $C_6H_2$), 7.23 (s, 1H, $C_6H_2$), 4.7–4.2 (br m, 2H, N$CH_2C_6H_2$), 3.3–3.1 (br m, 2H, $Me_2CH$), 2.8–2.1 (br m, 4H, $N(CH_2)_2N$), 2.1–2.6 (br m, 14H, $N(CH_2)_2N$ and MeN), 1.75 (s, 9H, Bu$^t$), 1.52 (s, 9H, Bu$^t$).

### [Al(κ$^4$-L$^c$)$Cl_2$] 3c

$AlCl_3$ (0.24 g, 1.8 mmol) was dissolved in THF (30 cm$^3$) and stirred for the dropwise addition of KL$^c$ (0.76 g, 1.8 mmol) in THF (20 cm$^3$). After 2 h a white precipitate formed, stirring was continued for a further 14 h. The solid was isolated by filtration and dried *in vacuo*. The product was then extracted into dichloromethane (30 cm$^3$), filtered and dried under reduced pressure affording **3c** as a white solid. Yield: 0.27 g (31%).

Data for **3c**. $^1$H NMR ($CD_2Cl_2$, 125.7 MHz, 298 K): $\delta$ 7.20 (d, $J = 2.5$, 1H, $C_6H_2Bu^t$), 6.73 (d, $J = 2.5$, 1H, $C_6H_2Bu^t$), 5.05 (d, $J = 13.5$, 1H, C$H_2$Ar), 3.55 (d, $J = 13.5$ Hz, 1H, C$H_2$Ar), 3.40 (m, 1H, N$CH_2CH_2N$), 3.30 (m, 1H, $NCH_2CH_2N$), 3.20 (m, 3H, $NCH_2CH_2N$), 2.98 (s, 3H, NMe), 2.87 (s, 3H, NMe), 2.85–2.60 (m, 7H, $NCH_2CH_2N$), 1.40 (s, 9H, $CMe_3$), 1.24 (s, 9H, $CMe_3$). $^{13}$C-{$^1$H} NMR ($CD_2Cl_2$, 500 MHz, 298 K): $\delta$ 157.0 (2-$C_6H_2Bu^t$), 139.3 and 137.7 (1-$C_6H_2$ and 3-$C_6H_2$), 123.4 and 123.3 (4-$C_6H_2$ and 6-$C_6H_2$), 119.7 (5-$C_6H_2$), 66.0 (N$C$H$_2$Ar), 57.4, 56.6, 56.4, 54.6 and 53.8 ($NCH_2CH_2N$), 50.5 and 49.9 (NMe), 35.4, 34.2 (2 × $C$Me$_3$), 31.8, 30.4 (2 × C$Me_3$). $^{27}$Al NMR ($CD_2Cl_2$, 78.19 MHz, 298 K): $\delta$ 30.0 (br s). EI-MS: *m*/*z* = 471 [M]$^+$, 456 [M − Me]$^+$, 456 [M − Cl]$^+$, 420 [M − Cl − Me]$^+$,

407 [M − 2Me − Cl]$^+$. Anal. Found (calc. for $C_{23}H_{40}AlCl_2N_3O$): C, 57.5 (58.5); H, 8.8 (8.6); N, 8.4 (8.9)%.

### NMR-tube scale synthesis of {[Al(κ$^4$-L$^c$)Cl][AlCl$_4$]} 7c

Compound **3c** (0.01 g, 0.021 mmol) was dissolved in $CD_2Cl_2$ (500 μl) and transferred into a Young's NMR tube. $AlCl_3$ (0.028 g, 0.021 mmol) was then added to this solution and the mixture was vigorously shaken until no solid $AlCl_3$ remained. The product was characterised immediately by $^1$H and $^{27}$Al NMR spectroscopy. The product decomposes completely in solution over 2 d and also on removal of the volatiles under reduced pressure.

Data for **7c**. $^1$H NMR ($CD_2Cl_2$, 125.7 MHz, 298 K): $\delta$ 7.32 (br s, 1H, $C_6H_2$), 6.85 (br s, 1H, $C_6H_2$), 4.23 (br s, 2H, C$H_2$Ar), 3.5–3.0 (br m, 12H, $NCH_2CH_2N$), 2.86 (s br, 6H, NMe), 1.43 (s br, 9H, Bu$^t$), 1.29 (s br, 9H, Bu$^t$). $^{27}$Al NMR ($CD_2Cl_2$, 78.19 MHz, 298 K): $\delta$ 102.2 (s, $AlCl_4$), 45.3 (br s, Al(κ$^4$-L$^c$)Cl).

### NMR-tube scale synthesis of {[CPh$_3$][AlCl$_4$]}

$Ph_3CCl$ (0.010 g, 0.036 mmol) was dissolved in $CD_2Cl_2$ (500 μl) and transferred into a Young's NMR tube. Aluminium trichloride (0.048 g, 0.036 mmol) was added to the colourless solution and the mixture was shaken. The resulting yellow–green solution was analysed by $^{27}$Al NMR spectroscopy. $^{27}$Al NMR ($CD_2Cl_2$, 78.19 MHz, 298 K): $\delta$ 102.0 (s, $AlCl_4$).

### [Ga(κ$^4$-L$^a$)Cl$_2$] (4a)

$GaCl_3$ (0.19 g, 1.1 mmol) was dissolved in benzene (10 cm$^3$) and stirred for the dropwise addition of KL$^a$ (0.35 g, 1.0 mmol) in benzene (10 cm$^3$). The mixture was stirred at room temp. for 16 h. The volatiles were removed under reduced pressure and the residue was extracted with $CH_2Cl_2$ (30 cm$^3$). Dichloromethane was removed under reduced pressure, the residue was washed with benzene (15 cm$^3$) and dried *in vacuo* to give the product as a white solid. Yield: 0.30 g (61%).

Data for **4a**. $^1$H NMR ($CDCl_3$, 300 MHz, 298 K): $\delta$ 6.92 (s, 1H, $C_6H_2$), 6.60 (s, 1H, $C_6H_2$), 4.12 (s, 2H, $NCH_2C_6H_2$), 4.04 (sept, $J$ = 6.2, 2H, $Me_2CH$), 3.45 (m, 4H, $N(CH_2)_2N$), 3.27 (m, 4H, $N(CH_2)_2N$), 3.15 (m, 2H, $N(CH_2)_2N$), 2.88 (m, 2H, $N(CH_2)_2N$), 2.18 (s, 3H, $C_6H_2Me_2$), 2.16 (s, 3H, $C_6H_2Me_2$), 1.22 (m, 12 H, $Me_2CH$). EI-MS: *m*/*z* 487 [M]$^+$. Anal. Found (calc. for $C_{21}H_{36}Cl_2GaN_3O$): C, 54.6 (51.8); H, 6.7 (7.4); Cl, 12.3 (14.5); N, 7.6 (8.6)%. A satisfactory elemental analysis could not be obtained by recrystallisation.

### [Ga(κ$^4$-L$^b$)Cl$_2$] 4b

$GaCl_3$ (0.26 g, 1.5 mmol) was dissolved in benzene (25 cm$^3$) and stirred for the dropwise addition of KL$^b$ (0.70 g, 1.5 mmol) in benzene (25 cm$^3$). The mixture was stirred at room temp. for 10 min, then the solution was filtered and allowed to react for a further 16 h. This resulted in the formation of a white precipitate which was isolated by filtration, washed with benzene (20 cm$^3$) and evaporated to dryness *in vacuo* to afford the product as a white solid. Yield: 0.51 g (60%).

Data for **4b**: $^1$H NMR ($CD_2Cl_2$, 500 MHz, 218 K): $\delta$ 7.08 (s, 1H, $C_6H_2$), 6.62 (s, 1H, $C_6H_2$), 5.03 (d, $J$ = 14.4, 1H, $NCH_2C_6H_2$), 4.21 (sept, $J$ = 6.2, 1H, $Me_2CH$), 4.14 (sept, $J$ = 6.2, 1H, $Me_2CH$), 3.67 (m, 1H, $N(CH_2)_2N$), 3.64 (d, $J$ = 14.4, 1H, $NCH_2C_6H_2$), 3.15 (m, 3H, $N(CH_2)_2N$), 3.01 (m, 2H, $N(CH_2)_2N$), 2.70 (m, 1H, $N(CH_2)_2N$), 2.58 (m, 2H, $N(CH_2)_2N$), 2.46 (m, 2H, $N(CH_2)_2N$), 1.58 (d, $J$ = 6.3, 3H, $Me_2CH$), 1.35 (d, $J$ = 6.3, 3H, $Me_2CH$), 1.29 (s, 9H, Bu$^t$), 1.61 (s, 9H, Bu$^t$), 1.03 (d, $J$ = 6.3, 3H, $Me_2CH$), 0.97 (d, $J$ = 6.3 Hz, 3H, $Me_2CH$). $^{13}$C-{$^1$H} NMR ($CD_2Cl_2$, 500 MHz, 218 K): $\delta$ 157.2 (2-$C_6H_2$), 138.5 and 135.9 (1-$C_6H_2$ and 3-$C_6H_2$), 122.9 and 122.6 (4-$C_6H_2$ and 6-$C_6H_2$), 117.2 (5-$C_6H_2$), 64.9 ($NCH_2C_6H_2$), 54.7, 54.3 ($Me_2CH$), 53.9, 52.2, 50.9, 49.5, 40.4, 39.3 ($N(CH_2)_2N$), 34.8, 33.4 (2 × $Me_3C$), 31.0, 29.6 (2 × $Me_3C$), 20.6, 20.3, 17.7, 16.1 ($Me_2CH$). EI-MS: *m*/*z* 571 [M]$^+$. Anal. Found (calc. for $C_{27}H_{48}Cl_2GaN_3O$): C, 56.7 (56.8); H, 8.3 (8.5); N, 7.0 (7.3); Cl, 12.1 (12.4)%.

### [Ga(κ$^4$-L$^c$)Cl$_2$] 4c

$GaCl_3$ (0.13 g, 0.76 mmol) was dissolved in benzene (20 cm$^3$) and stirred for the dropwise addition of KL$^c$ (0.3 g, 0.76 mmol) in benzene (25 cm$^3$). The mixture was stirred at room temp. for 2 h which led to formation of white precipitate. The solution was filtered and the precipitate washed with benzene (20 cm$^3$) and extracted with $CH_2Cl_2$ (15 cm$^3$). Insolubles were removed by filtration and the solvent was removed under reduced pressure to yield the product as a white solid. Yield: 0.27 g (72%).

Data for **4c**. $^1$H NMR ($CDCl_3$, 300 MHz, 298 K): $\delta$ 7.19 (s, 1H, $C_6H_2$), 6.67 (s, 1H, $C_6H_2$), 4.33 (br s, 2H, $NCH_2C_6H_2$), 3.28 (br s, 2H, $N(CH_2)_2N$), 3.13 (br s, 2H, $N(CH_2)_2N$), 2.92 (br s, 8H, $N(CH_2)_2N$), 2.86 (s, 6H, MeN), 1.41 (s, 9H, Bu$^t$), 1.23 (s, 9H, Bu$^t$). EI-MS: *m*/*z* 515.3 [M]$^+$, 500 [M − Me]$^+$, 478 [M − Cl]$^+$, 443 [M − 2Cl]$^+$. Anal. Found (calc. for $C_{23}H_{40}Cl_2GaN_3O$): C, 53.1 (53.6); H, 7.6 (7.8); N, 7.9 (8.2)%.

### [In(κ$^4$-L$^a$)Cl$_2$] 5a

$InCl_3$ (0.28 g, 1.28 mmol) was suspended in benzene (15 cm$^3$) and stirred for the dropwise addition of KL$^a$ (0.45 g, 1.17 mmol) in benzene (25 cm$^3$). The mixture was stirred at room temp. for 24 h in which time a white precipitate formed. The solid was isolated by filtration, washed with benzene (2 × 20 cm$^3$) and extracted with $CH_2Cl_2$ (30 cm$^3$). Dichloromethane was removed under reduced pressure yielding the product as a white solid. Yield: 0.31 g (50%).

Data for **5a**: $^1$H NMR ($CDCl_3$, 300 MHz, 298 K): $\delta$ 6.86 (s, 1H, $C_6H_2$), 6.53 (s, 1H, $C_6H_2$), 5.15 (d, $J$ = 12.6, 1H, $NCH_2C_6H_2$), 3.89 (sept, $J$ = 6.3, 1H, $Me_2CH$), 3.72 (sept, $J$ = 6.3, 1H, $Me_2CH$), 3.52 (m, 1H, $N(CH_2)_2N$), 3.34 (m, 2H, $N(CH_2)_2N$), 3.30 (d, $J$ = 12.6, 1H, $NCH_2C_6H_2$), 3.04 (m, 2H, $N(CH_2)_2N$), 2.83 (m, 2H, $N(CH_2)_2N$), 2.73 (m, 2H, $N(CH_2)_2N$), 2.53 (m, 2H, $N(CH_2)_2N$), 2.28 (m, 1H, $N(CH_2)_2N$), 2.16 (s, 3H, $C_6H_2Me_2$), 2.12 (s, 3H, $C_6H_2Me_2$), 1.60 (d, $J$ = 6.0, 3 H, $Me_2CH$), 1.44 (d, $J$ = 6.6, 3 H, $Me_2CH$), 1.22 (d, $J$ = 6.0, 3 H, $Me_2CH$), 1.04 (d, $J$ = 6.6 Hz, 3 H, $Me_2CH$). EI-MS: *m*/*z* 532 [M]$^+$. Anal. Found (calc. for $C_{21}H_{36}Cl_2InN_3O$): C, 45.0 (47.4); H, 6.4 (6.8); Cl, 14.5 (13.3); N, 7.3 (7.9)%. A satisfactory elemental analysis could not be obtained by recrystallisation.

### [In(κ$^4$-L$^b$)Cl$_2$] 5b

$InCl_3$ (0.17 g, 0.77 mmol) was suspended in benzene (12 cm$^3$) and stirred for the dropwise addition of KL$^b$ (0.40 g, 0.85 mmol) in benzene (25 cm$^3$). The mixture was stirred at room temp. for 48 h in which time a white precipitate formed. The solution was isolated by filtration, the precipitate was washed with benzene (2 × 25 cm$^3$) and extracted with $CH_2Cl_2$ (35 cm$^3$). The solution was filtered from the insolubles, the volatiles were removed under reduced pressure and the residue was dried *in vacuo* to afford the product as a white solid. Yield: 0.39 g (82%). Crystals of **5b**·3$CH_2Cl_2$ suitable for X-ray diffraction study were grown at room temp. from $CH_2Cl_2$.

Data for **5b**. $^1$H NMR ($CDCl_3$, 300 MHz, 298 K): $\delta$ 7.18 (s, 1H, $C_6H_2$), 6.59 (s, 1H, $C_6H_2$), 5.21 (d, $J$ = 14.0, 1H, $NCH_2C_6H_2$), 4.10 (sept, $J$ = 6.7, 1H, $Me_2CH$), 3.99 (sept, $J$ = 6.7, 1H, $Me_2CH$), 3.61 (m, 1H, $N(CH_2)_2N$), 3.48 (d, $J$ = 14.0, 1H, $NCH_2C_6H_2$), 3.33 (m, 1H, $N(CH_2)_2N$), 3.12 (m, 2H, $N(CH_2)_2N$), 2.94 (m, 3H, $N(CH_2)_2N$), 2.59 (m, 5H, $N(CH_2)_2N$), 1.59 (d, $J$ = 6.7, 3 H, $Me_2CH$), 1.39 (s, 9H, Bu$^t$), 1.38 (d, $J$ = 6.7, 3 H, $Me_2CH$), 1.19 (s, 9H, Bu$^t$), 1.07 (d, $J$ = 6.7, 3 H, $Me_2CH$), 1.05 (d, $J$ = 6.7 Hz, 3 H, $Me_2CH$). $^{13}$C-{$^1$H} NMR ($CDCl_3$, 500 MHz, 298K): $\delta$ 160.3 (2-$C_6H_2$), 139.4 and 135.5 (1-$C_6H_2$ and 3-$C_6H_2$), 124.1 and 123.7 (4-$C_6H_2$ and 6-$C_6H_2$), 117.0 (5-$C_6H_2$), 65.8 ($NCH_2C_6H_2$), 56.1, 56.0 ($Me_2CH$), 52.6, 51.8, 51.5, 50.2, 41.6,

41.4 ($N(CH_2)_2N$), 35.2, 33.8 (2 × $Me_3C$), 31.8, 30.3 (2 × $Me_3C$), 21.1, 21.0, 15.7, 15.6 ($Me_2CH$). EI-MS: *m/z* 615 $[M]^+$, 600 $[M - Me]^+$, 582 $[M - Cl]^+$. Anal. Found (calc. for $C_{27}H_{48}Cl_2InN_3O$): C, 52.6 (52.6); H, 7.9 (7.9); Cl, 13.1 (13.5); N, 6.6 (6.8)%.

### [In(κ⁴-L^c)Cl₂] 5c

$InCl_3$ (0.1 g, 0.46 mmol) was suspended in benzene (40 $cm^3$) and stirred for the dropwise addition of $KL^c$ (0.2 g, 0.48 mmol) in benzene (15 $cm^3$). The mixture was stirred at room temp. for 48 h in which time a white precipitate formed. The solution was removed by filtration, the residue was washed with benzene (2 × 25 $cm^3$) and extracted into $CH_2Cl_2$ (70 $cm^3$). The solution was filtered from insolubles and the solvent was removed under reduced pressure to yield the product as a white solid. Yield: 0.19 g (82%).

Data for **5c**. $^1H$ NMR ($CDCl_3$, 300 MHz, 298 K): $\delta$ 7.23 (s, 1H, $C_6H_2$), 6.72 (s, 1H, $C_6H_2$), 5.09 (d, $J$ = 12.7, 1H, $NCH_2C_6H_2$), 3.78 (m, 1H, $N(CH_2)_2N$), 3.49 (m, 1H, $N(CH_2)_2N$), 3.39 (d, $J$ = 12.7 Hz, 1H, $NCH_2C_6H_2$), 3.06 (m, 3H, $N(CH_2)_2N$), 2.94 (s, 3H, MeN), 2.88 (m, 2H, $N(CH_2)_2N$), 2.77 (s, 3H, MeN), 2.62 (m, 4H, $N(CH_2)_2N$), 2.35 (m, 1H, $N(CH_2)_2N$), 1.45 (s, 9H, $Bu^t$), 1.25 (s, 9H, $Bu^t$). $^{13}C$-{$^1H$} NMR ($CDCl_3$, 500 MHz, 298 K): $\delta$ 162.9 (2-$C_6H_2$), 138.4 and 136.0 (1-$C_6H_2$ and 3-$C_6H_2$), 125.8 and 124.2 (4-$C_6H_2$ and 6-$C_6H_2$), 118.7 (5-$C_6H_2$), 63.9 ($NCH_2C_6H_2$), 56.1, 54.1, 52.4, 51.5, 50.8, 48.4 ($N(CH_2)_2N$), 48.2, 47.3 (MeN), 35.4, 33.8 (2 × $Me_3C$), 31.8, 30.1 (2 × $Me_3C$). EI-MS: *m/z* 559 $[M]^+$, 544 $[M - Me]^+$, 524 $[M - Cl]^+$. Anal. Found (calc. for $C_{23}H_{40}Cl_2InN_3O$): C, 46.8 (49.3); H, 6.5 (7.2); N, 7.0 (7.5)%. A satisfactory elemental analysis could not be obtained upon recrystallisation.

### [Tl(κ⁴-L^a)] 13a

TlOEt (0.25 g, 1.0 mmol) and $HL^a$ (0.35 g, 1.0 mmol) were dissolved in benzene (40 $cm^3$) and the mixture was stirred at room temp. for 16 h. The volatiles were removed under reduced pressure to yield the product as a white solid. Yield: 0.41 g (75%).

Data for **13a**. $^1H$ NMR ($C_6D_6$, 300 MHz, 298 K): $\delta$ 7.27 (s, 1H, $C_6H_2$), 6.98 (s, 1H, $C_6H_2$), 4.01 (br s, 2H, $NCH_2C_6H_2$), 2.95 (br s, 4H, $Pr^iNCH_2CH_2NCH_2C_6H_2$), 2.69 (s, 3H, $C_6H_2Me_2$), 2.62 (sept, $J$ = 6.6, 2H, $Me_2CH$), 2.45 (s, 3H, $C_6H_2Me_2$), 2.31 (br s, 4H, $Pr^iNCH_2CH_2NCH_2C_6H_2$), 2.02 (s, 4H, $Pr^iN(CH_2)_2NPr^i$), 0.77 (d, $J$ = 6.5 Hz, 12 H, $Me_2CH$). EI-MS: *m/z* 551 $[M]^+$. Anal. Found (calc. for $C_{21}H_{36}N_3OTl$): C, 45.5 (45.8); H, 6.3 (6.6); N, 6.9 (7.6)%.

### [Tl(κ⁴-L^b)] 13b

TlOEt (0.25 g, 1.0 mmol) and $HL^b$ (0.43 g, 1.0 mmol) were dissolved in benzene (40 $cm^3$) and the mixture was stirred at room temp. for 16 h. The volatiles were removed under reduced pressure affording the product as a white solid. Yield: 0.56 g (88%). Crystals of **13b** suitable for X-ray diffraction study were grown at room temp. from hexanes.

Data for **13b**. $^1H$ NMR ($C_6D_6$, 300 MHz, 298 K): $\delta$ 7.74 (s, 1H, $C_6H_2$), 7.11 (s, 1H, $C_6H_2$), 3.54 (s, 2H, $NCH_2C_6H_2$), 2.65 (br s, 4H, $Pr^iNCH_2CH_2NCH_2C_6H_2$), 2.20 (m, 2H, $Me_2CH$), 1.99 (s, 9H, $Bu^t$), 1.96 (br s, 4H, $Pr^iNCH_2CH_2NCH_2C_6H_2$), 1.74 (br s, 4H, $Pr^iN(CH_2)_2NPr^i$), 1.51 (s, 9H, $Bu^t$), 0.64 (br s, 12 H, $Me_2CH$). EI-MS: *m/z* 635 $[M]^+$. Anal. Found (calc. for $C_{27}H_{48}N_3OTl$): C, 50.9 (51.1); H, 7.5 (7.6); N, 6.5 (6.6)%.

### [Tl(κ⁴-L^c)] 13c

TlOEt (0.25 g, 1.0 mmol) and $HL^c$ (0.38 g, 1.0 mmol) were dissolved in benzene (40 $cm^3$) and the mixture was stirred at room temp. for 16 h. The volatiles were removed under reduced pressure to give the product as a white solid. Yield: 0.47 g (81%). Crystals of **13c** suitable for X-ray diffraction study were grown at room temp. from hexanes.

Data for **13c**. $^1H$ NMR ($C_6D_6$, 300 MHz, 298 K): $\delta$ 7.76 (s, 1H, $C_6H_2$), 7.14 (s, 1H, $C_6H_2$), 3.53 (s, 2H, $NCH_2C_6H_2$), 2.57 (br s, 2H, $N(CH_2)_2N$), 2.02 (s, 9H, $Bu^t$), 1.96 (br s, 2H, $N(CH_2)_2N$), 1.89 (br s, 2H, $N(CH_2)_2N$), 1.74 (br m, 10H, 2 × MeN and $N(CH_2)_2N$), 1.65 (br s, 2H, $N(CH_2)_2N$), 1.55 (s, 9H, $Bu^t$). EI-MS: *m/z* 579 $[M]^+$. Anal. Found (calc. for $C_{23}H_{40}N_3OTl$): C, 47.6 (47.7); H, 6.4 (6.7); N, 7.0 (7.3)%.

### [Tl(κ⁴-L^a)Cl₂]₂ 6a

$TlCl_3$ (0.34 g, 1.1 mmol) was dissolved in THF (20 $cm^3$) and stirred for the dropwise addition of $KL^a$ (0.42 g, 1.1 mmol) in THF (20 $cm^3$) over a period of 3 h. The mixture was stirred at room temp. for 16 h. The solution was removed by filtration, the residue was washed with pentane (2 × 20 $cm^3$) and extracted with $CH_2Cl_2$ (200 $cm^3$). The volatiles were removed under reduced pressure to afford the product as an orange solid. Yield: 0.2 g (29%).

Data for **6a**. $^1H$ NMR ($CD_2Cl_2$, 300 MHz, 298 K): $\delta$ 7.05 (s, 1H, $C_6H_2$), 6.78 (s, 1H, $C_6H_2$), 6.63 (s, 1H, $C_6H_2$), 6.53 (s, 1H, $C_6H_2$), 5.51 (d, $J$ = 12.4, 1H, $NCH_2C_6H_2$), 4.77 (d, $J$ = 12.4, 1H, $NCH_2C_6H_2$), 3.92 (m, 2H, $Me_2CH$ and $NCH_2C_6H_2$), 3.70 (m, 2H, $Me_2CH$), 3.55 (m, 2H, $Me_2CH$ and $N(CH_2)_2N$), 3.35 (m, 3H, $N(CH_2)_2N$), 3.28–2.93 (m, 5H, $N(CH_2)_2N$), 2.84 (m, 1H, $N(CH_2)_2N$), 2.78–2.58 (m, 2H, $N(CH_2)_2N$), 2.66 (d, $J$ = 12.4 Hz, 1H, $NCH_2C_6H_2$), 2.53 (m, 2H, $N(CH_2)_2N$), 2.38 (m, 2H, $N(CH_2)_2N$), 2.31–1.86 (m, 7H, $N(CH_2)_2N$), 2.22 (s, 3H, $C_6H_2Me_2$), 2.10 (s, 3H, $C_6H_2Me_2$), 2.15 (s, 3H, $C_6H_2Me_2$), 2.06 (s, 3H, $C_6H_2Me_2$), 1.78 (m, 1H, $N(CH_2)_2N$), 1.54 (m, 6 H, $Me_2CH$), 1.34 (m, 6 H, $Me_2CH$), 1.21 (m, 6 H, $Me_2CH$), 1.02 (m, 6 H, $Me_2CH$). ES-MS: *m/z* 1244.0 $[M + H]^+$, 1206 $[M + H, - Cl]^+$, 623 $[\frac{1}{2}M + H]^+$, 586 $[\frac{1}{2}M - Cl]^+$. Anal. Found (calc. for $C_{42}H_{72}Cl_4N_6O_2Tl_2$): C, 40.3 (40.6); H, 5.4 (5.8); Cl, 11.3 (11.4); N, 6.4 (6.7)%.

### [Tl(κ⁴-L^b)Cl₂]₂ 6b

$TlCl_3$ (0.19 g, 0.6 mmol) was dissolved in THF (20 $cm^3$) and stirred for the dropwise addition of $KL^b$ (0.28 g, 0.6 mmol) in THF (20 $cm^3$) over a period of 2 h. The mixture was stirred at room temp. for 48 h. The solution was filtered from insolubles, the residue was washed with THF (2 × 35 $cm^3$) and the combined extracts were reduced in volume to 8 $cm^3$, which led to the formation of an orange precipitate. The precipitate was washed with pentane (20 $cm^3$) and dried *in vacuo* to give the product as a bright orange solid. Yield: 0.23 g (55%).

Data for **6b**. $^1H$ NMR ($CD_2Cl_2$, 300 MHz, 298 K): $\delta$ 7.38 (s, 1H, $C_6H_2$), 7.09 (s, 1H, $C_6H_2$), 6.74 (s, 1H, $C_6H_2$), 6.63 (s, 1H, $C_6H_2$), 5.34 (d, $J$ = 13.5, 1H, $NCH_2C_6H_2$), 4.99 (d, $J$ = 13.5, 1H, $NCH_2C_6H_2$), 4.14 (sept, $J$ = 6.6, 1H, $Me_2CH$), 4.01 (d, $J$ = 13.5, 1H, $NCH_2C_6H_2$), 3.85–3.99 (m, 2H, $Me_2CH$), 3.73 (sept, $J$ = 6.6 Hz, 1H, $Me_2CH$), 3.21–3.66 (m, 10H, $N(CH_2)_2N$), 3.10 (m, 1H, $N(CH_2)_2N$), 2.59–3.01 (m, 9H, $N(CH_2)_2N$ + $NCH_2C_6H_2$), 2.42 (m, 2H, $N(CH_2)_2N$), 2.25 (m, 1H, $N(CH_2)_2N$), 1.94 (m, 1H, $N(CH_2)_2N$), 1.80 (m, 1H, $N(CH_2)_2N$), 1.58 (m, 6 H, $Me_2CH$), 1.41 (s, 9H, $Bu^t$), 1.40 (s, 9H, $Bu^t$), 1.38 (m, 6 H, $Me_2CH$), 1.27 (s, 18H, $Bu^t$), 1.10–1.20 (m, 12 H, $Me_2CH$). ES-MS: *m/z* 1413 $[M + H]^+$, 1376 $[M - Cl]^+$, 706 $[\frac{1}{2}M + H]^+$, 671 $[\frac{1}{2}M - Cl]^+$. Anal. Found (calc. for $C_{54}H_{96}Cl_4N_6O_2Tl_2$): C, 46.0 (45.9); H, 6.9 (6.8); N, 6.0 (6.0)%.

### [Tl(κ⁴-L^c)Cl₂]₂ (6c)

$TlCl_3$ (0.23 g, 0.73 mmol) was dissolved in THF (15 $cm^3$) and stirred for the dropwise addition of $KL^c$ (0.30 g, 0.73 mmol) in THF (15 $cm^3$) over a period of 3 h. The mixture was stirred at room temp. for 72 h. The supernatant was filtered from insolubles, the residue was washed with THF (120 $cm^3$), and the combined extracts were reduced in volume to 10 $cm^3$, which led

to formation of an orange precipitate. The precipitate was washed with pentane (2 × 20 $cm^3$) and dried *in vacuo* to yield the product as an yellow–orange solid. Yield 0.30 g (60%).

Data for **6c**. $^1$H NMR ($CD_2Cl_2$, 300 MHz, 298 K): $\delta$ 7.25 (s, 1H, $C_6H_2$), 6.93 (s, 1H, $C_6H_2$), 4.55 (d, $J$ = 12.8, 1H, NC$H_2$-$C_6H_2$), 3.81 (m, 1H, $N(CH_2)_2N$), 3.59 (m, 1H, $N(CH_2)_2N$), 3.39 (d, $J$ = 12.8 Hz, 1H, NC$H_2C_6H_2$), 3.19 (m, 1H, $N(CH_2)_2N$), 3.07 (m, 1H, $N(H_2)_2N$), 2.98 (s, 3H, MeN), 2.82 (m, 3H, $N(CH_2)_2N$), 2.69 (s, 3H, MeN), 2.60 (m, 3H, $N(CH_2)_2N$), 2.39 (m, 1H, $N(CH_2)_2N$), 2.23 (m, 1H, $N(CH_2)_2N$), 1.44 (s, 9H, Bu$^t$), 1.26 (s, 9H, Bu$^t$). ES-MS: *m*/*z* 1298 $[M + H]^+$, 1263 $[M - Cl]^+$, 650 $[\frac{1}{2} M + H]^+$, 614 $[\frac{1}{2} M - Cl]^+$. Anal. Found (calc. for $C_{46}H_{80}Cl_4N_6O_2Tl_2$): C, 42.7 (42.5); H, 6.4 (6.2); N, 6.0 (6.5)%.

### [Sc(κ$^4$-L$^a$)Cl$_2$] 8a

$ScCl_3$ (0.2 g, 1.3 mmol) was refluxed in THF (30 $cm^3$) for 25 min. The solution was allowed to cool and was then stirred for the dropwise addition of KL$^a$ (0.50 g, 1.3 mmol) in THF (25 $cm^3$) over a period of 2 h. The mixture was stirred at room temp. for 16 h in which time a white precipitate formed. The supernatant was removed by filtration, the residue was washed with pentane (25 $cm^3$) and extracted with $CH_2Cl_2$ (70 $cm^3$). Dichloromethane was removed under reduced pressure to give the product as a white solid. Yield: 0.36 g (59%).

Data for **8a**. $^1$H NMR ($CD_2Cl_2$, 300 MHz, 298 K): $\delta$ 6.89 (s, 1H, $C_6H_2$), 6.66 (s, 1H, $C_6H_2$), 4.86 (d, $J$ = 13.3, 1H, NC$H_2$-$C_6H_2$), 3.94 (sept, $J$ = 6.7, 1H, $Me_2CH$), 3.82 (sept, $J$ = 6.7, 1H, $Me_2CH$), 3.44 (m, 1H, $N(CH_2)_2N$), 3.28 (m, 3H, $N(CH_2)_2N$- + $NCH_2C_6H_2$), 3.08 (m, 1H, $N(CH_2)_2N$), 2.95 (m, 1H, $N(CH_2)_2N$), 2.86 (m, 1H, $N(CH_2)_2N$), 2.80 (m, 2H, $N(CH_2)_2N$), 2.64 (m, 2H, $N(CH_2)_2N$), 2.50 (m, 1H, $N(CH_2)_2N$), 2.41 (m, 1H, $N(CH_2)_2N$), 2.16 (s, 3H, $C_6H_2Me_2$), 2.11 (s, 3H, $C_6H_2Me_2$), 1.60 (d, $J$ = 6.0, 3 H, $Me_2CH$), 1.39 (d, $J$ = 6.6, 3 H, $Me_2CH$), 1.14 (d, $J$ = 6.0, 3 H, $Me_2CH$), 0.97 (d, $J$ = 6.6 Hz, 3 H, $Me_2CH$). EI-MS: *m*/*z* 461 $[M]^+$, 426 $[M - Cl]^+$. Anal. Found (calc. for $C_{21}H_{36}ScCl_2N_3O$): C, 54.1 (54.5); H, 7.80 (7.8); N, 9.0 (9.1)%.

### [Sc(κ$^4$-L$^b$)Cl$_2$] 8b

$ScCl_3$ (0.2 g, 1.3 mmol) was refluxed in THF (40 $cm^3$) for 25 min. The solution was allowed to cool and was then stirred for the dropwise addition of KL$^b$ (0.61 g, 1.3 mmol) in THF (25 $cm^3$) over a period of 2 h. The mixture was stirred at room temp. for 24 h, then the solution was filtered from insolubles and the volatiles removed under reduced pressure. The residue was washed with pentane (25 $cm^3$) and dried *in vacuo* to yield the product as a light-yellow solid. Yield: 0.49 g (69%).

Data for **8b**. $^1$H NMR ($CD_2Cl_2$, 300 MHz, 298 K): $\delta$ 7.24 (s, 1H, $C_6H_2$), 6.85 (s, 1H, $C_6H_2$), 4.89 (d, $J$ = 14.0, 1H, $NCH_2C_6H_2$), 4.10 (sept, $J$ = 6.3, 2H, $Me_2CH$), 3.74 (m, 1H, $N(CH_2)_2N$), 3.45 (d, $J$ = 14.0, 1H, $NCH_2C_6H_2$), 3.33 (m, 1H, $N(CH_2)_2N$), 3.99–3.25 (m, 4H, $N(CH_2)_2N$), 2.63–2.98 (m, 6H, $N(CH_2)_2N$), 2.37 (m, 1H, $N(CH_2)_2N$), 1.65 (d, $J$ = 6.8, 3 H, $Me_2CH$), 1.44 (s, 9H, Bu$^t$), 1.35 (d, $J$ = 6.8, 3 H, $Me_2CH$), 1.28 (s, 9H, Bu$^t$), 1.10 (d, $J$ = 6.5, 3 H, $Me_2CH$), 1.04 (d, $J$ = 6.5 Hz, 3 H, $Me_2CH$). $^{13}$C-{$^1$H} NMR ($CD_2Cl_2$, 300 MHz, 298 K): $\delta$ 157.3 (2-$C_6H_2$), 139.5 and 136.3 (1-$C_6H_2$ and 3-$C_6H_2$), 124.2 and 123.9 (4-$C_6H_2$ and 6-$C_6H_2$), 123.1 (5-$C_6H_2$), 65.8 ($NCH_2$-$C_6H_2$), 57.6, 56.9 ($Me_2CH$), 55.3, 55.8, 53.5, 52.8, 43.4, 43.1 ($N(CH_2)_2N$), 35.2, 34.2 (2 × $Me_3C$), 31.7, 30.4 (2 × $Me_3C$), 21.8, 21.2, 14.8, 14.7 ($Me_2CH$). EI-MS: *m*/*z* 545 $[M]^+$, 530 $[M - Me]^+$, 510 $[M - Cl]^+$, 494 $[M - Cl - Me]^+$, 466.2 $[M - Cl - Pr^i]^+$. Anal. Found (calc. for $C_{27}H_{48}ScCl_2N_3O$): C, 59.1 (59.3); H, 9.1 (8.9); N, 7.4 (7.7)%.

### [Sc(κ$^4$-L$^c$)Cl$_2$] 8c

$ScCl_3$ (0.2 g, 1.34 mmol) was refluxed in THF (25 $cm^3$) for 25 min. The solution was allowed to cool and was then stirred for the dropwise addition of KL$^c$ (0.55 g, 1.34 mmol) in THF (25 $cm^3$) over a period of 2 h. The mixture was stirred at room temp. for 24 h, then the solution was filtered from insolubles and the volatiles removed under reduced pressure. The residue was washed with pentane (30 $cm^3$) and dried *in vacuo* to afford the product as a white solid. Yield: 0.51 g (77%).

Data for **8c**. $^1$H NMR ($CD_2Cl_2$, 300 MHz, 298 K): $\delta$ 7.27 (s, 1H, $C_6H_2$), 6.94 (s, 1H, $C_6H_2$), 4.76 (d, $J$ = 13.1, 1H, NC$H_2$-$C_6H_2$), 3.85 (m, 1H, $N(CH_2)_2N$), 3.66 (m, 1H, $N(CH_2)_2N$), 3.43 (d, $J$ = 13.1 Hz, 1H, $NCH_2C_6H_2$), 3.08–3.34 (m, 2H, $N(CH_2)_2N$), 3.02 (s, 3H, MeN), 2.82–2.98 (m, 3H, $N(CH_2)_2N$), 2.78 (s, 3H, MeN), 2.51–2.76 (m, 4H, $N(CH_2)_2N$), 2.37 (m, 1H, $N(CH_2)_2N$), 1.47 (s, 9H, Bu$^t$), 1.29 (s, 9H, Bu$^t$). $^{13}$C-{$^1$H} NMR ($CD_2Cl_2$, 300 MHz, 298 K): $\delta$ 158.9 (2-$C_6H_2$), 139.6 and 135.8 (1-$C_6H_2$ and 3-$C_6H_2$), 125.2 and 124.2 (4-$C_6H_2$ and 6-$C_6H_2$), 123.7 (5-$C_6H_2$), 64.8 ($NCH_2C_6H_2$), 58.8, 57.3, 52.4, 56.8, 54.1, 50.5 ($N(CH_2)_2N$), 50.4, 50.1 (2 × MeN), 35.1, 34.2 (2 × $Me_3C$), 31.7, 30.1 (2 × $Me_3C$). EI-MS: *m*/*z* 489 $[M]^+$, 474.4 $[M - Me]^+$, 454 $[M - Cl]^+$, 438 $[M - Me - Cl]^+$ Anal. Found (calc. for $C_{23}H_{40}ScCl_2N_3O$): C, 56.1 (56.3); H, 8.0 (8.2); N, 8.2 (8.6)%.

### [Y(κ$^4$-L$^b$)Cl$_2$] 9b

$YCl_3$ (0.2 g, 1.0 mmol) was refluxed in THF (15 $cm^3$) for 5 min. The solution was allowed to cool and was then stirred for the dropwise addition of KL$^b$ (0.47 g, 1.0 mmol) in THF (25 $cm^3$) over a period of 2 h. The mixture was stirred at room temp. for 24 h, then the solution was filtered from insolubles and the volatiles removed under reduced pressure. The residue was dried *in vacuo* to give the product as a white solid. Yield 0.43 g (73%).

Data for **9b**. $^1$H NMR ($CD_2Cl_2$, 300 MHz, 298 K): $\delta$ 7.26 (s, 1H, $C_6H_2$), 6.89 (s, 1H, $C_6H_2$), 4.77 (d, $J$ = 13.5, 1H, NC$H_2$-$C_6H_2$), 4.07 (sept, $J$ = 6.6, 1H, $Me_2CH$), 3.89 (sept, $J$ = 6.6, 1H, $Me_2CH$), 3.56 (m, 1H, $N(CH_2)_2N$), 3.40 (d, $J$ = 13.5, 1H, $NCH_2C_6H_2$), 3.29 (m, 1H, $N(CH_2)_2N$), 2.87 (m, 8H, $N(CH_2)_2N$), 2.43 (m, 2H, $N(CH_2)_2N$), 1.61 (d, $J$ = 6.8, 3 H, $Me_2CH$), 1.46 (s, 9H, Bu$^t$), 1.29 (s, 9H, Bu$^t$), 1.27 (d, $J$ = 6.8, 3 H, $Me_2CH$), 1.13 (d, $J$ = 6.4, 3 H, $Me_2CH$), 1.09 (d, $J$ = 6.4, 3 H, $Me_2CH$). $^{13}$C-{$^1$H} NMR ($CD_2Cl_2$, 300 MHz, 298 K): $\delta$ 158.5 (2-$C_6H_2$), 138.6 and 136.3 (1-$C_6H_2$ and 3-$C_6H_2$), 125.2 and 124.3 (4-$C_6H_2$ and 6-$C_6H_2$), 123.0 (5-$C_6H_2$), 65.0 ($NCH_2C_6H_2$), 56.7, 56.3 ($Me_2CH$), 54.6, 53.5, 51.9, 44.4, 43.2 ($N(CH_2)_2N$), 35.1, 34.1 (2 × $Me_3C$), 31.7, 30.2 (2 × $Me_3C$), 22.1, 21.0, 15.0, 14.0 ($Me_2CH$). EI-MS: *m*/*z* 589 $[M]^+$, 554 $[M - Cl]^+$. Anal. Found (calc. for $C_{27}H_{48}Cl_2N_3OY$): C, 54.6 (54.9); H, 8.2 (8.2); N, 6.8 (7.1)%.

### [Y(κ$^4$-L$^c$)Cl$_2$] 9c

$YCl_3$ (0.98 g, 0.5 mmol) was refluxed in THF (15 $cm^3$) for 5 min. The solution was allowed to cool and then was stirred for the dropwise addition of KL$^c$ (0.21 g, 0.5 mmol) in THF (15 $cm^3$) over a period of 2 h. The mixture was stirred at room temp. for 24 h, then the solution was filtered from insolubles and the volatiles removed under reduced pressure. The residue was dried *in vacuo* to give the product as a white solid. Yield 0.21 g (79%).

Data for **9c**. $^1$H NMR ($CD_2Cl_2$, 300 MHz, 298 K): $\delta$ 7.27 (s, 1H, $C_6H_2$), 6.96 (s, 1H, $C_6H_2$), 4.58 (d, $J$ = 13.8, 1H, NC$H_2$-$C_6H_2$), 3.84 (m, 1H, $N(CH_2)_2N$), 3.61 (m, 1H, $N(CH_2)_2N$), 3.41 (d, $J$ = 13.8 Hz, 1H, $NCH_2C_6H_2$), 3.22 (m, 1H, $N(CH_2)_2N$), 3.09 (m, 1H, $N(CH_2)_2N$), 3.00 (s, 3H, MeN), 2.85 (m, 3H, $N(CH_2)_2N$), 2.72 (s, 3H, MeN), 2.63 (m, 3H, $N(CH_2)_2N$), 2.42 (m, 1H, $N(CH_2)_2N$), 2.25 (m, 1H, $N(CH_2)_2N$), 1.47 (s, 9H, Bu$^t$), 1.29 (s, 9H, Bu$^t$). $^{13}$C-{$^1$H} NMR ($CD_2Cl_2$, 300 MHz, 298 K): $\delta$ 159.6 (2-$C_6H_2$), 138.8 and 136.0 (1-$C_6H_2$ and 3-$C_6H_2$), 126.2 and 124.5 (4-$C_6H_2$ and 6-$C_6H_2$), 123.4 (5-$C_6H_2$), 63.4 ($NCH_2$-$C_6H_2$), 59.0, 57.1, 56.2, 52.4, 48.9 ($N(CH_2)_2N$), 48.8, 48.7 (MeN), 35.2, 34.1 (2 × $Me_3C$), 31.7, 30.0 (2 × $Me_3C$). EI-MS: *m*/*z* 533 $[M]^+$, 518 $[M - Me]^+$, 498 $[M - Cl]^+$. Anal. Found

**Table 1** X-Ray data collection and processing parameters for $[In(\kappa^4\text{-}L^b)Cl_2]\cdot 3CH_2Cl_2$ **5b**·$3CH_2Cl_2$, $[Tl(\kappa^4\text{-}L^b)]$ **13b** and $[Tl(\kappa^4\text{-}L^c)]$ **13c**

| | **5b**·$3CH_2Cl_2$ | **13b** | **13c** |
|---|---|---|---|
| Formula | $C_{27}H_{48}Cl_2InN_3O\cdot 3CH_2Cl_2$ | $C_{27}H_{48}N_3OTl$ | $C_{23}H_{40}N_3OTl$ |
| Formula weight | 871.23 | 635.07 | 578.96 |
| Crystal system | Monoclinic | Triclinic | Monoclinic |
| Space group | $P2_1/c$ | $P\bar{1}$ | $P2_1/c$ |
| $a$/Å | 10.285(8) | 9.5230(4) | 9.140(3) |
| $b$/Å | 14.613(6) | 11.1850(3) | 16.921(5) |
| $c$/Å | 26.906(4) | 13.5600(6) | 15.533(2) |
| $\alpha$/° | — | 79.328(3) | — |
| $\beta$/° | 99.539(6) | 74.964(2) | 93.939(6) |
| $\gamma$/° | — | 78.089(3) | — |
| $V$/Å$^3$ | 3987.9 | 1360.5 | 2396.6 |
| $Z$ | 4 | 2 | 4 |
| $\mu$(Mo-K$\alpha$)/mm$^{-1}$ | 1.16 | 5.96 | 6.76 |
| Total reflections | 7300 | 5135 | 4718 |
| Observed reflections [$I > 3\sigma(I)$] | 3480 | 4847 | 4097 |
| Final $R$,[a] $R_w$ [b] | 0.0958, 0.0780 | 0.0297, 0.0361 | 0.0201, 0.0241 |

[a] $R = \Sigma\big||F_o| - |F_c|\big|/\Sigma|F_o|$. [b] $R_w = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2\}^{\frac{1}{2}}$.

(calc. for $C_{23}H_{40}Cl_2N_3OY$): C, 51.2 (51.7); H, 7.3 (7.5); N, 7.5 (7.9)%.

### $[Ti(\kappa^4\text{-}L^b)Cl_2]$ 10b

$[TiCl_3(THF)_3]$ (0.17 g, 0.46 mmol) was dissolved in THF (35 cm$^3$) and a solution of $KL^b$ (0.21 g, 0.46 mmol) in THF (25 cm$^3$) was added dropwise over a period of 2 h. The mixture was stirred at room temp. for 16 h, then the solution was filtered and the solids extracted with $CH_2Cl_2$ (10 cm$^3$). The volatiles were removed under reduced pressure and the residue dried *in vacuo* for 16 h to give the product as a pale blue solid. Yield 0.18 g (72%).

Data for **10b**. $^1$H NMR ($CD_2Cl_2$, 300 MHz, 298 K): $\delta$ 1.15 (br s, 18H, Bu$^t$). EI-MS: *m*/*z* 548 $[M]^+$, 505 $[M - Pr^i]^+$, 470 $[M - Cl - Pr^i]^+$. Anal. Found (calc. for $C_{27}H_{48}N_3OCl_2Ti$): C, 62.3 (59.0); H, 9.6 (8.8); N, 6.5 (7.6)%. A satisfactory elemental analysis could not be obtained by recrystallisation.

### $[Ti(\kappa^4\text{-}L^c)Cl_2]$ 10c

$[TiCl_3(THF)_3]$ (0.56 g, 1.5 mmol) was dissolved in THF (40 cm$^3$) and a solution of $KL^c$ (0.62 g, 1.5 mmol) in THF (30 cm$^3$) was added dropwise over a period of 1.5 h. The mixture was stirred at room temp. for 16 h, then the solution was filtered and the solids extracted with $CH_2Cl_2$ (25 cm$^3$). The volatiles were removed under reduced pressure and the residue dried *in vacuo* for 16 h to give the product as a pale-violet solid. Yield 0.55 g (74%).

Data for **10c**. $^1$H NMR ($CD_2Cl_2$, 500 MHz, 298 K): $\delta$ 1.12 (br s, 18H, Bu$^t$). EI-MS: *m*/*z* 492 $[M]^+$, 457 $[M - Cl]^+$. Anal. Found (calc. for $C_{23}H_{40}Cl_2N_3OTi$): C, 55.5 (56.0); H, 8.0 (8.2); N, 8.3 (8.5)%.

### $[V(\kappa^4\text{-}L^b)Cl_2]$ 11b

$[VCl_3(THF)_3]$ (0.45 g, 1.2 mmol) was dissolved in THF (30 cm$^3$) and a solution of $KL^b$ (0.56 g, 1.2 mmol) in THF (35 cm$^3$) was added dropwise over a period of 2 h. The mixture was stirred at room temp. for 16 h, then the solution was filtered . The solids were washed with THF (30 cm$^3$) and extracted with $CH_2Cl_2$ (30 cm$^3$). The volatiles were removed under reduced pressure and the residue dried *in vacuo* for 16 h to give the product as a brown solid. Yield 0.24 g (39%).

Data for **11b**. $^1$H NMR ($CD_2Cl_2$, 300 MHz, 298 K): $\delta$ 1.08 (s, 18H, Bu$^t$). EI-MS: *m*/*z* 551 $[M]^+$, 516 $[M - Cl]^+$, 473 $[M - Cl - Pr^i]^+$. Anal. Found (calc. for $C_{27}H_{48}Cl_2N_3OV$): C, 58.3 (58.7); H, 8.8 (8.7); N, 7.2 (7.6)%.

### $[V(\kappa^4\text{-}L^c)Cl_2]$ 11c

$[VCl_3(THF)_3]$ (0.41 g, 1.1 mmol) was dissolved in THF (30 cm$^3$) and a solution of $KL^c$ (0.46 g, 1.1 mmol) in THF (30 cm$^3$) was added dropwise over a period of 3 h. The mixture was stirred at room temperature for 16 h, then the solution was filtered. The solids were washed with pentane (25 cm$^3$) and extracted with $CH_2Cl_2$ (20 cm$^3$). The volatiles were removed under reduced pressure and the residue dried *in vacuo* for 16 h to give the product as a yellow-brown solid. Yield 0.26 g (53%).

Data for **11c**. $^1$H NMR ($CD_2Cl_2$, 500 MHz, 298 K): $\delta$ 1.03 (br s, 18H, Bu$^t$). EI-MS: *m*/*z* 495 $[M]^+$, 460 $[M - Cl]^+$. Anal. Found (calc. for $C_{23}H_{40}Cl_2N_3OV$): C, 55.0 (55.6); H, 8.0 (8.1); N, 8.0 (8.5)%.

### $[Cr(\kappa^4\text{-}L^b)Cl_2]$ 12b

$[CrCl_3(THF)_3]$ (0.41 g, 1.1 mmol) was dissolved in THF (50 cm$^3$) and a solution of $KL^b$ (0.52 g, 1.1 mmol) in THF (35 cm$^3$) was added dropwise over a period for 2 h. The mixture was stirred at room temperature for 16 h, then the solution was filtered. The solids were washed with THF (10 cm$^3$) and extracted with $CH_2Cl_2$ (35 cm$^3$). The volatiles were removed under reduced pressure and the residue dried *in vacuo* for 16 h to give the product as a dark-grey solid. Yield 0.16 g (27%).

Data for **12b**. $^1$H NMR ($CD_2Cl_2$, 300 MHz, 298 K): $\delta$ 2.17 (br s, 18H, $(CH_3)_3CC_6H_2$). EI-MS: *m*/*z* 552 $[M]^+$, 517 $[M - Cl]^+$. Anal. Found (calc. for $C_{27}H_{48}Cl_2CrN_3O$): C, 58.2 (58.6); H, 8.5 (8.7); N, 7.3 (7.6)%.

### $[Cr(\kappa^4\text{-}L^c)Cl_2]$ 12c

$[CrCl_3(THF)_3]$ (0.42 g, 1.1 mmol) was dissolved in THF (50 cm$^3$) and a solution of $KL^c$ (0.46 g, 1.1 mmol) in THF (25 cm$^3$) was added dropwise over a period of 2 h. The mixture was stirred at room temperature for 16 h, then the solution was filtered. The solids were washed with THF (30 cm$^3$) and extracted with $CH_2Cl_2$ (60 cm$^3$). The volatiles were removed under reduced pressure and the residue dried *in vacuo* for 16 h to give the product as a grey–green solid. Yield 0.32 g (59%).

Data for **12c**. $^1$H NMR ($CD_2Cl_2$, 500 MHz, 298 K): $\delta$ 2.12 (s, 18H, Bu$^t$). EI-MS: *m*/*z* 496 $[M]^+$, 481 $[M - Me]^+$, 461 $[M - Cl]^+$. Anal. Found (calc. for $C_{23}H_{40}Cl_2CrN_3O$): C, 55.1 (55.5); H, 8.2 (8.1); N, 8.3 (8.4)%.

### Crystal structure determinations of $[In(\kappa^4\text{-}L^b)Cl_2]\cdot 3CH_2Cl_2$ (**5b**·$3CH_2Cl_2$), $[Tl(\kappa^4\text{-}L^b)]$ (13b) and $[Tl(\kappa^4\text{-}L^c)]$ (13c)

Crystal data collection and processing parameters 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.[14] Data were collected at 150 K using Mo-K$\alpha$ radiation; equivalent reflections were merged and

the images were processed with the DENZO and SCALEPACK programs.[15] Corrections for Lorentz-polarisation effects and absorption were performed and the structures were solved by direct methods using either SIR92[16] or SHELXS-86.[17] Subsequent difference Fourier syntheses revealed the positions of all other non-hydrogen atoms, and hydrogen atoms were placed geometrically. Extinction corrections were applied as required.[18] Crystallographic calculations were performed using SHELXS-86, SIR92 and CRYSTALS-PC.[19] The relatively large *R* factor for **5b**·$3CH_2Cl_2$ is attributed to the presence of three dichloromethane molecules of crystallisation.

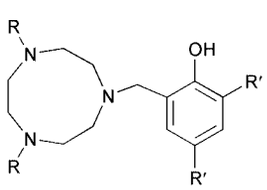
CCDC reference number 186/2285.

See http://www.rsc.org/suppdata/dt/b0/b008267h/ for crystallographic files in .cif format.

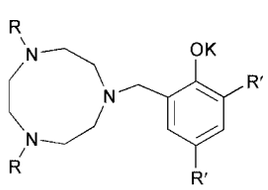
## Results and discussion

### Ligand precursors and their potassium salts

Previous work on the aluminium systems **B** and **C** above showed that use of alkoxide pendant arms were less likely to lead to the desired monomeric products than 3,5-disubstituted-2-hydroxybenzyl groups.[6] We therefore decided in future studies to use triazacyclononane ligands featuring pendant aryloxide groups bearing 3,5-substituents in the aromatic ring. The use of 3,5-ring substituents was expected to enhance complex solubility and provide some measure of steric protection around the M–O(Ar) linkage, thereby promoting the formation of mononuclear products. The ligand precursors, abbreviated as $HL^a$, $HL^b$ and $HL^c$ **1a**–**c** shown below have been reported previously



| R | R′ | Abbrev. |
|---|---|---|
| $Pr^i$ | Me | $HL^a$ **1a** |
| $Pr^i$ | $Bu^t$ | $HL^b$ **1b** |
| Me | $Bu^t$ | $HL^c$ **1c** |



| R | R′ | Abbrev. |
|---|---|---|
| $Pr^i$ | Me | $KL^a$ **2a** |
| $Pr^i$ | $Bu^t$ | $KL^b$ **2b** |
| Me | $Bu^t$ | $KL^c$ **2c** |

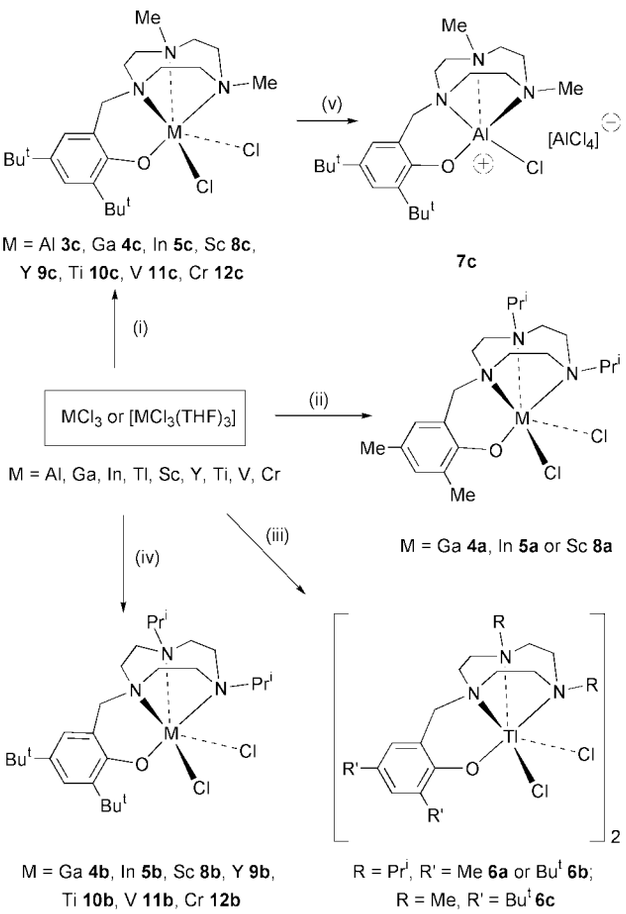
by Tolman and co-workers (for **1a**,**b**)[11] and Flassbeck and Wieghardt (**1c**).[13] With one very recent exception,[20] complexes of these ligands have been reported only for the later transition metals,[11,13,21–23] There has also been a report of vanadium oxo derivatives of the N- and aryl ring-unsubtituted ligand precursor 1-(2-hydroxybenzyl)-4,7-triazacyclononane.[24]

The precursors $HL^{a,b}$ **1a**–**b** were prepared according to Tolman's method.[11] However, we have developed an improved and more convenient synthesis of $HL^c$ **1c**. Wieghardt's synthesis[13] for **1c** uses the reaction of $HMe_2$[9]$aneN_3$[10] and 3,5-di-*tert*-butyl-2-hydroxybenzyl bromide to give **1c** as a yellow–brown viscous oil (no yield given). This was then used for complex synthesis without further purification. We have found that Tolman's general procedure (*via* an intermediate Mannich base)[11] can be adopted for the synthesis of **1c**. Thus reaction of $HMe_2$[9]$aneN_3$[10] with aqueous formaldehyde in methanol followed by subsequent addition of 2,4-di-*tert*-butylphenol afforded $HL^c$ **1c** as a white solid in 80% isolated yield.

As discussed below, we have prepared a range of dichloride complexes $[M(L^{a–c})Cl_2]$ from either the corresponding $MCl_3$ or $[MCl_3(THF)_3]$ precursors. While it is, in principle, possible to react these trichlorides directly with the ligand precursors $HL^{a–c}$ (*e.g.* in the presence of an amine base to take up the liberated HCl), it is thermodynamically and experimentally more favourable to use salt-elimination reactions. Thus the potassium, O-metallated salts of $HL^{a–c}$ were prepared from the ligand precursors and 3 to 4 equivalents of potassium hydride in THF at −30 °C. The compounds $KL^{a–c}$ **2a**–**c** were obtained as spectroscopically pure, off-white solids in 87–98% yield. The air- and moisture-sensitive new compounds are soluble in benzene and THF, and could be used without further purification. They are formulated as "$KL^{a–c}$" although their solution and/or solid state structures could be polynuclear.

### Group 13 complexes of the type $[M(\kappa^4\text{-}L^{a–c})Cl_2]_n$

Apart from our own work on aluminium systems such as $[Al(\kappa^2\text{-}L^b)Me_2]$ **B** and $[Al(\kappa^2\text{-}L^b)Me]^+$ **C**,[6] there has been only one other report (without structural authentication) of a mono-pendant arm triazacyclononane complex of a Group 13 metal.[20] A number of derivatives of these metals with tris-pendant arm homologues have, however, been described.[25–28] The syntheses of the new compounds $[M(\kappa^4\text{-}L^{a–c})Cl_2]_n$ ($n = 1$, M = Al, Ga or In; $n = 2$, M = Tl) are summarised in Scheme 1.




**Scheme 1** Synthesis and structures of mononuclear *cis*-dichloride complexes with mono-pendant arm triazacyclononane ligands. Reagents and conditions: (i) $KL^c$ **2c**, THF or benzene, room temp., 31–82%; (ii) $KL^a$ **2a**, THF or benzene, room temp., 50–61%; (iii) $KL^{a–c}$ **2a**–**c**, THF, room temp., 29–60%; (iv) $KL^b$ **2b**, room temp., 27–82%; (v) $AlCl_3$, $CD_2Cl_2$, room temp., >95%.

Full characterising data for these and all the new compounds described herein are reported in the Experimental section; they will not be discussed in detail unless interpretation is not straightforward.

Reactions of $MCl_3$ (M = Al, Ga, In or Tl) were carried out in THF (M = Al) or benzene for all three potassium salts **2a**–**c**. For reactions with $AlCl_3$ only $[Al(\kappa^4\text{-}L^c)Cl_2]$ **3c** could be isolated as a pure product. Although NMR analysis of the crude reaction product with $KL^b$ **2b** suggested that an aluminium complex had formed, attempts to work up this reaction further gave decomposition products that could not be separated. The reactions of $KL^{a–c}$ **2a**–**c** with $GaCl_3$ or $InCl_3$ gave the

**Table 2** Selected bond distances (Å) and angles (°) for [In($\kappa^4$-L$^b$)Cl$_2$] **5b**

| | | | |
|---|---|---|---|
| In(1)–Cl(1) | 2.439(2) | In(1)–N(4) | 2.366(7) |
| In(1)–Cl(2) | 2.489(3) | In(1)–N(7) | 2.401(7) |
| In(1)–N(1) | 2.271(8) | In(1)–O(18) | 2.076(5) |
| Cl(1)–In(1)–Cl(2) | 95.52(9) | N(1)–In(1)–N(7) | 78.8(3) |
| Cl(1)–In(1)–N(1) | 166.12(19) | N(4)–In(1)–N(7) | 79.0(3) |
| Cl(2)–In(1)–N(1) | 97.70(19) | Cl(1)–In(1)–O(18) | 91.36(17) |
| Cl(1)–In(1)–N(4) | 106.8(2) | Cl(2)–In(1)–O(18) | 90.45(17) |
| Cl(2)–In(1)–N(4) | 88.0(2) | N(1)–In(1)–O(18) | 84.3(2) |
| N(1)–In(1)–N(4) | 78.0(3) | N(4)–In(1)–O(18) | 161.8(2) |
| Cl(1)–In(1)–N(7) | 89.2(2) | N(7)–In(1)–O(18) | 101.6(2) |
| Cl(2)–In(1)–N(7) | 166.94(18) | | |

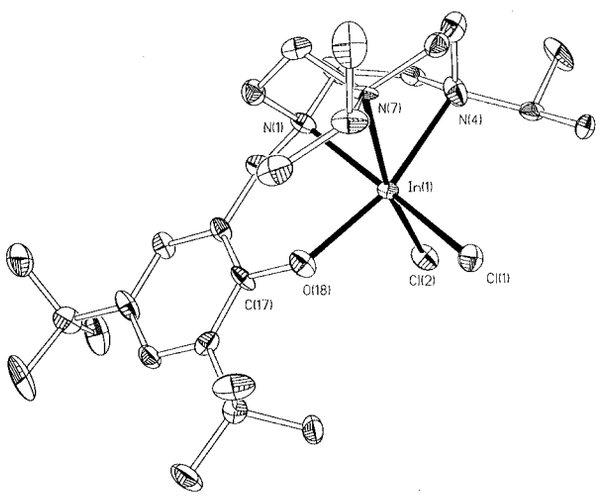



**Fig. 1** Displacement ellipsoid (30%) plot of [In($\kappa^4$-L$^b$)Cl$_2$] **5b** with H atoms omitted.

corresponding products [Ga($\kappa^4$-L$^{a–c}$)Cl$_2$] **4a**–**c** and [In($\kappa^4$-L$^{a–c}$)-Cl$_2$] **5a**–**c** as white solids in 61–82% isolated yield. The reaction of KL$^{a–c}$ **2a**–**c** with TlCl$_3$ gave the binuclear products [Tl-($\kappa^4$-L$^{a–c}$)Cl$_2$]$_2$ **6a**–**c** (discussed further below) in 29–60% yield. In general, the complexes of ligands L$^b$ and L$^c$ are considerably more soluble than their L$^a$ counterparts, and this is attributed to the presence of lipophilic *tert*-butyl substituents on the aryloxide rings of the former. Our failure to isolate aluminium dichloride complexes of the ligands L$^a$ and L$^b$ is possibly due to the increased steric crowding imposed by the triazacyclic N-isopropyl groups compared to that of the N-methyl substituents in L$^c$.

The mononuclear, solid state structures proposed in Scheme 1 for [M($\kappa^4$-L$^{a–c}$)Cl$_2$] **3**–**6** are supported by the crystal structure of [In($\kappa^4$-L$^b$)Cl$_2$] **5b**. Diffraction-quality crystals of **5b**·3CH$_2$Cl$_2$ were obtained from dichloromethane. Data collection and processing parameters are given in Table 1, a view of the molecular structure is given in Fig. 1 and selected bond lengths and angles are listed in Table 2.

Molecules of [In($\kappa^4$-L$^b$)Cl$_2$] **5b** contain pseudo-octahedral In(III) centres. The coordination sphere is comprised of a monoanionic $\kappa^4$-L$^b$ group and two mutually *cis* chloride ligands. The bond lengths and angles within the $\kappa^4$-L$^b$ ligand are comparable to those previously reported for transition metal complexes.[11,22,23] The slightly different In–Cl distances of 2.439(2) and 2.489(3) Å presumably reflect the unsymmetrical coordination environment at indium, which is also revealed in the variation in the In–N distances of 2.271(8), 2.366(7) and 2.401(7) Å. The range of In–N(triazacyclononane) distances in previous structurally characterised H$_3$[9]aneN$_3$ or tris-pendant arm functionalised triazacyclononane complexes of indium is *ca.* 2.25–2.41 Å (av. 2.32 Å) for 7 examples listed in the Cambridge Structural Database.[29,30] Compound **5b** is only the second structurally characterised compound of the type [M(L)X$_2$] (L = anionic mono-pendant arm triazacyclononane, X = halogen).[9]

The room-temperature solution NMR data for [Al($\kappa^4$-L$^c$)Cl$_2$] **3c** and [In($\kappa^4$-L$^{a–c}$)Cl$_2$] **5a**–**c** and the low temperature NMR data for [Ga($\kappa^4$-L$^{b,c}$)Cl$_2$] **4b**,**c** (see below) are fully consistent with the solid state structure of **5b**. For example, the $^1$H spectra typically show four doublets and two apparent septets for the two inequivalent N-isopropyl groups, and a pair of mutually coupled doublets for the diastereotopic benzylic methylene H atoms. The spectra also show a series of multiplets for the triazacyclononane ring methylene H atom along with characteristic resonances for the 3,5-disubstituted aryloxide rings.

Although the dimethyl analogue of [Al($\kappa^4$-L$^c$)Cl$_2$] **3c**, namely [Al($\kappa^2$-L$^b$)Me$_2$] **B**, posseses a bidentate, N,O-coordinated L$^b$ ligand, we nonetheless propose that **3c** possesses the six-coordinate geometry shown in Scheme 1. This interpretation is based on the significant differences between the NMR spectra for the two complexes. The $^1$H and $^{13}$C spectra for the dichloride **3c** are sharp at room temperature, whereas those of [Al-($\kappa^2$-L$^b$)Me$_2$] **B** and all the other $\kappa^2$-coordinated mono-pendant arm macrocycles of this type (including four structurally characterised examples)[6] are very broad at room temperature indicative of fluxional behaviour. In the low-temperature, slow-exchange limit, the $^1$H NMR spectra of these $\kappa^2$-coordinated dialkyl aluminium complexes sharpen up and show a pair of triazacyclononane methylene resonances in the region $\delta$ 4–5. Such unusually low-field resonances (which are apparently characteristic of the $\kappa^2$-coordination mode) are entirely absent from the spectra of **3c** and any of the $\kappa^4$-L$^{a–c}$ complexes described herein.

The room-temperature $^1$H NMR spectra of the gallium complexes [Ga($\kappa^4$-L$^{a–c}$)Cl$_2$] **4a**–**c** show only one septet and one pair of doublets for the N-isopropyl groups, and one singlet for the benzylic methylene protons. One cooling the samples to −80 °C these resonances decoalesce and appear as described above for **3c** and **5a**–**c** (the complex **4a** is too insoluble for low temperature NMR studies). The low temperature NMR data therefore suggest that [Ga($\kappa^4$-L$^{a–c}$)Cl$_2$] **4a**–**c** possess the $\kappa^4$-coordinated structures shown in Scheme 1. The nature of the fluxional process which gives rise to the implied $C_s$-symmetrical structures on the room-temperature NMR timescale is unknown. Possibly there is a dynamic equilibrium between $\kappa^4$- and $\kappa^1$(O)-coordinated species (the latter being the higher energy isomer) and this would give rise the exchange processes seen. A fluxional process involving loss of chloride from [Ga($\kappa^4$-L$^{a–c}$)Cl$_2$] to give a $C_s$-symmetrical cation [Ga($\kappa^4$-L$^{a–c}$)-Cl]$^+$ is in principle feasible, especially given the formation of [Al($\kappa^4$-L$^b$)Me]$^+$ **C** or [Al($\kappa^4$-L$^c$)Cl]$^+$ **7c** (see below). However, the fluxional process for **4b** was not affected (as judged by $^1$H signal linewidths) by the addition of several equivalents of [N(PPh$_3$)$_2$]Cl and so a rate-determining step involving loss of Cl$^-$ appears to be unlikely.

The NMR spectra of the binuclear products [Tl($\kappa^4$-L$^{a–c}$)Cl$_2$]$_2$ **6a**–**c** are sharp at room temperature but feature two individual sets of resonances (in a 1:1 ratio) for the $\kappa^4$-L$^{a–c}$ ligands. Each set of L$^{a–c}$ resonances is consistent with an unsymmetrical geometry at thallium. For example, there are two pairs of mutually-coupled doublets for the benzylic methylene H atoms and two pairs of apparent septets for the NPr$^i$ methine H atoms. Compounds **6a**–**c** are formed reproducibly in analytically pure form; the ratio between the two sets of resonances is always 1:1. The dimeric structures proposed for **6a**–**c** are supported by their electrospray mass spectra which all show weak intensity molecular ions consistent with this. The base peaks in these spectra correspond to monomeric [Tl($\kappa^4$-L$^{a–c}$)Cl$_2$] suggesting that each thallium centre has a triazacyclic ligand and two chlorides associated with it (ruling out a possible structure with two L$^{a–c}$ ligands bound to one thallium). We have not been able to obtain diffraction-quality crystals of **6a**–**c** but tentatively propose a chloride bridged dimeric structure since the aryloxide

oxygens (the only other likely bridging atoms) are sterically well protected by the neighbouring aryl ring substituents, especially for **6b**,**c**. A number of chloride-bridged dithallium complexes have been structurally characterised.[29,30] Examination of molecular models of chloride-bridged dimers show that the least crowded structures have inequivalent, unsymmetrical $L^{a-c}$ ligands consistent with the NMR data for **6a**–**c**. It is probably the increased atomic radius of thallium compared to the lighter congeners that leads to the dimeric structure formed.

There is continuing current interest in cationic aluminium complexes[31] and we have recently reported on the synthesis of the organometallic cationic complex $[Al(\kappa^4\text{-}L^b)Me]^+$ **C** and some homologues.[6] In an attempt to prepare an aluminochloride analogue of **C**, $[Al(\kappa^4\text{-}L^c)Cl_2]$ **3c** was reacted with $AlCl_3$ in $CD_2Cl_2$ in an NMR tube scale experiment (Scheme 1) to form the complex $\{[Al(\kappa^4\text{-}L^c)Cl]\ [AlCl_4]\}$ **7c**. Compound **7c** decomposes completely in solution over 2 d and also on removal of the volatiles under reduced pressure. It was characterised *in situ* only by $^1H$ and $^{27}Al$ NMR spectroscopy.

The $^1H$ NMR spectrum of $[Al(\kappa^2\text{-}L^c)Cl]^+$ resembles the $L^b$ sub-spectrum in $[Al(\kappa^2\text{-}L^b)Me]^+$ **C** which has been isolated as its $MeB(C_6F_5)_3^-$ salt and fully characterised.[6] The $^1H$ resonances for $L^c$ are consistent with $C_s$ symmetry. For example, there is only a singlet for the two $ArCH_2N$ methylene protons of the pendant arm, and only one singlet for the triazacyclic NMe groups. Most significantly, all of the triazacyclic $NCH_2CH_2N$ resonances appear in the range $\delta$ 3.5–3.0 (*i.e.* there are none at $\delta >$ *ca.* 4 that would indicate a $\kappa^2$-coordinated $L^c$ ligand). We propose that the cation in **7c** therefore posseses a $\kappa^4$-coordinated $L^c$ ligand. In support of the structure proposed for $[Al(\kappa^2\text{-}L^c)Cl]^+$ in Scheme 1, we note that Tolman and co-workers have reported the crystal structures of trigonal-bipyramidal complexes $[M(L^b)X]$ and $[M(L^a)X]^+$ (M = Cu or Zn; X = Cl, MeCN)[11] that have the same geometry as that proposed for $[Al(\kappa^2\text{-}L^c)Cl]^+$. Moreover, the diamagnetic complexes give $^1H$ NMR spectra that are consistent with $C_s$ symmetrical structures on the NMR timescale.[11] The $^{27}Al$ NMR spectrum of **7c** shows a broad singlet at $\delta$ 45.3 assigned to $[Al(\kappa^2\text{-}L^c)Cl]^+$ and a sharp singlet at $\delta$ 102.2 assigned to $AlCl_4^-$. The $^{27}Al$ NMR spectrum of $\{[CPh_3][AlCl_4]\}$ in the same solvent shows a sharp singlet at $\delta$ 102.0. Further studies and characterisation of **7c** were inhibited by its low stability in the solution and solid states.

### Group 3 and early transition metal complexes of the type $[M(\kappa^4\text{-}L^{a-c})Cl_2]$

Triazacyclonoane complexes of the Group 3 elements have been very little studied. Bercaw and co-workers have reported the non-pendant arm complexes $[M(Me_3[9]aneN_3)X_3]$ (X = Me or Cl).[32] All of the other Group 3 compounds feature tris-pendant arm triazacyclononanes.[25,26,33,34] Furthermore, while there is an extensive triazacyclononane complex chemistry in general of the early transition metals (defined here as the Ti, V and Cr triads), there have been only two reports of mono-pendant arm derivatives of these metals, these being vanadium oxo or μ-oxo derivatives.[24,35] We thus wished to extend our successful syntheses of the Group 13 complexes $[M(\kappa^4\text{-}L^{a-c})Cl_2]_n$ to the pre- and early-transition metals since such species would be potentially useful synthons for new organometallic and catalytic chemistry.

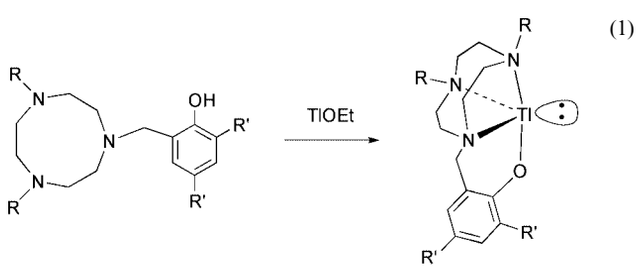
As summarised in Scheme 1, reaction of $ScCl_3$ with $KL^{a-c}$ **2a**–**c** in THF gives the corresponding triazacyclononane derivatives $[Sc(L^{a-c})Cl_2]$ **8a**–**c** in 59–77% isolated yield. The new complexes are proposed to have the monomeric structures shown by comparison with that of $[In(L^b)Cl_2]$ **5b** and Bercaw's $[Sc(Me_3[9]aneN_3)Cl_3]$.[32] The $^1H$ and $^{13}C$ NMR data are analogous to those for the mononuclear Group 13 complexes and all three compounds give rise to molecular ions in their electron-impact mass spectra. While reaction of $YCl_3$ with $KL^a$ in THF gave ill defined products, with $KL^{b,c}$ **2b**,**c** the white compounds $[Y(L^{b,c})Cl_2]$ **9b**,**c** were obtained in 73–79% isolated yield. The proposed structures are shown in Scheme 1, and the $^1H$ and $^{13}C$ NMR and EI-mass spectra are entirely consistent with them. As mentioned, we hoped that the compounds $[Sc(L^{a-c})Cl_2]$ **8a**–**c** and $[Y(L^{b,c})Cl_2]$ **9b**,**c** would be useful precursors to other new complexes and reaction chemistry. Indeed, we have found in preliminary experiments that new scandium and yttrium *cis*-dialkyl derivatives are readily accessible by reaction of **8c** or **9b** with organolithium reagents.[36] A full account of these and related organometallic studies will be published in due course.

Finally in this section we report the syntheses of the Ti, V and Cr complexes $[M(L^b)Cl_2]$ (M = Ti **10b**, V **11b** or Cr **12b**) and $[M(L^c)Cl_2]$ (M = Ti **10c**, V **11c** or Cr **12c**) as shown in Scheme 1. Attempts to prepare derivatives of $L^a$ for these metals were unsuccessful. The compounds are obtained in moderate to good yield on reaction of $KL^{b,c}$ with the corresponding $[MCl_3(THF)_3]$. The new compounds are paramagnetic as indicated by their broad $^1H$ NMR spectra and all showed parent molecular ions in their EI mass spectra. The monomeric structures shown in Scheme 1 are assigned based on those for the Group 3 and 13 analogues and those of the previously reported complexes of the type $[M(L)Cl_2]$ (M = Ti, V, Cr, L = non-pendant arm- or tris-pendant-arm-functionalised triazacyclononane ligand).[29,30]

### Thallium(I) complexes of mono-pendant arm triazacyclononanes

Thallium has an extensive chemistry of both the +III and +I oxidation states,[37] a characteristic that is frequently attributed to the so-called "inert pair effect".[38] Only one thallium(I) triazacyclonane complex has been structurally characterised previously;[39] [9]ane$S_3$ and [9]ane$N_2S$ homologues have also been described.[40,41] All of these $R_3$[9]ane$E_3$ (R = Me or none; E = N, S) complexes are cationic. No mononuclear thallium(I) aryloxide has yet been reported, all examples to date being dimeric, tetrameric or oligomeric in the solid state.[42,43] We hoped that use of the pendant arm, tetradentate ligands $L^{a-c}$ would give rise to neutral, mononuclear thallium(I) aryloxide complexes of a type not previously prepared.

Reaction of $HL^{a-c}$ **1a**–**c** with thallium(I) ethoxide in benzene leads to elimination of ethanol and the formation of the new complexes $[Tl(L^{a-c})]$ **13a**–**c** in 78–88% isolated yield [eqn. (1)].




(1)

R = Pr$^i$, R' = Me **1a** or Bu$^t$ **1b**; R = Me, R' = Bu$^t$ **1c**

R = Pr$^i$, R' = Me **13a** or Bu$^t$ **13b**; R = Me, R' = Bu$^t$ **13c**

These light-, air- and moisture-sensitive compounds are soluble in benzene and dichloromethane, but rapidly decompose in chloroform. Diffraction-quality crystals of $[Tl(L^b)]$ **13b** and $[Tl(L^c)]$ **13c** were obtained from hexanes. The molecular structures are shown in Fig. 2(a) and (b), and selected bond lengths and angles are in Table 3.

The structures can be viewed as being derived from very distorted trigonal bipyramids in which the atoms O(18) and N(4) occupy the axial positions. Two of the remaining equatorial sites are taken up by N(1) and N(7). Depending on the actual electronic structure (hybridisation) of thallium, a lone pair may be considered to occupy the remaining equatorial site

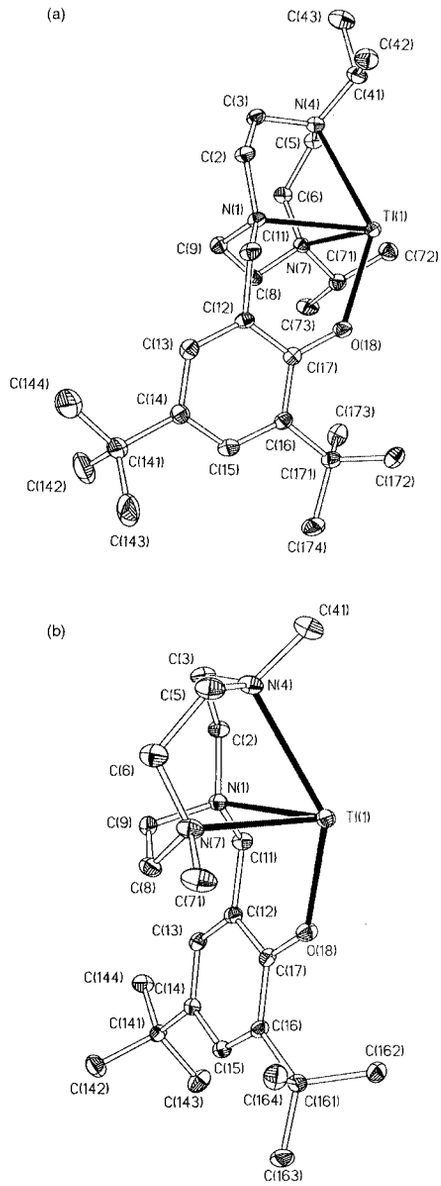



**Fig. 2** Displacement ellipsoid (30%) plots of (a) [Tl(κ⁴-L^b)] **13b** and (b) [Tl(κ⁴-L^c)] **13c**. H atoms are omitted.

as illustrated in eqn. (1). The compounds **13b**,**c** are the first monomeric thallium(I) aryloxides and also the first neutral thallium(I) $R_3$[9]ane$E_3$ complexes. The Tl(I)–O(aryloxide) distances of 2.419(3) and 2.4006(16) Å are shorter than any previously found (av. *ca.* 2.62 Å), although this is not surprising since other values are for bridging aryloxide groups.[42,43] The Tl–N distances lie the range 2.622(4)–2.948(4) Å; the average for previous Tl(I)–N(amine) distances of 2.72 Å is spanned by these values.[29,30] The cation $[Tl(Me_3[9]aneN_3)]^+$ possesses Tl(I)–N distances in the range 2.59(2)–2.63(1) Å. The narrower range of values and shorter average Tl–N distances in this cation can be attributed to the approximate $C_3$-symmetrical binding of the $Me_3$[9]ane$N_3$ ligand and the positive charge on the metal centre. Although the Tl(1)–N(4) distances in particular for **13b**,**c** are long compared to those in previous thallium(I) amine complexes (av. 2.72 Å), they are well within the sum of the van der Waals radii of N and Tl (3.55 Å).[44] There are no intermolecular contacts between molecules of **13b**,**c** in the solid state.

The compounds [Tl(L^[4a–c])] **13a**–**c** give rise to broad $^1$H NMR spectra which change with temperature but do not sharpen even at −90 °C. This is indicative of one or more fluxional processes, the nature of which are unknown. The broadening of the spectra may also be partly attributable to coupling to $^{203}$Tl and/or $^{205}$Tl. All three compounds give the expected molecular ion envelopes in their EI-mass spectra.

**Table 3** Selected bond distances (Å) and angles (°) for [Tl(κ⁴-L^b)] **13b** and [Tl(κ⁴-L^c)] **13c**

| | **13b** | **13c** |
|---|---|---|
| Tl(1)–O(18) | 2.419(3) | 2.4006(16) |
| Tl(1)–N(1) | 2.622(4) | 2.6744(18) |
| Tl(1)–N(4) | 2.948(4) | 2.811(2) |
| Tl(1)–N(7) | 2.776(4) | 2.696(2) |
| N(1)–Tl(1)–N(4) | 64.83(12) | 65.15(6) |
| N(1)–Tl(1)–N(7) | 66.37(12) | 66.41(6) |
| N(4)–Tl(1)–N(7) | 63.63(12) | 65.24(6) |
| N(1)–Tl(1)–O(18) | 75.41(12) | 74.99(5) |
| N(4)–Tl(1)–O(18) | 137.21(12) | 138.61(6) |
| N(7)–Tl(1)–O(18) | 86.92(12) | 89.45(6) |

Thallium(I) complexes (*e.g.* $TlPF_6$ and $[Tl(C_5H_5)]$) are often used in halide elimination reactions because of the low solubility of the thallium halide side-products. In certain instances, thallium reagents show decreased tendency for competing redox process compared to alkali metal analogues. Preliminary results have shown that **13a**–**c** are, like the potassium salts **4a**–**c**, useful ligand-delivery agents in reactions with certain transition metal halides.[36]

## Concluding remarks

We have described a series of new mono-pendant arm triazacyclononane complexes of main group and early transition metals. All of the compounds are either the first, or at least rare, examples of this class for the metals studied. The dichloride complexes for Groups 3 to 6 promise to be useful precursors to further new chemistry. Complexes **13a**–**c** are the first structurally characterised, monomeric thallium(I) aryloxides and are also potentially useful ligand transfer reagents. We are currently developing the organometallic and catalytic chemistry of these and related triazacyclononane-supported metal complexes.

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