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Synthesis and styrene polymerisation catalysis of η^5- and η^1-pyrrolyl-ligated cationic rare earth metal aminobenzyl complexes†

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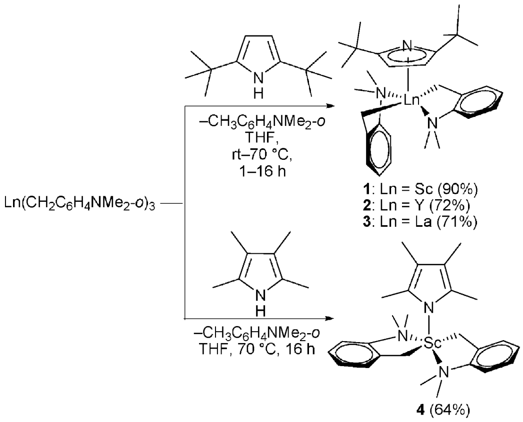
The cationic rare earth metal aminobenzyl complexes bearing mono(pyrrolyl) ligands are synthesised and structurally characterised, and the coordination mode of the pyrrolyl ligands is found to show significant influence on the polymerisation of styrene.

The cationic rare earth (group 3 and lanthanide metals) alkyl complexes bearing mono(cyclopentadienyl) ligands have attracted growing interest due to their high potential in polymerisation catalysis.[1,2] For the stabilisation of such half-sandwich alkyl complexes, cyclopentadienyl derivatives with bulky substituents or with side arms that have amino or ether functional groups have often been employed.[3] In contrast, studies on the influence of heteroatom-containing cyclopentadienyl ligands on the olefin polymerisation activity of the rare earth complexes remained scarce.[4]

Pyrrolyl is isoelectronic with cyclopentadienyl and can show more flexible metal-coordination modes (ranging from N-η^1 (σ) to η^5 (π)) than the cyclopentadienyl analogues. Although a number of pyrrolyl-ligated divalent[5] and trivalent[6] rare earth complexes and group 4 metal complexes[7,8] have been reported, the influence of the coordination mode of the pyrrolyl ligands on the polymerisation activity of a metal complex catalyst has hardly been examined, and a structurally characterised cationic pyrrolyl metal complex has not been reported previously. We report herein the synthesis, structural characterisation, and styrene polymerisation catalysis of the cationic rare earth (*o*-dimethylaminobenzyl) complexes bearing η^5- and η^1-pyrrolyl ligands. We found that the coordination mode (η^1 or η^5) of the pyrrolyl ligands can show dramatic influence on the polymerisation activity.

The acid–base reaction of the rare earth tris(*o*-dimethylaminobenzyl) complexes $Ln(CH_2C_6H_4NMe_2\text{-}o)_3$ with 1 equiv of 2,5-*t*-$Bu_2C_4H_2NH$ gave in high yields the corresponding mono(pyrrolyl)-ligated bis(aminobenzyl) complexes (η^5-2,5-*t*-$Bu_2C_4H_2N)Ln(CH_2C_6H_4NMe_2\text{-}o)_2$ (Ln = Sc (**1**), Y (**2**), La (**3**)) from the smallest scandium to the largest lanthanum (Scheme 1).‡ X-Ray analyses revealed that all of these complexes adopt a similar overall structure. As a typical example, the X-ray structure of **1** is shown in Fig. 1(a). The pyrrolyl ligand is bonded to the metal centre in an η^5-fashion as an azacyclopentadienyl ligand and the two aminobenzyl ligands are all bonded to the metal centre in a chelating fashion *via* both the benzyl CH_2 carbon atom and the amino unit. The average bond length of the Sc–pyrrolyl ring atoms (2.531(2) Å) is almost the same as that of the Sc–Cp ring carbons (2.539(2) Å) found in $(Me_3SiC_5Me_4)Sc(CH_2C_6H_4NMe_2\text{-}o)_2$.[2a] In complexes **1–3**, the bond distances around the metal centres decrease in the order of **3** (La) > **2** (Y) > **1** (Sc) as the decrease in their metal size (*e.g.*, Ln–pyrrolyl bond (av.) **1**: 2.531(2), **2**: 2.678(2), **3**: 2.829(8) Å).

The similar reaction of $Sc(CH_2C_6H_4NMe_2\text{-}o)_3$ with 1 equiv of tetramethylpyrrole C_4Me_4NH gave (η^1-$C_4Me_4N)Sc(CH_2C_6H_4NMe_2\text{-}o)_2$ (**4**) in 64% isolated yield. An X-ray crystallographic study revealed that the pyrrolyl ligand in **4** is in an η^1-N-σ coordination fashion and the scandium atom lies in the pyrrolyl plane with an average deviation of only 0.017 Å (Fig. 1(b)). The Sc(1)–N(3) (pyrrolyl) bond distance in **4** (2.119(3) Å) is much shorter than that in **1** (2.478(2) Å), consistent with the difference in pyrrolyl coordination modes between **4** and **1**. The η^1-bonding fashion of the tetramethylpyrrolyl ligand in **4** is in sharp contrast with what was observed previously in other tetramethylpyrrolyl-coordinated metal complexes such as (η^5-$NC_4Me_4)Ti(SPh)_3$,[8a] (η^5-$NC_4Me_4)TiCl_3$,[8a] (η^5-$NC_4Me_4)TaMe_2Cl_2$,[8b] and $Ru(\eta^5\text{-}NC_4Me_4)_2$,[8c] in which the pyrrolyl ligands all adopted an η^5-bonding mode. As far as we are aware, complex **4** represents the first example of a structurally characterized η^1-bonding tetramethylpyrrolyl complex.



Scheme 1 Synthesis of rare earth metal bis(*o*-dimethylaminobenzyl) complexes bearing mono η^5- and η^1-pyrrolyl ligands.

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† Electronic supplementary information (ESI) available: Experimental details, and scanned NMR spectra of syndiotactic polystyrene. Crystallographic data for CCDC 659963–659966 and 668429. See DOI: 10.1039/b719182k

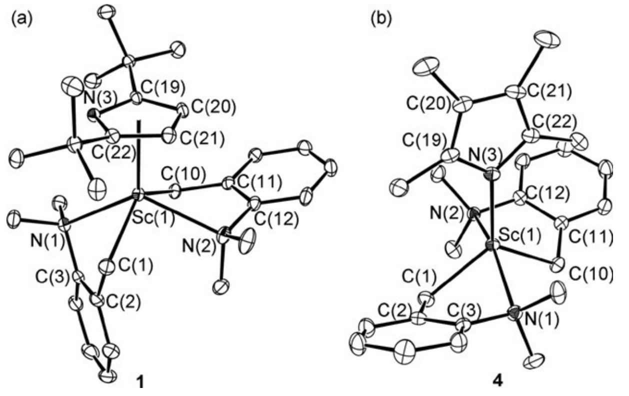


Fig. 1 ORTEP drawings of **1** (a) and **4** (b) with 30% probability of thermal ellipsoids. Selected bond lengths (Å) and angles (°): **1**: Sc(1)–C(1) 2.290(2), Sc(1)–C(10) 2.285(2), Sc(1)–N(1) 2.489(2), Sc(1)–N(2) 2.471(2), Sc(1)–N(3) 2.478(2), Sc(1)–C(19) 2.527(2), Sc(1)–C(20) 2.561(2), Sc(1)–C(21) 2.556(2), Sc(1)–C(22) 2.532(2), Sc(1)–C(1)–C(2) 101.4(2), Sc(1)–C(10)–C(11) 107.7(2). **4**: Sc(1)–C(1) 2.223(4), Sc(1)–C(10) 2.221(4), Sc(1)–N(1) 2.309(3), Sc(1)–N(2) 2.306(3), Sc(1)–N(3) 2.119(3) Sc(1)–C(1)–C(2) 103.2(2), Sc(1)–C(10)–C(11) 105.0(2).

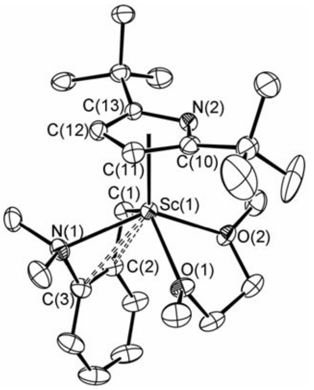
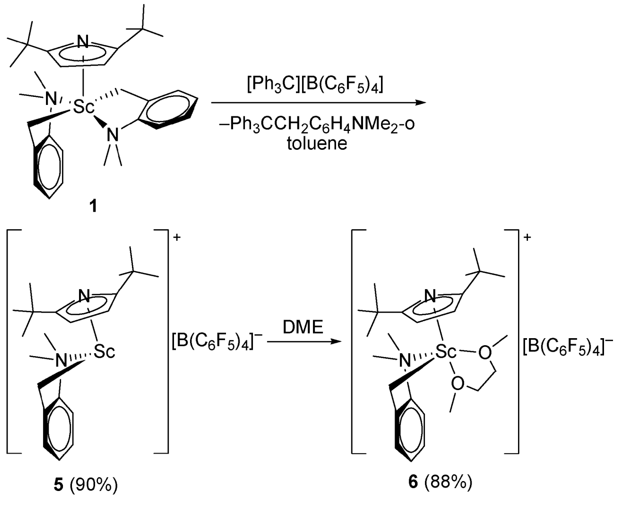


Fig. 2 ORTEP drawing of the cationic part of **6** with 30% probability of thermal ellipsoids. Selected bond lengths (Å): Sc(1)–C(1) 2.228(2), Sc(1)–C(2) 2.654(2), Sc(1)–C(3) 2.751(2), Sc(1)–O(1) 2.242(2), Sc(1)–O(2) 2.216(2), Sc(1)–N(1) 2.368(2), Sc(1)–N(2) 2.382(2), Sc(1)–C(10) 2.482(2), Sc(1)–C(11) 2.541(2), Sc(1)–C(12) 2.523(2), Sc(1)–C(22) 2.453(2) Sc(1)–C(1)–C(2) 89.3(2).

Addition of 1 equiv of $[Ph_3C][B(C_6F_5)_4]$ to **1** in toluene at 25 °C gave the corresponding cationic mono(aminobenzyl) complex $[(2,5\text{-}t\text{-}Bu_2C_4H_2N)Sc(CH_2C_6H_4NMe_2\text{-}o)][B(C_6F_5)_4]$ (**5**) in *ca.* 90% yield (Scheme 2). Recrystallisation of **5** from a mixed hexane–toluene–DME solution afforded single crystals of $[(2,5\text{-}t\text{-}Bu_2C_4H_2N)Sc(CH_2C_6H_4NMe_2\text{-}o)(dme)][B(C_6F_5)_4]$ (**6**). An X-ray diffraction study established that **6** is a separated ion pair that possesses a chelating dme ligand at the Sc centre (Fig. 2). The pyrrolyl ligand is bonded to the Sc atom in an η^5-fashion as observed in its neutral precursor **1**. Because of the greater electron deficiency of the cationic metal centre in **6**, the bond distances of the Sc–pyrrolyl ring bonds in **6** (2.476(2) Å) are significantly shorter than that in **1** (2.531(2) Å), and so are the Sc–benzyl (**6**: 2.228(2) Å, **1**: av. 2.288(2) Å) and Sc–amino (**6**: 2.368(2) Å, **1**: av. 2.480(2) Å) bond distances. Moreover, interactions between the Sc centre and some phenyl atoms of the benzyl group are also observed in **6** (Sc–C2: 2.654(2) Å, Sc–C3: 2.751(2) Å), and therefore, the Sc–C1–phenyl(C2) angle in **6** (89.3(2)°) is significantly smaller than those in **1** (101.4(2) and 107.7(2)°). To our knowledge, complex **6** represents the first example of a structurally characterised cationic pyrrolyl complex for any metal.

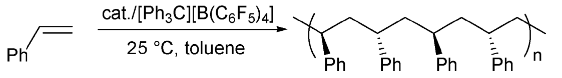
The reaction of the η^1-tetramethylpyrrolyl-ligated complex **4** with 1 equiv of $[Ph_3C][B(C_6F_5)_4]$ in THF afforded $[(C_4Me_4N)Sc(CH_2C_6H_4NMe_2\text{-}o)(thf)_3][B(C_6F_5)_4]$ (**7**), which possessed three thf ligands as shown by ^1H NMR analysis. Attempts to obtain single crystals of **7** were, however, not successful.

In the presence of 1 equiv of $[Ph_3C][B(C_6F_5)_4]$, the scandium bis(aminobenzyl) complex **1** showed high activity for the polymerisation of styrene, yielding syndiotactic polystyrene with high molecular weight and moderate molecular distribution (Table 1, run 1).† The yttrium complex **2** could also produce syndiotactic polystyrene but with much lower activity, whereas the lanthanum analogue **3** showed no activity under the same conditions. These results, including the trend in metal-effect, are comparable with those observed in the case of the $C_5Me_4SiMe_3$-based complexes $(C_5Me_4SiMe_3)$-



Scheme 2 Synthesis of a cationic scandium aminobenzyl complex bearing an η^5-pyrrolyl ligand.

Table 1 Syndiospecific polymerisation of styrene by complexes **1–6**,**8**[a]



Run	Cat.	Ln	t/min	Yield (%)	Activity[b]	sPS	M_n (10^4)[c]	M_w/M_n[c]
1	**1**	Sc	<1	100	>3100	100	14.7	1.99
2	**2**	Y	30	13	17	100	1.7	2.09
3	**3**	La	30	0	—	—	—	—
4	**5**[d]	Sc	<1	100	>3100	100	20.6	1.83
5	**6**[d]	Sc	30	0	—	—	—	
6	**4**	Sc	30	0	—	—	—	
7	**8**	Sc	25	95	118	100	6.8	2.46

[a] Conditions: 25 μmol Ln, 25 μmol $[Ph_3C][B(C_6F_5)_4]$; Ln : monomer = 1 : 500 (mol : mol), V = 7.2 mL (toluene), unless otherwise noted. [b] kg of polymer per mol-Sc h. [c] Determined by GPC in *o*-dichlorobenzene at 145 °C against polystyrene standard. [d] Borate compound was not used.

Ln(CH$_2$SiMe$_3$)$_2$(thf).[2e,9] The isolated cationic benzyl species **5** alone also showed high activity for the syndiospecific polymerisation of styrene, while the neutral complex **1** was inactive under the same conditions. The cationic complex **6** showed no activity, apparently due to the strong coordination of the dme ligand to the metal centre. The η^1-C$_4$Me$_4$N-ligated Sc complex **4** did not show any activity for the polymerisation of styrene either in the presence or absence of [Ph$_3$C][B(C$_6$F$_5$)$_4$]. In comparison, the analogous η^5-tetramethylcyclopentadienyl scandium complex (C$_5$Me$_4$H)Sc(CH$_2$C$_6$H$_4$NMe$_2$-*o*)$_2$ (**8**)[2a] afforded syndiotactic polystyrene in the presence of 1 equiv of [Ph$_3$C][B(C$_6$F$_5$)$_4$] (Table 1, run 7). These results demonstrate that an η^5-π-bonding ligand system is superior to an η^1-bonding analogue for such types of polymerisation catalysts.

In summary, we have demonstrated that the pyrrolyl-ligated rare earth bis(*o*-dimethylaminobenzyl) complexes ranging from the largest La to the smallest Sc can be prepared by the acid–base reaction between the tris(*o*-dimethylaminobenzyl) complexes Ln(CH$_2$C$_6$H$_4$NMe$_2$-*o*)$_3$ and a pyrrole ligand such as 2,5-*t*-Bu$_2$C$_4$H$_2$NH (or C$_4$Me$_4$NH). The reaction of the Sc complex (η^5-2,5-*t*-Bu$_2$C$_4$H$_2$N)Sc(CH$_2$C$_6$H$_4$NMe$_2$-*o*)$_2$ (**1**) with [Ph$_3$C][B(C$_6$F$_5$)$_4$] has afforded the first structurally characterized cationic pyrrolyl–metal complex, [(η^5-2,5-*t*-Bu$_2$C$_4$H$_2$N)Sc(CH$_2$C$_6$H$_4$NMe$_2$-*o*)(dme)][B(C$_6$F$_5$)$_4$] (**6**). The coordination mode (η^1 or η^5) of the pyrrolyl ligands has been found to show a dramatic influence on the polymerisation of styrene.

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Notes and references

‡ **(2,5-*t*-Bu$_2$C$_4$H$_2$N)Sc(CH$_2$C$_6$H$_4$NMe$_2$-*o*)$_2$** (**1**). A THF solution (5 mL) of 2,5-*t*-Bu$_2$C$_4$H$_2$NH (0.540 g, 3.0 mmol) was added to a THF solution (20 mL) of Sc(CH$_2$C$_6$H$_4$NMe$_2$-*o*)$_3$ (1.343 g, 3.0 mmol) at room temperature. After stirring for 12 h at 70 °C, the solvent was removed under reduced pressure. The residue was washed by diethyl ether. Recrystallisation by toluene–hexane gave **1** as yellow crystals (1.329 g, 90%). CCDC 659963. **(2,5-*t*-Bu$_2$C$_4$H$_2$N)Y(CH$_2$C$_6$H$_4$NMe$_2$-*o*)$_2$** (**2**). To a THF solution (6 mL) of Y(CH$_2$C$_6$H$_4$NMe$_2$-*o*)$_3$ (0.492 g, 1.0 mmol) was added a THF solution (4 mL) of 2,5-*t*-Bu$_2$C$_4$H$_2$NH (0.179 g, 1.0 mmol) at room temperature. After stirring overnight at 50 °C, the solvent was removed under reduced pressure. The residue was washed by diethyl ether to give **2** as a light-yellow powder (0.385 g, 72%). Single crystals suitable for X-ray analysis were obtained by recrystallisation from hexane solution. CCDC 668429. **(2,5-*t*-Bu$_2$C$_4$H$_2$N)La(CH$_2$C$_6$H$_4$NMe$_2$-*o*)$_2$** (**3**). To a THF solution (10 mL) of La(CH$_2$C$_6$H$_4$NMe$_2$-*o*)$_3$ (0.542 g, 1.0 mmol) was added a THF solution (5 mL) of 2,5-*t*-Bu$_2$C$_4$H$_2$NH (0.179 g, 1.0 mmol) at room temperature. After stirring for 1 h at room temperature, the solvent was removed under reduced pressure. The residue was washed by hexane and dissolved in 30 mL of toluene. Slow evaporation of solvent gave **3** as orange cubic crystals (0.338 g, 69%). CCDC 659964. **(2,3,4,5-Me$_4$C$_4$N)Sc(CH$_2$C$_6$H$_4$NMe$_2$-*o*)$_2$** (**4**). To a THF solution (20 mL) of Sc(CH$_2$C$_6$H$_4$NMe$_2$-*o*)$_3$ (1.343 g, 3.0 mmol) was added a THF solution (5 mL) of 2,3,4,5-Me$_4$C$_4$NH (0.478 g, 3.3 mmol) at room temperature. After stirring for 12 h at 70 °C, the solvent was removed under reduced pressure. The residue was washed by hexane to give **4** as a yellow powder (0.833 g, 64%). Single crystals suitable for X-ray analysis were obtained from a concentrated hexane solution at −30 °C. CCDC 659965. **[(2,5-*t*-Bu$_2$C$_4$H$_2$N)Sc(CH$_2$C$_6$H$_4$NMe$_2$-*o*)][B(C$_6$F$_5$)$_4$]** (**5**). A toluene solution (10 mL) of **1** (0.246 g, 0.50 mmol) was added to [(Ph$_3$C)][B(C$_6$F$_5$)$_4$] (0.461 g, 0.50 mmol) in toluene (15 mL) at room temperature. After stirring for 5 min, the solvent was removed under reduced pressure. The residue was washed by hexane. Drying under vacuum gave a dark brown powder of **5** (0.471 g, *ca.* 90%) with a small amount of an unidentified impurity. **[(2,5-*t*-Bu$_2$C$_4$H$_2$N)Sc(CH$_2$C$_6$H$_4$NMe$_2$-*o*)(dme)][B(C$_6$F$_5$)$_4$]** (**6**). DME (0.50 mL) was added to a toluene solution (2 mL) of **5** (0.103 g, 0.10 mmol) at room temperature. After stirring for 5 min, the solvent was removed under reduced pressure. The residue was washed by hexane. Drying under vacuum gave **6** (0.101 g, 88%) as an orange powder. Single crystals suitable for X-ray analysis were obtained from a hexane–toluene–DME solution at room temperature. CCDC 659966. **[(2,3,4,5-Me$_4$C$_4$N)Sc(CH$_2$C$_6$H$_4$NMe$_2$-*o*)(thf)$_3$][B(C$_6$F$_5$)$_4$]** (**7**). To a benzene solution (2 mL) of **4** (0.044 g, 0.10 mmol) was added a benzene solution (2 mL) of [(Ph$_3$C)][B(C$_6$F$_5$)$_4$] (0.092 g, 0.10 mmol) at room temperature. After stirring for 5 min, 0.5 mL of THF was added and the solvent was removed under reduced pressure. The residue was washed by hexane. Drying under vacuum gave **7** (0.091 g, 76%) as a dark brown powder with a small amount of an unidentified impurity.

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9 As mentioned previously,[2a] the Ln–CH$_2$C$_6$H$_4$NMe$_2$-*o* unit is as active as Ln–CH$_2$SiMe$_3$ for the initiation of olefin polymerization. After olefin insertion, the benzyl (or alkyl) group will get away from the metal center and show little influence on the propagation.