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Organolanthanide chemistry with bis(trimethylsilyl)methyl- and *tert*-butyldimethylsilyl-substituted cyclopentadienyl ligands. Synthesis and characterisation of tris(cyclopentadienyl)lanthanide(III) complexes, including crystal structures of $[Ln\{\eta^5\text{-}C_5H_4CH(SiMe_3)_2\}_3]$ (Ln = Nd or Tm) and $[Ce\{\eta^5\text{-}C_5H_3(SiMe_2Bu^t)_2\text{-}1,3\}_3]$[☆]

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Abstract

The homoleptic tris(substituted cyclopentadienyl)lanthanide(III) complexes $[LnCp^R_3]$ (Ln = La (**1**), Ce (**2**), Pr (**3**), Nd (**4**), Sm (**5**), Gd (**6**), Tb (**7**), Dy (**8**), Er (**9**), Tm (**10**) and Yb (**11**)], $[NdCp^t_3]$ (**12**), $[CeCp^{tt}_3]$ (**13**) and $[NdCp^{tt}_3]$ (**14**) [$Cp^R = \eta^5\text{-}C_5H_4\{CH(SiMe_3)_2$, $Cp^t = \eta^5\text{-}C_5H_4(SiMe_2Bu^t)$, $Cp^{tt} = \eta^5\text{-}C_5H_3(SiMe_2Bu^t)_2\text{-}1,3$], have been synthesised by the reaction of the anhydrous lanthanide(III) halide with the appropriate sodium or potassium cyclopentadienide in THF. The characterisation of these complexes was established by ^1H-, ^{13}C- and ^{29}Si-NMR spectroscopy (for **1–5** and **12–14**), elemental analysis and mass spectrometry. The early paramagnetic lanthanide complexes **2**–**5**, and **12**–**14** had very sharp ^1H-NMR spectral signals, and the paramagnetic shifts were temperature-dependent. The molecular structures of **4, 10** and **13** have been determined by single crystal X-ray diffraction studies. The attempted syntheses of organoneodymium(II) and organothulium(II) complexes are also described. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Cerium; Cyclopenadienyls; Lanthanides; Neodymium; Thulium; X-rays

1. Introduction

Although tris(cyclopentadienyl)lanthanide complexes with three $[C_5H_5]^-$ ligands have been studied in great detail, the corresponding derivatives with substituted cyclopentadienyl ligands have received less attention [1]. As an important class of organolanthanide compounds, tris(cyclopentadienyl)lanthanide or tris(substituted cyclopentadienyl)lanthanide complexes are used as starting materials for the synthesis of other organolanthanide compounds [2], as reducing agents [3], as catalysts [4], and as precursors for electronic doping materials [5]. In the past, we have extensively investigated 1,3-bis(trimethylsilyl)cyclopentadienyl- (≡Cp″) Ln compounds. We have recently synthesised a series of new $(Me_3Si)_2CH$- and Bu^tMe_2Si-substituted cyclopentadienyl ligands as their alkali metal compounds [6]. We now report the synthesis and characterisation of various tris(cyclopentadienyl)lanthanide(III) derivatives with these ligands, including the X-ray structures of $[Nd\{\eta^5\text{-}C_5H_4CH(SiMe_3)_2\}_3]$, $[Tm\{\eta^5\text{-}C_5H_4CH(SiMe_3)_2\}_3]$ and $[Ce\{\eta^5\text{-}C_5H_3(SiMe_2Bu^t)_2\text{-}1,3\}_3]$.

[☆] Dedicated to Professor Peter Jutzi, an excellent chemist and a good friend to M.F.L., to mark his 60th birthday.

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2. Results and discussion

2.1. Synthesis and characterisation of complexes **1-14**

The reaction of the anhydrous lanthanide(III) chloride or iodide with three equivalents of [bis(trimethylsilyl)methyl]cyclopentadienyl-potassium (≡KCp^R) in THF, followed by removal of the solvent in vacuo and extraction of the residue with hexane, yielded crystalline $[LnCp^R_3]$ in good yield $[Cp^R = \eta^5\text{-}C_5H_4CH(SiMe_3)_2]$ (Eq. (1)).

$$LnX_3 + 3\,KCp^R \xrightarrow{THF} [LnCp^R{}_3] + 3\,KX_3 \qquad (1)$$

X = Cl and Ln = La (**1**), Ce (**2**), Pr (**3**), Nd (**4**), Sm (**5**), Gd (**6**), Tb (**7**), Dy (**8**), Er (**9**) or Yb (**11**); X = I, Ln = Tm (**10**)

Due to the potential importance of neodymium(III) and Ce(III) complexes, possible precursors of organoneodymium(II) or Ce(II) species (see Section 2.3), three other tris(cyclopentadienyl)metal complexes, $[NdCp^t_3]$ (**12**), $[CeCp^{tt}_3]$ (**13**) and $[NdCp^{tt}_3]$ (**14**), were synthesised similarly, from the appropriate lanthanide(III) chloride and $NaCp^t$ or KCp^{tt}, (Eqs. (2,3)) $[Cp^t = \eta^5\text{-}C_5H_4(SiMe_2Bu^t)$, $Cp^{tt} = \eta^5\text{-}C_5H_3(SiMe_2Bu^t)_2\text{-}1,3]$.

$$NdCl_3 + 3\,NaCp^t \xrightarrow{THF} \underset{\mathbf{12}}{[NdCp^t{}_3]} + 3\,NaCl \qquad (2)$$

$$NdCl_3 + 3\,KCp^{tt} \xrightarrow{THF} [LnCp^{tt}{}_3] + 3\,KCl \qquad (3)$$

Ln = Ce (**13**), Nd (**14**)

Complexes **1**–**12** were extremely hydrocarbon-soluble, which allowed them to be easily separated from the by-products (KCl, KI or NaCl) by extraction with hexane rather than by sublimation. Concentration of the hexane solution and cooling to −30°C afforded crystalline products. Unlike **4** and **12**, complexes **13** and **14** were only slightly soluble in hexane and sparingly soluble in toluene. While not every single compound has been examined as to whether it would bind THF, this is unlikely perhaps for steric reasons; in any event, the Ce complex **13** was even recrystallised from THF and the Yb complex **11** (although unusual in being red) did not change colour in THF. In view of the colour, the ^{1}H-NMR spectrum of **11** in C_6D_6 at 20°C was examined. A broad signal centred at δ 29.7 was observed, with no evidence of a diamagnetic Yb(II) impurity.

Complexes **1**–**14** have been characterised by C and H elemental analysis, and, for the most part, by ^{1}H-, ^{13}C- and ^{29}Si-NMR and mass spectroscopy. Due to their $4f^n$ ground state electronic configuration, most lanthanide complexes in the +3 oxidation state are paramagnetic, except those of La^{3+} ($4f^0$) and Lu^{3+} ($4f^{14}$). This sometimes makes their NMR spectroscopic studies difficult. NMR spectral data on paramagnetic lanthanide(III) complexes are quite scant. However, we have found that complexes of the early lanthanides (e.g. **2**, **3**, **4**, **5**, **12** and **13**) showed very sharp ^{1}H-NMR signals, although their chemical shifts varied a great deal, whereas complexes of the middle and late lanthanides, **6**–**11** had very broadened NMR signals which were not readily assigned.

The ^{1}H-NMR spectrum of the diamagnetic ($4f^0$) lanthanum(III) complex **1** was quite similar to that of $LiCp^R$ or KCp^R [6], comprising a singlet at δ 0.14 due to the $SiMe_3$ protons, a singlet at δ 1.72 attributed to the methyne proton, and six resonances centred at δ 5.85 and 6.07 due to the protons of the Cp ring, with $^3J(^1H-^1H) = 2.6$ Hz. The ^{1}H-NMR spectrum of **3** showed two Cp ring proton signals, at δ 31.93 and 11.77, separated by ca. 20 ppm; the $SiMe_3$ proton signal had shifted to δ −15.12.

The ^{1}H-NMR spectral chemical shifts of **2**–**5** showed an almost linear dependence on the reciprocal of the absolute temperature, thus following the Curie–Weiss law. Fig. 1 shows the chemical shifts of the ^{1}H-NMR signals of $[PrCp^R_3]$ (**3**) as a function of temperature. The general features are very similar to those previously observed for $[Pr(\eta^5\text{-}C_5H_4SiMe_3)_3]$ [7].

2.2. The X-ray single crystal structures of $[NdCp^R_3]$ (**4**), $[TmCp^R_3]$ (**10**) and $[CeCp^{tt}_3]$ (**13**)

X-ray quality single crystals were obtained by recrystallisation of $[NdCp^R_3]$ (**4**) or $[TmCp^R_3]$ (**10**) from hexane or of $[CeCp^{tt}_3]$ (**13**) from THF. The molecular structure and the atom numbering schemes of **10** and **13** are shown in Figs. 2 and 3, respectively. Selected bond distances and angles for **4**, **10** and **13** are pre-

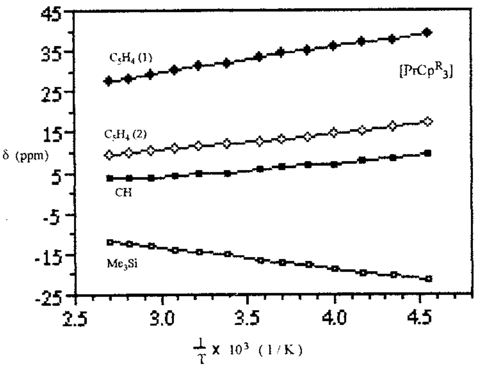


Fig. 1. Chemical shift of the ^{1}H-NMR signals of $[PrCp^R_3]$ (**3**) as a function of temperature (360 MHz, $C_6D_5CD_3$).

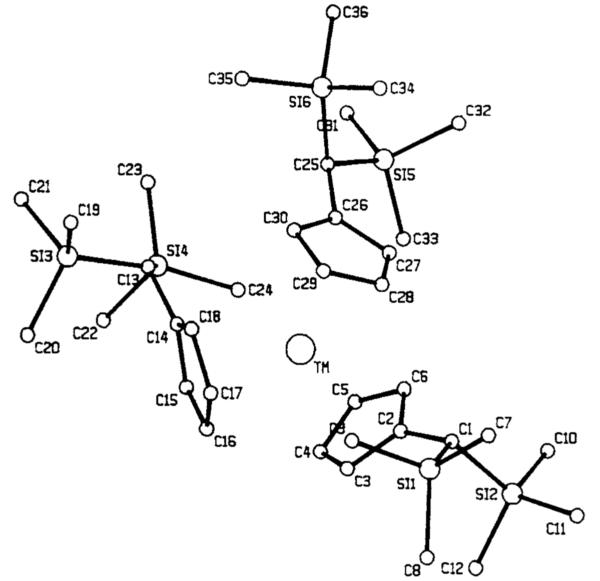


Fig. 2. Molecular structure and atom numbering scheme for [TmCp$_3^R$] (**10**).

sented in Table 1 and fractional atomic coordinates in Tables 2–4, respectively.

Each of the crystalline complexes **4**, **10** and **13** is monomeric; **4** and **10** are isostructural and only **13** has approximate C_3 symmetry. The coordination number of the central metal is 9, if each Cp^R or Cp^{tt} is regarded as occupying three coordination sites. The average Cp–M–Cp (Cp here representing the ring centroid) angle is ca. 120°. Agostic interactions are unlikely; for example in **13**, the shortest Ce···C non-bonding contact is 4.7 Å.

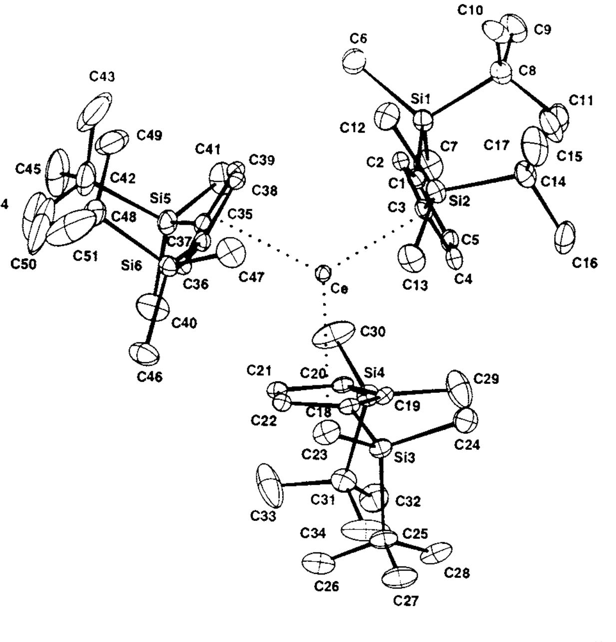


Fig. 3. Molecular structure and atom numbering scheme for [CeCp$_3^{tt}$] (**13**).

Table 1
Selected intramolecular distances (Å) and angles (°) with estimated standard deviations for [NdCp$_3^R$] (**4**), [TmCp$_3^R$] (**10**) and [CeCp$_3^{tt}$] (**13**) [a]

Bonds	**4**	**10**	**13**
Ln–Cp1	2.51	2.39	2.55
Ln–Cp2	2.51	2.39	2.55
Ln–Cp3	2.53	2.42	2.55
C(1)–C(2) av.	1.525(6)	1.518(4)	1.407(6)
C(1)–Si(1) av.	1.884(5)	1.891(3)	1.872(5)
Angles			
Cp1–Ln–Cp2	120.7	121.2	119.4
Cp1–Ln–Cp3	120.7	120.0	121.0
Cp2–Ln–Cp3	117.0	117.9	119.6

[a] Cp1, Cp2 and Cp3 are the centroids of the C(2) to C(6), C(14) to C(18), and C(26) to C(30) cyclopentadienyl rings.

The structures of tris(cyclopentadienyl)lanthanide and tris(substituted cyclopentadienyl)lanthanide complexes have been intensively investigated by X-ray crystallography. Due to their unsaturated character, nearly all the structurally characterised tris(cyclopentadienyl)lanthanide complexes (Ln = Sc [8a], Y [8b], La [9], Pr [10], Nd [11], Sm [12], Er [13], Tm [13] and Lu [14]) are polymers, except for the monomeric [Yb(η^5-C_5H_5)$_3$] [15]. For instance, lanthanum, praseodymium and neodymium complexes form polymeric zigzag chains of distinct (η^5-C_5H_5)$_2$Ln(μ-η^5:η^x-C_5H_5) units (La, $x = 2$ [9a] or 1 [9b]; Pr, $x = 1$-2; Nd, $x = 1$) involving two inequivalent terminal cyclopentadienyl ligands. The samarium derivative crystallises in two different polymeric chains, together with severely disordered cyclopentadienyl ligands. The scandium and lutetium complexes are isostructural, crystallising in chains [(η^5-C_5H_5)$_2$Ln(μ-η^1:η^1-C_5H_5)]$_\infty$ in which (η^5-C_5H_5)$_2$Ln units are bridged in a monohapto fashion by two other cyclopentadienyl ligands.

Structural data for some tris(methylcyclopentadienyl)lanthanide complexes have also been reported, including those of La [16], Ce [17,18], Nd [19] and Yb [20]. The crystalline complexes La(C_5H_4Me)$_3$, Ce(C_5H_4Me)$_3$ and Nd(C_5H_4Me)$_3$ are tetramers, with three pentahapto ligands and one additional, longer monohapto contact. By contrast, crystalline [Yb(η^5-C_5H_4Me)$_3$] is a monomer, due to the small size of Yb. Lanthanide complexes with more sterically demanding substituted cyclopentadienyl ligands are monomeric, e.g. [Ce{η^5-C_5H_3(SiMe$_3$)$_2$-1,3}$_3$] (≡[CeCp$''_3$]) [17], [Ce{η^5-$C_5H_3Bu^t_2$-1,3}$_3$] [18], [SmCp$''_3$] [21], [Sm(η^5-C_5Me_5)$_3$] [22], [La(η^5-C_5Me_4H)$_3$] [23], [Sm(η^5-C_5Me_4H)$_3$] [23], [Tb(η^5-C_5Me_4H)$_3$] [24] and [Nd{η^5-C_5H_2Me(CH$_2$)$_5$}$_3$] [25]. Comparative structural data for some monomeric tris(substituted cyclopentadienyl)lanthanide complexes and the new compounds **4**, **10** and **13** are listed in Table 5. The average Ce–C(Cp) bond length, as well as Ce–Cp(centroid) distances, in **13** are almost indentical to those in [CeCp$''_3$] [17], being shorter than in [Ce{η^5-$C_5H_3Bu^t_2$-1,3}$_3$] [18].

2.3. Attempted synthesis of organoneodymium(II) and organothulium(II) complexes

The chemistry of the lanthanide elements is dominated by the + 3 oxidation state. A multitude of both inorganic and organometallic compounds of the lanthanides in this oxidation state are stable and well established. Although lanthanide(II) halides for almost all the elements in the series are known, only samarium, europium and ytterbium have the + 2 oxidation state chemically accessible in organometallic system under normal conditions. The organolanthanide(II) chemistry of elements other than Sm, Eu and Yb remains essentially unexplored, although an organocerium(II) [26], and an organoneodymium(II) complex [27] have been reported, but these claims remain to be structurally confirmed. X-ray data have been provided for $[TmI_2(DME)_3]$ [28]. We had previously shown that $[LnCp^x_3]$ with K or Li in dimethoxyethane (DME) at ambient temperature gave in high yield the crystalline (X-ray structures) $[\{LnCp^x_2(\mu\text{-}OMe)\}_2]$ $\{Cp^x = \eta^5\text{-}C_5H_3(SiMe_3)_2\text{-}1,3{\equiv}Cp''$ and Ln = La [29], Ce or Nd [30];

Table 2
Fractional atomic coordinates (× 10^4) and equivalent isotropic thermal parameters ($Å^2 \times 10^3$) for $[NdCp^R_3]$ (**4**) [a]

Atom	*x*	*y*	*z*	U_{eq}
Nd	1888.9(2)	2779.0(2)	4798.3(2)	44.1(1)
Si(1)	1487.2(13)	1741.4(11)	7560.5(9)	65(1)
Si(2)	4200.4(14)	2837.0(11)	8639.0(10)	73(1)
Si(3)	1890.0(13)	4193.5(11)	2340.9(10)	70(1)
Si(4)	−933.7(13)	3247.4((11)	1260.6(9)	67(1)
Si(5)	5396.8(12)	2039.7(12)	3661.8(11)	79(1)
Si(6)	3317.9(16)	416.1(13)	2248.0(12)	100(1)
C(1)	3003(4)	2303(3)	7464(3)	55(2)
C(2)	3007(4)	3051(3)	6799(3)	51(2)
C(3)	2241(4)	3741(3)	6613(3)	60(2)
C(4)	2719(5)	4411(3)	6122(3)	76(2)
C(5)	3753(5)	4127(3)	5980(3)	72(2)
C(6)	3928(4)	3295(4)	6384(3)	61(2)
C(7)	972(5)	2434((6)	8463(4)	118(4)
C(8)	235(5)	1630(4)	6431(4)	75(2)
C(9)	1613(6)	506(4)	7864(4)	106(3)
C(10)	4196(6)	2084(5)	9598(4)	107(3)
C(11)	5752(6)	2939(6)	8506(5)	127(4)
C(12)	3933(8)	4046(5)	9024(5)	145(4)
C(13)	530(4)	3274(3)	2263(3)	52(2)
C(14)	224(4)	3229(3)	3185(3)	49(2)
C(15)	−409(4)	2448(3)	3433(3)	53(2)
C(16)	−596(4)	2725(4)	4306(3)	62(2)
C(17)	−113(4)	3676(3)	4593(3)	67(2)
C(18)	401(4)	4003(3)	3916(3)	60(2)
C(19)	3097(5)	4144(4)	3466(4)	83(3)
C(20)	2543(5)	3883(6)	1355(4)	116(4)
C(21)	1555(6)	5444(4)	2343(4)	111(3)
C(22)	−1883(6)	2038(5)	998(4)	109(3)
C(23)	−1806(5)	4131(4)	1611(5)	110(3)
C(24)	−622(6)	3509(6)	141(4)	131(4)
C(25)	3701(4)	1573(3)	3121(3)	63(2)
C(26)	2932(4)	1417(3)	3798(3)	48(2)
C(27)	3348(4)	1304(3)	4754(3)	58(2)
C(28)	2341(4)	962(3)	5047(3)	56(2)
C(29)	1302(4)	872(3)	4275(3)	56(2)
C(30)	1657(4)	1165(3)	3512(3)	52(2)
C(31)	4435(6)	278(5)	1565(4)	136(4)
C(32)	1833(7)	387(7)	1305(5)	164(5)
C(33)	3217(7)	−630(5)	2897(5)	151(4)
C(34)	6252(5)	1056(5)	4092(5)	127(4)
C(35)	5956(5)	2602(5)	2750(4)	108(3)
C(36)	5809(5)	3010(5)	4699(4)	102(3)

[a] U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

Table 3
Fractional atomic coordinates (× 10^4) and equivalent isotropic thermal parameters ($Å^2 \times 10^3$) for $[TmCp^R_3]$ (**10**) [a]

Atom	*x*	*y*	*z*	U_{eq}
Tm	3108.9(1)	7245.0(1)	5163.3(1)	20.66(3)
Si(1)	3562.0(7)	8351.6(6)	2458.3(6)	29.1(2)
Si(2)	858.2(8)	7190.9(6)	1298.4(6)	33.0(2)
Si(3)	5880.8(7)	6742.8(6)	8713.9(6)	30.9(2)
Si(4)	3019.9(8)	5782.2(7)	7634.8(6)	34.7(2)
Si(5)	−475.6(7)	7957.4(7)	6308.8(6)	36.6(2)
Si(6)	1666.4(9)	9569.1(7)	7777.6(7)	45.0(4)
C(1)	2019(3)	7776(2)	2524(2)	28(1)
C(2)	2014(2)	7044(2)	3195(2)	25(1)
C(3)	2776(3)	6321(2)	3370(2)	31(1)
C(4)	2280(3)	5663(2)	3856(2)	38(1)
C(5)	1242(3)	5988(2)	4012(2)	41(1)
C(6)	1070(3)	6829(2)	3606(2)	32(1)
C(7)	3380(3)	9592(3)	2183(3)	48(1)
C(8)	4101(3)	7676(3)	1529(2)	52(1)
C(9)	4845(3)	8449(2)	3612(2)	37(1)
C(10)	−742(3)	6988(3)	1386(3)	64(2)
C(11)	802(3)	7962(3)	349(2)	46(1)
C(12)	1249(4)	6001(3)	901(2)	51(1)
C(13)	4368(2)	6723(2)	7716(2)	26(1)
C(14)	4649(2)	6754(2)	6773(2)	25(1)
C(15)	4419(3)	5975(2)	5999(2)	29(1)
C(16)	4972(3)	6274(2)	5330(2)	32(1)
C(17)	5529(3)	7226(2)	5666(2)	33(1)
C(18)	5355(2)	7523(2)	6558(2)	28(1)
C(19)	6815(3)	7976(3)	9039(3)	53(2)
C(20)	6772(3)	5858(3)	8293(3)	51(1)
C(21)	5611(3)	6434(3)	9836(2)	56(2)
C(22)	3417(4)	4537(3)	7633(3)	57(2)
C(23)	2386(3)	6101(3)	8645(2)	58(2)
C(24)	1746(3)	5787(3)	6489(2)	44(1)
C(25)	1258(3)	8390(2)	6873(2)	30(1)
C(26)	2036(2)	8529(2)	6207(2)	25(1)
C(27)	1620(3)	8665(2)	5233(2)	29(1)
C(28)	2639(3)	9002(2)	4966(2)	30(1)
C(29)	3712(2)	9068(2)	5755(2)	26(1)
C(30)	3346(2)	8768(2)	6517(2)	25(1)
C(31)	−1045(3)	7435(3)	7227(3)	52(1)
C(32)	−1308(3)	8969(3)	5893(3)	57(2)
C(33)	−922(3)	6968(3)	5241(3)	52(2)
C(34)	1757(4)	10608(3)	7124(3)	73(2)
C(35)	3190(4)	9601(4)	8731(3)	81(2)
C(36)	551(4)	9744(3)	8475(3)	62(2)

[a] U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

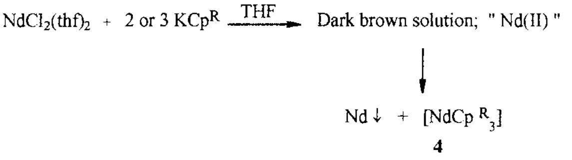
Table 4
Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($Å^2 \times 10^3$) for [CeCp$^{tt}_3$] (**13**) [a]

	x	y	z	U_{eq}
Ce	1032.5 (2)	2316.7 (1)	2157.8 (1)	19 (1)
Si(l)	−1474 (1)	889 (1)	1442 (1)	30 (1)
Si(2)	3087(1)	1139(1)	1254(1)	29(1)
Si(3)	4186(1)	2277(1)	3344(1)	28(1)
Si (4)	−306 (1)	2069 (1)	3695 (1)	30 (1)
Si(5)	−1856(1)	3568(1)	1849(1)	34(1)
Si(6)	2595(1)	3869(1)	1393(1)	28(1)
C(1)	−1 (4)	1155 (2)	1693(2)	27 (1)
C(2)	759 (4)	1305 (2)	1336 (2)	24(1)
C(3)	1874 (4)	1239 (2)	1636 (2)	25(1)
C(4)	1799(4)	1041(2)	2193(2)	27(1)
C(5)	664(4)	993(2)	2232(2)	28(1)
C(6)	−2212(4)	1404(3)	848(2)	45(1)
C(7)	−2271(5)	896(3)	2040(3)	53(2)
C(8)	−1420(4)	29(2)	1163(2)	36(1)
C(9)	−2600 (5)	−246 (3)	998 (3)	57 (2)
C(10)	−847(5)	22(3)	644(2)	50(2)
C(11)	−760(5)	−402(3)	1622(3)	49(1)
C(12)	2611(4)	1432(3)	513(2)	44(1)
C(13)	4385(4)	1583(3)	1578(2)	47(1)
C(14)	3455(4)	250(2)	1244(2)	40(1)
C(15)	2415 (5)	−158 (3)	1051 (3)	63 (2)
C(16)	3996(5)	22(3)	1842(3)	58(2)
C(17)	4278(6)	139(3)	841(3)	71(2)
C(18)	2651(4)	2421(2)	3170(2)	26(1)
C(19)	1826(3)	2015(2)	3320(2)	24(1)
C(20)	811(4)	2351(2)	3308(2)	24(1)
C(21)	1022(4)	3004(2)	3153(2)	26(1)
C(22)	2127(4)	3043(2)	3067(2)	26(1)
C(23)	4939(4)	2810(3)	2910(2)	42(1)
C(24)	4542(4)	1413(3)	3221(2)	41(1)
C(25)	4646(4)	2465(3)	4131(2)	36(1)
C(26)	4235(5)	3131(3)	4275(2)	52(2)
C(27)	5923(4)	2452(3)	4284(2)	54(2)
C(28)	4177(4)	1960(3)	4487(2)	48(1)
C(29)	−126(6)	1181(3)	3828(3)	66(2)
C(30)	−1751(5)	2207(4)	3310(3)	72(2)
C(31)	−95(4)	2496(3)	4399(2)	38(1)
C(32)	−831(5)	2203(3)	4788(2)	52(2)
C(33)	−397(8)	3211(3)	4323(3)	97(3)
C(34)	1133(6)	2447(4)	4690(3)	86(3)
C(35)	−497(4)	3295(2)	1680(2)	26(1)
C(36)	535(4)	3627(2)	1829(2)	26(1)
C(37)	1303(4)	3425(2)	1497(2)	24(1)
C(38)	736(4)	2944(2)	1114(2)	25(1)
C(39)	−347(4)	1873(2)	1227(2)	26(1)
C(40)	−1675(5)	3900(3)	2584(3)	57(2)
C(41)	−2889(4)	2898(3)	1771(3)	49(1)
C42)	−2412(5)	4242(3)	1339(3)	60(2)
C(43)	−2509(11)	4010(5)	743(4)	158(6)
C(44)	−1676(6)	4840(4)	1438(4)	96(3)
C(45)	−3579(5)	4442(3)	1444(4)	98(3)
C(46)	3223(5)	4323(3)	2045(2)	52(2)
C(47)	3629(4)	3288(3)	1217(3)	50(1)
C(48)	2200(5)	4456(3)	780(2)	46(1)
C(49)	1679(7)	4113(4)	251(3)	83(2)
C(50)	1444(11)	4959(5)	930(4)	162(6)
C(51)	3274(8)	4765(5)	655(4)	135(5)

[a] U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

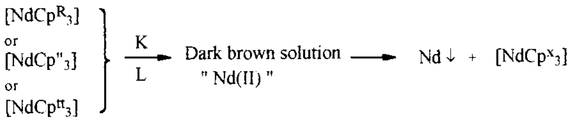
or Cp^x = η^5-$C_5H_3Bu^t_2$-1,3 and Ln = Ce [30]} or [NdCp$''_2$(μ-OMe)$_2$Li(DME)] [30]. In these reactions, LnCp$^x_2$ species were postulated to have been key intermediates [30], which for the case of the La experiment was confirmed by EPR spectroscopy [29]. Furthermore, [LnCp$''_3$] with K or C_8K and [18]-crown-6 in benzene at ambient temperature gave the X-ray-characterised salt [K([18]-crown-6)][LnCp$''_2$(C_6H_6)] (Ln = La or Ce), the anion containing the 1,4-cyclohexa-2,5-dienyl-ligated LnCp$''_2$ [31]. From [La(η^5-$C_5H_3Bu^t_2$-1,3)$_9$] and K with [18]-crown-6 in benzene, thus was obtained the X-ray characterised K([18]-crown-6)(η^2-C_6H_6)$_2$[{La(η^5-C_5H_3-Bu^t_2-1,3)$_2$}$_2$(μ-C_6H_6)] [32].

One of our present objectives was to synthesise and structurally characterise organoneodymium(II) and organothulium(II) complexes by using sterically demanding substituted cyclopentadienyl ligands. Reaction of $NdCl_2(THF)_2$ [33] with two or three equivalents of $KC_5H_4CH(SiMe_3)_2$ (≡KCp^R) in THF yielded a dark brown solution. After filtration and extraction with toluene, the extract was set aside at −30°C for several days. A black precipitate (Nd metal) resulted and the solution changed to blue, from which [NdCp$^R_3$] (**4**) was isolated. We believe that the dark brown solution may have contained a Nd(II) species, such as [K(THF)$_n$][Nd^{II}Cp$^R_2$Cl], [K(THF)$_n$][Nd^{II}Cp$^R_3$], [K(THF)$_n$]$_2$[Nd^{II}Cp$^R_2$Cl$_2$] or [K(THF)$_n$]$_2$[Nd^{II}Cp$^R_3$Cl], which gradually disproportionated to Nd and the homoleptic Nd(III) species (Eq. (4)).



(4)

Reduction of [NdCp$^R_3$] (**4**), [NdCp$''_3$] [30] or [NdCp$^{tt}_3$] (**14**) with potassium in THF also yielded a dark brown solution, which gradually decomposed to precipitate the black Nd metal and the appropriate tris(cyclopentadienyl)neodymium(III) complexes, Eq. (5). Addition of a neutral donor ligand, such as DME, TMEDA, PMDETA or [18]-crown-6, to the reaction systems also failed to stabilise the Nd(II) intermediates. The dark brown precipitate from **14** may have been an ionic species, since it was insoluble in pentane or hexane, sparingly soluble in toluene and very soluble in THF. Attempts to stabilise and isolate a Nd(II) species by adding [NBu^n_4][BF_4] to the "reduced" reaction mixture from **4** were also unsuccessful.



(5)

Table 5
Selected structural data on homoleptic monomeric tris(cyclopentadienyl)lanthanide complexes

Compounds	Ln–C(Cp)$_{av}$	Ln–Cent (Cp)	Cent–Ln–Cent	Reference
$[Yb(\eta^5\text{-}C_5H_5)_3]$	2.639	2.351, 2.359, 2.348	119.5, 120.5, 119.8	[15]
$[Yb(\eta^5\text{-}C_5H_4Me)_3]$	2.64	2.38, 2.38, 2.29	109.6, 121.4, 128.9	[19]
$[La(\eta^5\text{-}C_5Me_4H)_3]$	2.84(6)	2.616(6)	120(av)	[22]
$[Sm(\eta^5\text{-}C_5Me_4H)_3]$	2.76(2)	2.489(6)	120(av)	[22]
$[Tb(\eta^5\text{-}C_5Me_4H)_3]$	2.712(11)	2.445(5)	120(av)	[23]
$[Sm(\eta^5\text{-}C_5Me_5)_3]$	2.82(5)	–	120(av)	[21]
$[Ce\{\eta^5\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}_3]$	2.83	2.575, 2.579, 2.542	119.6, 119.6, 120.4	[17]
$[Ce\{\eta^5\text{-}C_5H_3Bu^t_2\text{-}1,3\}_3]$	2.86	2.59(av)	120(av)	[18]
$[Sm\{\eta^5\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}_3]$	2.76	2.484, 2.522, 2.473	119.9, 120.1, 120.0	[21]
$[Nd\{\eta^5\text{-}C_5H_2Me(CH_2)_5\}_3]$	2.779(2)	2.517, 2.502, 2.514	120.47, 119.47, 120.01	[25]
$[NdCp^R_3]$ (**4**)	2.783	2.512, 2.506, 2.533	120.7, 120.6, 117.0	This work
$[TmCp^R_3]$ (**10**)	2.678	2.39, 2.39, 2.42	121.2, 120.0, 177.9	This work
$[CeCp^{tt}_3]$ (**13**)	2.82	2.553, 2.545, 2.553	119.4, 121.0, 119.6	This work

The Nd complex **4** was allowed to react with lithium powder, but the reduction was slow; the result was similar to that observed with potassium. The reaction of yellow $[TmCp^R_3]$ (**10**) with potassium in THF gave a brown solution. As in the neodymium systems, the latter was unstable and readily decomposed, yielding a black precipitate (Tm). The attempted synthesis of a Tm(II) compound, using procedures similar to those described above for Nd(II), were also unsuccessful.

3. Experimental

3.1. Materials and procedures

All manipulations were carried out under vacuum or argon by Schlenk techniques. Solvents were dried and distilled over sodium–potassium alloy under argon prior to use. The following compounds were prepared by known procedures: $LnCl_3$ [34], TmI_3 [35], $NdCl_2(THF)_2$ [32], KCp^R [6], $NaCp^t$ [6], KCp^{tt} [6]. Others were purchased, and purified by standard procedures. Microanalyses were carried out by Medac (Brunel University). NMR spectra were recorded with Bruker WM250, WM360 or WM500 instruments. Melting points were determined in sealed capillaries under an atmosphere of argon and are uncorrected. Mass spectra were recorded on a VG Autospec mass spectrometer operating in the EI mode at 70 eV.

*3.2. Synthesis of $[LaCp^R_3]$ (**1**) $[Cp^R = \eta^5\text{-}C_5H_4CH(SiMe_3)_2]$*

A solution of KCp^R (2.4 g, 9.14 mmol) in THF (50 ml) was added to a stirred suspension of $LaCl_3$ (0.73 g, 2.98 mmol) in THF (100 ml). The mixture was stirred for 20 h at room temperature and then refluxed for 8 h, giving a slightly cloudy yellow suspension, which was then filtered. The solvent was removed from the filtrate in vacuo and the resultant solid residue was dried at 50°C in vacuo for 1 h to yield a pale white solid, which was extracted into hexane (ca. 50 ml) and filtered. The filtrate was concentrated and its volume was reduced under vacuum to ca. 3 ml. Cooling to −30°C afforded colourless crystals of compound **1** (1.85 g, 77%). M.p. (dec.) 162–164°C. Anal. Calc. for $C_{36}H_{69}LaSi_6$: C, 53.2; H, 8.59. Found: C, 52.2; H, 8.59%. ^{1}H-NMR: (C_6D_6, 20°C): δ 0.14 (s, 18H, $SiMe_3$); 1.72 (s, 1H, CH); 5.86 (t, 2H, Cp ring) and 6.08 (t, 2H, Cp ring). ^{13}C-NMR (C_6D_6, 20°C): δ 1.24 ($SiMe_3$); 21.03 (CH); 113.22, 114.61 and 130.51 (Cp ring). ^{29}Si-NMR (C_6D_6, 20°C): δ 2.1.

*3.3. Synthesis of $[CeCp^R_3]$ (**2**)*

The reaction of KCp^R (5.64 g, 21.5 mmol) and $CeCl_3$ (1.6 g, 6.49 mmol), using the procedure described for **1**, afforded red crystals of compound **2** (4.55 g, 87%). M.p. (dec.) 157–160°C. Anal. Calc. for $C_{36}H_{69}CeSi_6$: C, 53.4; H, 8.58. Found: C, 53.0; H, 8.55%. ^{1}H-NMR: ($C_6D_5CD_3$, 22°C): δ −5.36 (s, 18H, $SiMe_3$); 2.87 (s, 1H, CH); 8.61 (s, 2H, Cp ring) and 15.07 (s, 2H, Cp ring). ^{13}C-NMR ($C_6D_5CD_3$, 22°C): δ −5.81 ($SiMe_3$); 17.32 (CH); 165.38, 166.22 and 166.85 (Cp ring). ^{29}Si-NMR ($C_6D_5CD_3$, 22°C): δ 5.1.

*3.4. Synthesis of $[PrCp^R_3]$ (**3**)*

The reaction of KCp^R (1.35 g, 5.15 mmol) and $PrCl_3$ (0.42 g, 1.72 mmol), using the procedure described for **1**, afforded green–yellow crystals of compound **3** (1.06 g, 76%). M.p. (dec.) 147–150°C. Anal. Calc. for $C_{36}H_{69}PrSi_6$: C, 53.3; H, 8.57. Found: C, 52.9; H, 8.60%. ^{1}H-NMR: ($C_6D_5CD_3$, 22°C): δ −15.12 (s, 18H, $SiMe_3$); 4.94 (s, 1H, CH); 11.77 (s, 2H, Cp ring) and 31.93 (s, 2H, Cp ring). ^{13}C-NMR ($C_6D_5CD_3$, 22°C): δ −15.73 ($SiMe_3$); 8.22 (CH); 225.39, 266.49 and 271.635 (Cp ring). ^{29}Si-NMR ($C_6D_5CD_3$, 22°C): δ 16.8.

3.5. Synthesis of [NdCp$^R_3$] (**4**)

The reaction of KCp^R (17.1 g, 64.95 mmol) and NdCl$_3$ (4.75 g, 19.0 mmol), using the procedure described for **1**, afforded blue crystals of compound **4** (11.24 g, 73%). M.p. (dec.) 155–157°C. Anal. Calc. for $C_{36}H_{69}NdSi_6$: C, 53.1; H, 8.54. Found: C, 52.1; H, 8.73%. ^{1}H-NMR: ($C_6D_5CD_3$, 22°C): δ −9.31 (s, 18H, SiMe$_3$); 5.42 (s, 1H, CH); 1.76 (s, 2H, Cp ring) and 14.23 (s, 2H, Cp ring). ^{13}C-NMR ($C_6D_5CD_3$, 22°C): δ −13.52 (SiMe$_3$); 2.58 (CH); 238.42 (br) and 230.46 (Cp ring). ^{29}Si-NMR ($C_6D_5CD_3$, 22°C): δ 28.8.

3.6. Synthesis of [SmCp$^R_3$] (**5**)

The reaction of KCp^R (2.8 g, 10.66 mmol) and SmCl$_3$ (0.91 g, 3.54 mmol), using the procedure described for **1**, afforded orange crystals of compound **5** (1.91 g, 67%). M.p. (dec.) 136–139°C. Anal. Calc. for $C_{36}H_{69}Si_6Sm$: C, 52.7; H, 8.47. Found: C, 52.2; H, 8.44%. ^{1}H-NMR: ($C_6D_5CD_3$, 22°C): δ −2.73 (s, 18H, SiMe$_3$); 0.08 (s, 1H, CH); 14.52 (s, 2H, Cp ring) and 17.60 (s, 2H, Cp ring). ^{13}C-NMR ($C_6D_5CD_3$, 22°C): δ −0.98 (SiMe$_3$); 28.45 (CH); 105.00, 108.00 and 127.62 (Cp ring). ^{29}Si-NMR ($C_6D_5CD_3$, 22°C: δ −12.2.

3.7. Synthesis of [GdCp$^R_3$] (**6**)

The reaction of KCp^R (1.30 g, 4.95 mmol) and GdCl$_3$ (0.39 g, 1.48 mmol), using the procedure described for **1**, afforded yellow crystals of compound **6** (1.05 g, 85%). M.p. (dec.) 140–142°C. Anal. Calc. for $C_{36}H_{69}GdSi_6$: C, 52.2; H, 8.40. Found: C, 51.9; H, 8.38%. MS: *m*/*e* 828 ([*M*]$^+$, 0.06%); 813 ([*M*−Me]$^+$, 0.06%); 604 ([GdCp$^R_2$]$^+$, 38%); 224 ([Cp^R]$^+$, 27%); 73 ([SiMe$_3$]$^+$, 100%).

3.8. Synthesis of [TbCp$^R_3$] (**7**)

The reaction of KCp^R (1.75 g, 6.67 mmol) and TbCl$_3$ (0.53 g, 2.0 mmol), using the procedure described for **1**, afforded yellow crystals of compound **7** (0.95 g, 57%). M.p. (dec.) 138–140°C. Anal. Calc. for $C_{36}H_{69}Si_6Tb$: C, 52.1; H, 8.39. Found: C, 51.6; H, 8.43%. MS: *m*/*e* 829 ([*M*]$^+$, 0.10%); 814 ([*M*−Me]$^+$, 0.12%); 605 ([TbCp$^R_2$]$^+$, 100%); 224 ([Cp^R]$^+$, 22%); 73 ([SiMe$_3$]$^+$, 93%).

3.9. Synthesis of [DyCp$^R_3$] (**8**)

The reaction of KCp^R (4.3 g, 16.38 mmol) and DyCl$_3$ (1.42 g, 5.28 mmol), using the procedure described for **1**, afforded yellow crystals of compound **8** (3.67 g, 84%). M.p. (dec.) 139–141°C. Anal. Calc. for $C_{36}H_{69}DySi_6$: C, 51.5; H, 8.35. Found: C, 51.4; H, 8.35%. MS: *m*/*e* 832 ([*M*]$^+$, 0.07%); 817 ([*M*−Me]$^+$, 0.11%); 608 ([DyCp$^R_2$]$^+$, 54%); 224 ([Cp^R]$^+$, 20%); 73 ([SiMe$_3$]$^+$, 100%).

3.10. Synthesis of [ErCp$^R_3$] (**9**)

The reaction of KCp^R (2.5 g, 9.52 mmol) and ErCl$_3$ (0.80 g, 2.92 mmol), using the procedure described for **1**, afforded orange crystals of compound **9** (1.2 g, 49%). M.p. (dec.) 140–142°C. Anal. Calc. for $C_{36}H_{69}ErSi_6$: C, 51.6; H, 8.30. Found: C, 51.0; H, 8.26%. MS: *m*/*e* 838 ([*M*]$^+$, 0.08%); 614 ([ErCp$^R_2$]$^+$, 90%); 224 ([Cp^R]$^+$, 7%); 73 ([SiMe$_3$]$^+$, 100%).

3.11. Synthesis of [TmCp$^R_3$] (**10**)

The reaction of KCp^R (0.92 g, 3.50 mmol) and TmI$_3$ (0.75 g, 1.08 mmol), using the procedure described for **1**, afforded orange crystals of compound **10** (0.48 g, 53%). M.p. (dec.) 130–135°C. Anal. Calc. for $C_{36}H_{69}Si_6Tm$: C, 51.5; H, 8.29. Found: C, 50.5; H, 8.29%.

3.12. Synthesis of [YbCp$^R_3$] (**11**)

The reaction of KCp^R (1.90 g, 7.23 mmol) and YbCl$_3$ (0.61 g, 2.2 mmol), using the procedure described for **1**, afforded dark red crystals of compound **11** (0.6 g, 32%). M.p. (dec.) 130–134°C. Anal. Calc. for $C_{36}H_{69}Si_6Yb$: C, 51.3; H, 8.24. Found: C, 50.6; H, 8.24%.

3.13. Synthesis of [NdCp$^t_3$] (**12**)

A solution of NaCp^t (1.4 g, 7.7 mmol) in THF (50 ml) was added to a stirred suspension of NdCl$_3$ (0.5 g, 2.0 mmol) in THF (100 ml). The mixture was stirred for 2 days at room temperature, giving a green suspension, which was then filtered. The solvent was removed from the filtrate in vacuo and the resultant solid residue was dried at 50°C in vacuo for 1 h and then extracted into hexane (50 ml). The extract was filtered and the filtrate concentrated to ca. 5 ml. Cooling to −30°C afforded green crystals of compound **12** (1.1 g, 80%). M.p. (dec.) 122–125°C. Anal. Calc. for $C_{33}H_{66}NdSi_3$: C, 58.1; H, 8.42. Found: C, 58.2; H, 8.70%. ^{1}H-NMR: ($C_6D_5CD_3$, 20°C): δ 0.84 (s, 9H, CMe$_3$); −14.36 (s, 6H, SiMe$_2$); 20.03 (s, 2H, Cp ring) and −8.87 (s, 2H, Cp ring). ^{13}C-NMR ($C_6D_5CD_3$, 20°C: δ 24.55 [$\mathbf{C}(CH_3)_3$]; 27.00 [$C(\mathbf{C}H_3)_3$]; −23.4 (SiMe$_2$); 250.42, 240.84 and 228.70 (Cp ring). ^{29}Si-NMR ($C_6D_5CD_3$, 20°C: δ 52.6.

3.14. Synthesis of [CeCp$^{tt}_3$] (**13**)

KCp^{tt} (3.43 g, 10 mmol) was added by portions to a stirred suspension of the colourless CeCl$_3$ (0.82 g, 3.33

mmol) in THF (100 ml). The mixture was stirred for 12 h at room temperature. The green mixture was refluxed for 7 h. The THF was removed in vacuo and toluene (100 ml) was added to the residue. The mixture was heated under reflux for 7 h, filtered and the blue–green filtrate concentrated in vacuo to ca. 10 ml. Cooling to −20°C gave blue–green crystals of compound **13** (2.65 g, 78%). X-ray quality crystals of **13** were obtained by crystallisation from THF at room temperature. Anal. Calc. for $C_{51}H_{99}CeSi_6$: C, 60.1; H, 9.71. Found: C, 59.8; H, 9.44%. ^{1}H-NMR (C_6D_6, 21°C): δ 30.18 (brs, 1H, Cp ring), 18.02 (brs, 2H, Cp ring), 2.57 (s, 18H, CMe_3), −2.44 (s, 6H, $SiMe_2$), −12.29 (s, 6H, $SiMe_2$). MS: *m/e* 1019 ($[M]^+$, 0.3%), 1004 ($[M{-}Me]^+$, 0.5%), 962 ($[M{-}Bu^t]^+$, 1.2%), 904 ($[M{-}SiMe_2Bu^t]^+$, 4.3%), 726 ($[CeCp^{tt}_2]^+$, 70%), 293 ($[Cp^{tt}]^+$, 22%), 237 ($[Cp^{tt}{-}Bu^t]^+$, 86%), 73 ($[SiMe_3]^+$, 100%).

3.15. *Synthesis of [NdCp$^{tt}_3$]* (**14**)

A solution of KCp^{tt} (5.6 g, 16.87 mmol) in THF (100 ml) was added to a stirred suspension of $NdCl_3$ (1.4 g, 5.6 mmol) in THF (100 ml). The mixture was stirred for 2 days at room temperature and then refluxed for 8 h, giving a green suspension, which was then filtered. The solvent was removed from the filtrate in vacuo and the resultant solid residue was dried at 50°C in vacuo for 1 h to yield a green solid which was extracted into toluene (100 ml). The extract was filtered and concentrated to ca. 10 ml. Cooling to −30°C afforded green crystals of compound **13** (3.7 g, 65%). Anal. Calc. for $C_{51}H_{99}NdSi_6$: C, 59.8; H, 9.67. Found: C, 58.9; H, 8.56%. ^{1}H-NMR: ($C_6D_5CD_3$, 22°C): δ 4.40 (s, 18H, CMe_3); −17.93 (s, 6H, $SiMe_2$); −2.62 (s, 6H, $SiMe_2$); 15.25 (s, 2H, Cp ring) and 34.90 (s, 2H, Cp ring). MS: *m/e* 1024 ($[M]^+$, 0.01%); 1009 ($[M{-}Me]^+$, 0.3%); 967 ($[M{-}Bu^t]^+$, 4%); 731 ($[NdCp^{tt}_2]^+$, 100%); 237 ($[Cp^{tt}{-}Bu^t]^+$, 15%); 73 ($[SiMe_3]^+$, 62%).

3.16. *Reaction of NdCl$_2$(THF)$_2$ with 2 KCp^R*

A solution of KCp^R (1.6 g, 6.09 mmol) in THF (20 ml) was added to a suspension of $NdCl_2(THF)_2$ (1.06 g, 3.05 mmol) in THF (30 ml). The mixture was stirred at room temperature for 2 days, leaving a dark brown solution and a black precipitate which was filtered off. The solvent was removed from the filtrate in vacuo to give a dark brown solid which was extracted with toluene (3 × 20 ml) and filtered. The filtrate was concentrated in vacuo to ca. 5 ml and cooled at −30°C. Over the course of 2 days, the brown colour of the solution gradually changed to light blue and a fine black powder (Nd metal) was precipitated. After filtration, crystalline $[NdCp^R_3]$ **4** (0.5 g) was isolated from the filtrate.

3.17. *Reaction of NdCl$_2$(THF)$_2$ with 3KCp^R*

Reaction of $NdCl_2(THF)_2$ (0.7 g, 2.0 mmol) with KCp^R (1.6 g, 6.0 mmol), in a similar fashion, yielded Nd and $[NdCp^R_3]$ (**4**) (0.4 g).

3.18. *Reduction of [NdCp$^R_3$]* (**4**) *with K in tetrahydrofuran*

Potassium (0.05 g, 1.28 mmol) was heated under vacuum, forming a potassium mirror on the wall of a Schlenk tube. The light blue solution of **4** (1.05 g, 1.28 mmol) in THF (30 ml) was slowly introduced into a Schlenk tube. There was an immediate change from blue to brown. The mixture was stirred at room temperature for 24 h, leaving a dark brown solution; all of the potassium had disappeared. The solution was concentrated to ca. 5 ml and cooled to −30°C. After one week, a black precipitate had formed and the brown solution had changed to light blue, from which crystalline **4** (0.5 g) was isolated.

3.19. *Reduction of [NdCp$^R_3$]* (**4**) *with K in the presence of DME, TMEDA, PMDETA, [18]-crown-6 or [NBu$^n_4$][BF$_4$]*

Five parallel reduction reactions of **4** with potassium in THF in the presence of DME, TMEDA, PMDETA, [18]-crown-6 or $[NBu^n_4][BF_4]$ were performed in a similar way as for the previous reaction. In each case, **4** (ca. 0.8 g, 1.0 mmol) was reacted with a stoichiometric amount of potassium and an excess of the neutral donor. The final products were Nd and **4** (ca. 0.3–0.5 g).

3.20. *Reduction of [NdCp$^{tt}_3$]* (**14**) *with K in THF*

The reduction of **14** (1.2 g, 1.2 mmol) with potassium (0.045 g, 1.15 mmol) in THF occured in a similar way as described in Section 3.18, and resulted in the formation of Nd and **14** (0.6 g).

3.21. *Reduction of [NdCp$''_3$] with K in tetrahydrofuran*

The reduction of $[NdCp''_3]$ (1.0 g, 1.3 mmol) with K (0.05 g, 1.13 mmol) in THF occured in a similar fashion as described in Section 3.18, and yielded Nd and $[NdCp''_3]$ (0.45 g).

3.22. *X-Ray structure determination of crystalline* **4**, **10** *and* **13**

Data were measured on an Enraf–Nonius CAD4 diffractometer using monochromated Mo–K$_\alpha$ radiation. A crystal of compound **4** was sealed in a capillary under argon; crystals of compounds **10** and **13** were

Table 6
X-ray crystal structure details

	$[NdCp^R_3]$ (**4**)	$[TmCp^R_3]$ (**10**)	$[CeCp^{tt}_3]$ (**13**)
Empirical formula	$C_{36}H_{69}NdSi_4$	$C_{36}H_{69}Si_4Tm$	$C_{51}H_{99}Si_6Ce$
M	814.7	839.4	1021.0
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P2_1/n$ (no. 14)
a, b, c (Å)	11.597(3), 14.223(4), 14.903(2)	11.426(2), 14.127(4), 14.711(3)	12.206(5), 20.687(8), 23.993(6)
α, β, γ (°)	95.84(2), 106.87(1), 97.59(2)	97.24(2), 107.57(2), 96.46(2)	100.52(3)
U (Å^3), Z, D_c (g cm^{-3})	2306.2, 2, 1.17	2217.1, 2, 1.26	5957(4), 4, 1.14
T (K)	298	173	173
F(000)	858	876	2188
μ(Mo–K$_\alpha$) (cm^{-1})	13.0	22.02	9.1
Crystal size (mm^3)	$0.45 \times 0.35 \times 0.15$	$0.4 \times 0.3 \times 0.3$	$0.4 \times 0.4 \times 0.1$
Total unique reflections	4294 ($2 < \theta < 20°$)	7793 ($2 < \theta < 25°$)	10466 ($2 < \theta < 25°$)
Significant reflections [$I > 2\sigma(I)$]	3795	7177	8407
R, R' [a], or wR_2 [b]	0.027, 0.032	0.023, 0.027 [a]	0.046, 0.120

[a] $R = \Sigma(|F_o - |F_c|) = \Sigma(|F_o|)$; $R' = [\Sigma w(|F_o| - |F_o|)^2 = \Sigma w(|F_o|)^2]^{1/2}$, for $I = 2\sigma(I)$.
[b] $wR_2 = [\Sigma w(|F_o|^2 - |F_c|^2)^2 = \Sigma w(|F_o|^2)^2]^{1/2}$ for all data.

coated in oil and cooled. Corrections for absorption were made using DIFABS [36] for **4** and **10**, and using psi-scan measurements for **13**.

Structure solutions were made using SHELXS-86 [37]. For **4** and **10** refinement was based on F, with H atoms fixed at idealised positions, using programs from the Enraf–Nonius MOLEN package. For **13**, refinement was based on F^2, with H atoms in riding mode, using SHELXL-93 [38].

Further details are given in Table 6. Tables of atom positions and thermal parameters have been deposited at CCDC.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre for compounds **4**, **10** and **13**. Copies of the information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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