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Journal of Organometallic Chemistry 499 (1995) 213–219

Journal of Organometallic Chemistry

Activation of a C–O bond by reaction of a tris(cyclopentadienyl)lanthanide complex with an alkali metal in dimethoxyethane (DME); crystal structures of $[\mathrm{Nd}\{\eta\text{-}\mathrm{C_5H_3(SiMe_3)_2}\text{-}1,3\}_2(\mu\text{-}\mathrm{OMe})_2\mathrm{Li(DME)}]$ and $[\{\mathrm{Ce}(\eta\text{-}\mathrm{C_5H_3{}^tBu_2}\text{-}1,3)_2(\mu\text{-}\mathrm{OMe})\}_2]$ ☆

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Received 29 March 1995

Abstract

The reaction of $[\mathrm{LnCp''_3}]$ [Ln = Ce, Cp″ = η-$\mathrm{C_5H_3{}^tBu_2}$-1,3 or η-$\mathrm{C_5H_3(SiMe_3)_2}$-1,3; or Ln = Nd and Cp″ = η-$\mathrm{C_5H_3(SiMe_3)_2}$-1,3] with metallic lithium or potassium in dimethoxyethane (DME) at ambient temperature gave in high yield $[\{\mathrm{LnCp''_2}(\mu\text{-OMe})\}_2]$ [Ln = Ce and Cp″ = η-$\mathrm{C_5H_3(SiMe_3)_2}$-1,3 (**1**) or η-$\mathrm{C_5H_3{}^tBu_2}$-1,3 (**2**); or Ln = Nd and Cp″ = η-$\mathrm{C_5H_3(SiMe_3)_2}$-1,3 (**3**)] or $[\mathrm{NdCp''_2}(\mu\text{-OMe})_2\mathrm{Li(DME)}]$ (Cp″ = η-$\mathrm{C_5H_3(SiMe_3)_2}$-1,3) (**4**). The crystal structures of complexes **2** and **4** are reported. Complex **4** is the first structurally characterized heterobimetallic lanthanocene-alkoxo-lithium.

Keywords: Cerium; Silicon; Cyclopentadienyl; Neodymium; C–O cleavage; Crystal structure

1. Introduction

There is growing interest in the organic chemistry of the lanthanides (Ln). The oxidation state +3 is ubiquitous, and organic Ln(II) compounds are well known only for Sm (f^6), Eu (f^7) and Yb (f^{14}), although there are references to Ce(II) [1] and Nd(II) compounds [2]. The organoLn(II) compounds are often obtained by reduction of an appropriate Ln(III) precursor [3–11], usually with an alkali metal as a one-electron reducing agent.

Lanthanocene(III) alkoxides and yttrium analogues are known [12–17], generally being obtained from the appropriate complex $\mathrm{LnCp_2^xX}$ substrate (e.g. X = Cl, alkyl or $\mathrm{N(SiMe_3)_2}$) by a nucleophilic displacement reaction involving an alcohol or an alkoxide anion as reagent [18]. There are unusual recent examples of the formation of Yb(II) alkoxides from diethyl ether or dimethoxyethane (DME), shown in Eqs. (1) [19], (2) [20] and (3) [21], and of a Lu(III) ethoxide [14], Eq. (4).

$$\mathrm{YbI_2 + 2LiC(SiMe_3)_3} \xrightarrow[-2\mathrm{LiI}]{\mathrm{Et_2O}} [\mathrm{Yb\{C(SiMe_3)_3\}(\mu\text{-}OEt)(OEt_2)\}_2}] \qquad (1)$$

I

$$2[\mathrm{Yb\{C(SiMe_3)_3\}_2}] \xrightarrow{\mathrm{Et_2O}} \mathbf{I} + \mathrm{HC(SiMe_3)_3 + CH_2{=}CH_2} \qquad (2)$$

$$\mathrm{YbI_2} \xrightarrow[h\nu]{\mathrm{DME}} [\{\mathrm{Yb(\mu\text{-}OMe)I_2(DME)}\}_2] \qquad (3)$$

$$2\mathrm{Lu}(\eta\text{-}\mathrm{C_5Me_5})_2\mathrm{H} + \mathrm{Et_2O} \longrightarrow \mathrm{Lu}(\eta\text{-}\mathrm{C_5Me_5})_2(\mathrm{OEt}) + \mathrm{C_2H_6} \qquad (4)$$

An alkalide ion (e.g. $\mathrm{Na^-}$) has been shown to be formed by the reaction of a solution of a crown ether or cryptand with an alkali metal mirror; and such species, prepared in situ, have been used as powerful reducing agents [22]. For example, from K and the crown ether 15-c-5, polyethylene glycol (after hydrolysis), $\mathrm{C_2H_4}$, $\mathrm{C_2H_6}$(trace) and $\mathrm{C_4H_{10}}$ (minor component) were obtained [22]. Deoxygenation of an alcohol by reduction

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☆ Dedicated to Professor Hideki Sakurai as a mark of esteem and friendship.

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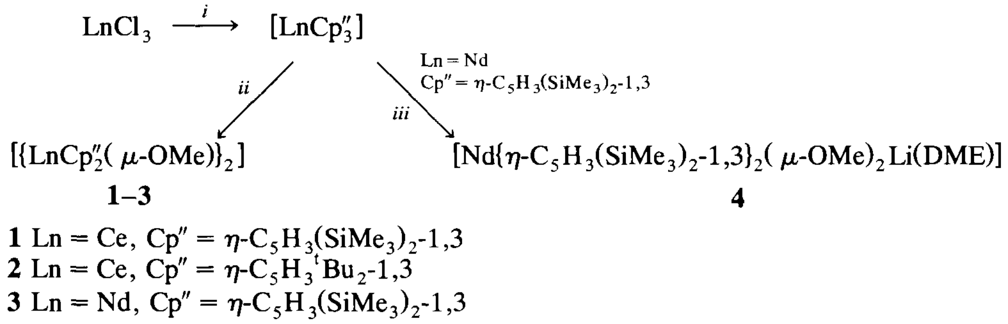


Scheme 1. Synthesis of complexes **1–4**. Reagents and conditions: (*i*) KCp'' or NaCp'', THF, ca. 20°C; (*ii*) Li for (for **1** and **2** only), DME, −33 to ca. 20°C; (*iii*) Li, DME, −33 to ca. 20°C.

with K and 18-c-6 in $^tBuNH_2$ is a valuable synthetic procedure [23].

2. Results and discussion

2.1. Synthesis and characterization of new Ln complexes and reaction pathway

Our objective was to obtain well characterized organocerium(II) and neodymium(II) complexes. The strategy was to use a tris(cyclopentadienyl)lanthanide(III) compound as substrate. We thought it would be advantageous to use a cyclopentadienyl ligand which would provide good lipophilicity and be sufficiently bulky to make the sought for Ln(II) complex kinetically stable. Accordingly, the choice fell on the 1,3-disubstituted ligands $[C_5H_3R_2\text{-}1,3]^-$ (R = $SiMe_3$ or ^tBu). Many $[LnCp''_3]$ complexes [Cp'' = η-$C_5H_3(SiMe_3)_2$-1,3] had already been made at Sussex [24], while the bis-t-butylcyclopentadienyl ligand was present in, for example, $[\{Ce(\eta\text{-}C_5H_3{}^tBu_2\text{-}1,3)_2(\mu\text{-}Cl)\}_2]$ [25].

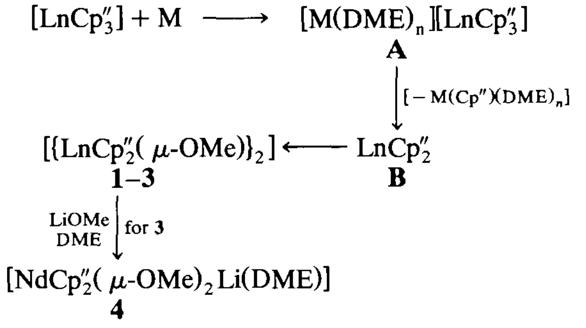
The substrates for the present investigation, $[\{Ce(\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}_3]$ (**5**), $[\{Ce(\eta\text{-}C_5H_3{}^tBu_2\text{-}1,3\}_3]$ (**6**) and $[\{Nd(\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}_3]$ (**7**), were prepared in good yield from the appropriate $LnCl_3$ and K (**5** and **7**) or Na (**6**) cyclopentadienide.

Our expectation was that the reaction of the tris(cyclopentadienyl)lanthanide complex **5**, **6** or **7** with K or Li in DME might form the lanthanate(II)-containing salt $[M(DME)_n][LnCp''_3]$ (M = K or Li). In the event, even under the exceedingly mild conditions that we employed, the reaction took a different course, the lanthanide-containing product obtained in high yield being a bis(cyclopentadienyl)lanthanide(III) methoxide $[\{LnCp''_2(\mu\text{-}OMe)\}_2]$ (Ln = Ce and Cp'' = η-$C_5H_3(SiMe_3)_2$-1,3 (**1**) or η-$C_5H_3{}^tBu_2$-1,3 (**2**); or Ln = Nd and Cp'' = η-$C_5H_3(SiMe_3)_2$-1,3 (**3**)) or $[NdCp''_2(\mu\text{-}OMe)_2Li(DME)]$ (**4**).

The nature of the coproducts of these reactions is not yet definitively established and requires further study. However, crystals of alkali metal cyclopentadienides $MCp''(DME)_n$ were isolated and identified by ^1H NMR spectroscopy ($n = 1$ for M = Li and $n = 2$ for M = K) and microanalysis. The gaseous products of the reaction were passed through Br_2 in CCl_4 and the resulting solution was shown to contain $BrCH_2CH_2Br$ (^1H NMR in $CDCl_3$ at 298 K: δ 3.67). The reactions leading to **1–4** are summarised in Scheme 1.

Compounds **1–7** gave satisfactory microanalytical, mass spectrometric and ^1H NMR spectroscopic data (see Experimental section). As these compounds are paramagnetic, the magnitudes of the ^1H NMR spectral chemical shifts are not particularly informative. It is interesting that for $[\{CeCp''_2(\mu\text{-}OMe)\}_2]$ (Cp = η-$C_5H_3(SiMe_3)_2$-1,3) (**1**), the cyclopentadienyl signal at $\delta - 1.06$ was very close to that derived from the $SiMe_3$ substituents at $\delta - 0.90$; the former, arising from a ligand closer to the paramagnetic metal, is the more shifted from the position in diamagnetic analogues.

The proposed pathway leading to complexes **1–4** is illustrated in Scheme 2. The first step is believed to be a one-electron transfer leading to the transient target salt **A**. The second is fragmentation of the latter to give a further labile intermediate $LnCp''_2$ (**B**), which, being not only a powerful reducing agent but also a strong oxophile, abstracts a methoxy radical from DME yielding $[\{LnCp''_2(\mu\text{-}OMe)\}_2]$ (**1–3**). The mode of formation of the Nd/Li methoxide **4** is more speculative, but it may have come from **3** + 2LiOMe; a related reaction is that



Scheme 2. Proposed reaction pathways to complexes **1–4**. The organic product generated in the OMe abstraction step may include C_2H_4, MeOEt and $(MeOCH_2CH_2)_2$.

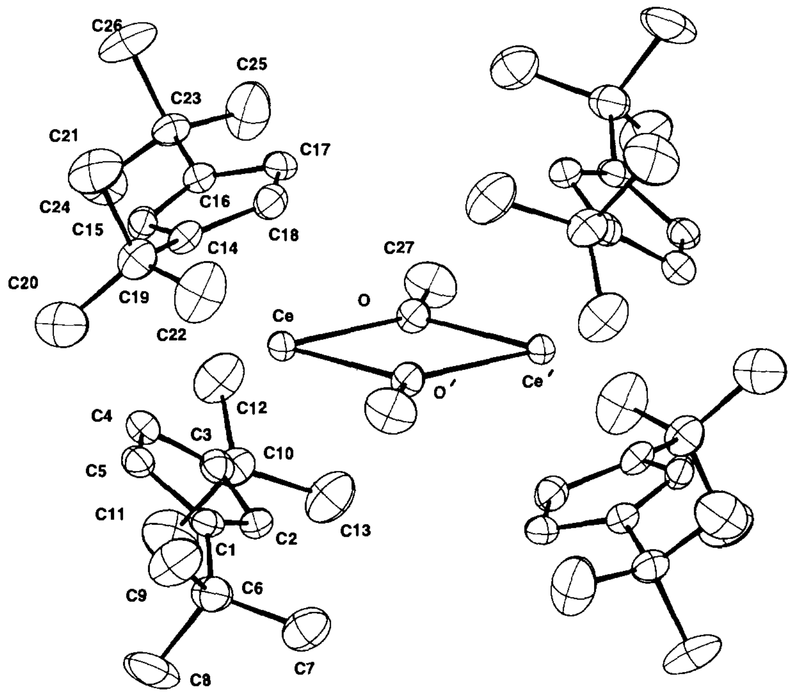


Fig. 1. Molecular structure of [{Ce(η-$C_5H_3{}^tBu_2$-1,3)$_2$(μ-OMe)}$_2$] (**2**) with the atom numbering scheme.

between [LnR_3] and LiCl(PMDETA) yielding [LnR_3-(μ-Cl)Li(PMDETA)] (R = $CH(SiMe_3)_2$, PMDETA = $MeN(CH_2CH_2NMe_2)_2$) [26].

2.2. Molecular structures of [{Ce{η-$C_5H_3{}^tBu_2$-1,3}$_2$(μ-OMe)}$_2$] (2) and [Nd{η-$C_5H_3(SiMe_3)_2$-1,3}$_2$(μ-OMe)$_2$-Li(DME)] (4)

The molecular structures, established by single-crystal X-ray diffraction studies, of complexes **2** and **4** are shown in Figs. 1 and 2, respectively. Selected bond lengths and angles are given in Tables 1 (**2**) and 2 (**4**) and atomic coordinates in Tables 3 (**2**) and 4 (**4**).

The dimeric structure of **2** was expected because its EI mass spectrum had shown a dimeric parent molecular ion. Furthermore, X-ray data are available for the yttrium compounds [{Y(η-C_5H_4R)$_2$(μ-OMe)}$_2$] (R = H or $SiMe_3$) [17b]. Other methoxides of cyclopentadienylyttrium or -gadolinium are often polynuclear, e.g. [Gd_5(η-C_5H_5)$_5$(μ-OMe)$_4$(μ_3-OMe)$_4$(μ_5-O) [16].

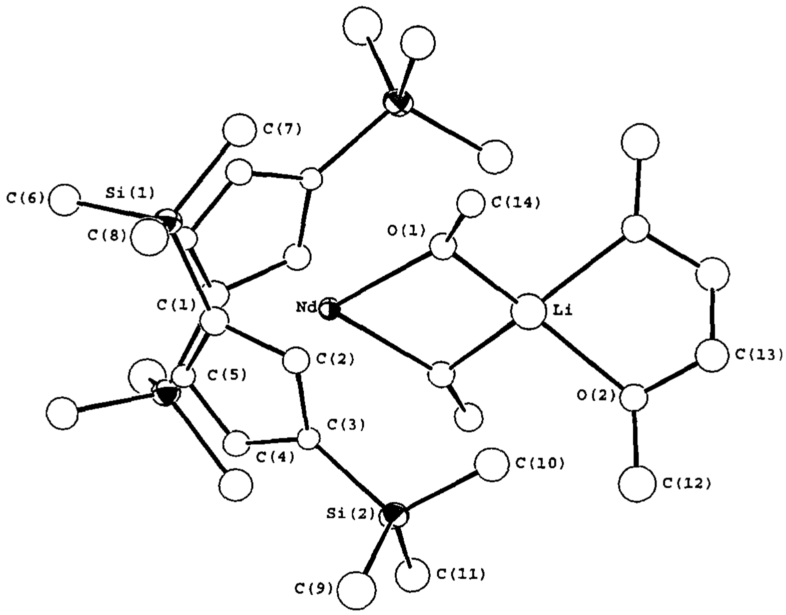


Fig. 2. Molecular structure of [Nd{η-$C_5H_3(SiMe_3)_2$-1,3}$_2$(μ-OMe)$_2$Li(DME)] (**4**) with the atom numbering scheme.

Table 1
Selected interatomic distances (Å) and bond angles (degrees) in complex **2**

Bond distance		Angle	
Ce–Cp1	2.596	Cp2–Ce–Cp1	126.2
Ce–Cp2	2.564	O–Ce–O′	70.2(2)
Ce–O	2.366(4)	O–Ce–Cp1	109.4
Ce–O′	2.386(4)	O′–Ce–Cp2	107.5
Ce–$C_{med.}$	2.83	O–Ce–Cp1	113.7
O–C(27)	1.395(7)	O′–Ce–Cp2	116.2
Ce · · · Ce	3.887	C(27)–O–Ce	133.9(4)
O(2)–C(14)	1.45(2)	C(27)–O–Ce′	116.3(4)
		Ce–O–Ce′	109.8(2)

Cp1 is the centroid of the C(1) to C(5) ring; Cp2 is the centroid of the C(14) to C(18) ring.

The closest analogues available for comparison with complex **2** are [{Ce(η-$C_5H_3{}^tBu_2$-1,3)$_2$(μ-Cl)}$_2$] [25] and [{Ce(η-$C_5H_3{}^tBu_2$-1,3)$_2$(μ-OTos)}$_2$] (Tos = $OSO_2C_6H_4Me$-*p*) [27]. The planar four-membered OCeOCe ring in **2** is essentially a square, with the methoxy-carbon atoms coplanar. The mean Ce–O bond distance in **2** of 2.376(4) Å is slightly shorter than that in the tosylate, 2.429(7) Å [27]. In contrast to the staggered conformation adopted by the two Cp″ rings in the latter complex, in **2** (as in the chloride) they are antiperiplanar; in **2** and the chloride, the relative orientation of the ^{t}Bu groups differs. The angle subtended at the metal by the centroids of the cyclopentadienyl rings Cp(2)–Ce–Cp(1) is wider in **2** (126.2°) than that for the tosylate (120.4°) [27] or the chloride (115.3°) [25]. The mean Ce–Cp(1 or 2) distance in **2** of 2.58 Å may be compared with the 2.54 Å in the tosylate and 2.52 Å in the chloride.

The structure of **4** is closely similar to that of [Nd{η-$C_5H_3(SiMe_3)_2$-1,3}$_2$(μ-Cl)$_2$Li(THF)$_2$] (**B**) [28]. The NdOLiO fragment in **4** is almost planar, the *O*-methyl groups being slightly out of this plane and *trans* to one another. The parameters for the $NdCp''_2$ fragments in **4** and in **B** are closely similar. Each of the metal atoms in both complexes is in a distorted tetrahedral environment if the Cp''^- ligand is regarded as occupying a single

Table 2
Selected interatomic distances (Å) and bond angles (degrees) in complex **4**

Bond distance		Angle	
Nd–Cp1	2.58	Cp–Nd–Cp′	122.0
Nd–O(1)	2.250(10)	Cp–Nd–O(1)	105.5
Nd–$C_{med.}$	2.84	O(1)–Nd–O(1)′	78.2(4)
Li–O(1)	1.95(3)	Cp–Nd–O(1)′	119.0(3)
Li–O(2)	2.11(3)	O(1)–Li–O(2)	150.5(6)
Nd · · · Li	3.09(4)	O(1)–Li–O(2)′	101.4(5)
O(1)–C(12)	1.39(2)	O(2)–Li–O(2)′	78(2)
O(2)–C(13)	1.44(7)	Nd–O(1)–Li	94(1)
O(2)–C(14)	1.45(2)	Nd–O(1)–C(14)	143.9(9)
		Li–O(1)–C(14)	118(1)
		Li–O(1)–C(12)	131(1)

Cp1 is the centroid of the C(1) to C(5) ring.

Table 3
Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters ($Å^2$ × 10^3) for **2**

Atom	x	y	z	U_{eq} [a]
Ce	1600.9(2)	−34.9(3)	142.3(2)	33(1)
O(1)	−143(3)	712(3)	−596(2)	41(1)
C(1)	2283(5)	−1977(4)	−326(4)	42(1)
C(2)	1517(5)	−1606(4)	−1059(3)	42(1)
C(3)	1974(5)	−755(5)	−1327(4)	43(1)
C(4)	3025(5)	−573(5)	−732(4)	48(2)
C(5)	3199(5)	−1314(4)	−134(4)	44(2)
C(6)	2243(7)	−3040(6)	1(4)	57(2)
C(7)	1040(6)	−3413(6)	−147(4)	73(2)
C(8)	2808(7)	−3746(5)	−463(5)	93(3)
C(9)	2905(7)	−3112(6)	897(5)	86(3)
C(10)	1566(6)	−313(5)	−2188(4)	52(2)
C(11)	2188(7)	−907(7)	−2684(5)	98(3)
C(12)	1812(7)	814(6)	−2213(5)	81(3)
C(13)	299(6)	−494(6)	−2583(4)	83(3)
C(14)	3189(5)	529(4)	1683(3)	41(1)
C(15)	3582(5)	1019(4)	1098(3)	41(1)
C(16)	2835(5)	1783(4)	704(4)	41(1)
C(17)	1934(5)	1755(4)	1025(4)	44(2)
C(18)	2157(5)	991(5)	1619(4)	49(2)
C(19)	3908(5)	−112(6)	2387(3)	53(2)
C(20)	4721(7)	−785(6)	2143(4)	82(3)
C(21)	4614(7)	653(6)	3035(4)	83(3)
C(22)	3213(7)	−736(7)	2777(5)	100(3)
C(23)	3097(6)	2647(5)	208(4)	49(2)
C(24)	3801(7)	2290(6)	−303(5)	85(3)
C(25)	2055(7)	3161(7)	−326(6)	104(4)
C(26)	3804(7)	3435(5)	818(5)	90(3)
C(27)	−472(7)	1427(6)	−1219(4)	75(2)

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

Table 4
Atomic coordinates and isotropic thermal parameters for **4**

Atom	x	y	z	U_{iso}
Nd	0.0000	0.14725(8)	0.2500	0.029(1) [a]
Si(1)	0.1758(5)	0.0086(3)	0.3895(3)	0.044(3) [a]
Si(2)	0.3025(5)	0.2039(3)	0.1467(3)	0.048(4) [a]
O(1)	0.0383(8)	0.2437(5)	0.3242(6)	0.040(4)
O(2)	0.0462(8)	0.4083(6)	0.1833(6)	0.043(4)
C(1)	0.1807(15)	0.0492(10)	0.2959(9)	0.045(6)
C(2)	0.2357(15)	0.1190(8)	0.2764(8)	0.041(6)
C(3)	0.2273(13)	0.1300(8)	0.1982(8)	0.029(5)
C(4)	0.1697(14)	0.0689(10)	0.1735(10)	0.040(5)
C(5)	0.1398(12)	0.0236(8)	0.2288(8)	0.030(5)
C(6)	0.0979(16)	−0.0790(11)	0.3847(11)	0.057(7)
C(7)	0.1092(17)	0.0689(11)	0.4578(11)	0.062(7)
C(8)	0.3218(16)	−0.0068(13)	0.4216(12)	0.079(7)
C(9)	0.4466(17)	0.1728(12)	0.1194(12)	0.086(9)
C(10)	0.3183(17)	0.2876(11)	0.2038(11)	0.067(7)
C(11)	0.2199(17)	0.2205(11)	0.0618(11)	0.066(7)
C(12)	0.1151(18)	0.4117(12)	0.1213(12)	0.079(8)
C(13)	0.0463(13)	0.4750(9)	0.2260(9)	0.064(8)
C(14)	0.1051(15)	0.2673(10)	0.3871(10)	0.044(6)
Li	0.0000	0.3179(24)	0.2500	0.072(14)

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

coordination site. The Nd–O bond length of 2.25(1) Å in **4** is slightly shorter than the mean Ce–O bond length in **2**, 2.376(4)°, but the O–Ln–O′ bond angle in **4** (Ln = Nd) of 78.2(4)° is substantially wider than that in **2** (Ln = Ce), 70.2(2)°.

3. Experimental

All operations were carried out either under vacuum or under an argon atmosphere using standard Schlenk techniques.

3.1. Preparation of $[Ce\{\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}_3]$ (5)

A mixture of $CeCl_3$ (2.7 g, 10.95 mmol) and $KC_5H_3(SiMe_3)_2$ (15.19 g, 61.25 mmol) in THF (150 ml) was stirred for 16 h at room temperature, during which it gradually changed colour to yellow–brown. The solvent was removed in vacuo, toluene (150 ml) was added and the mixture stirred for 5 h, the colour changing from yellow to deep blue. The solvent was removed in vacuo, the residue was stirred with hexane (200 ml) for 2 h and the solution was then filtered. The filtrate was evaporated in vacuo and the residue crystallized from hexane at −22°C to give blue crystals of $[Ce\{\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}_3]$ (**5**) (7.81g, 93%), m.p. 210–212°C. ^1H NMR (C_6D_6, 298 K): δ 27.51 (br, 1H), 17.42 (br, 2H), −4.60 (s, 18H). MS: m/z 767 (M^+, 46%), 695 ($[M-SiMe_3]^+$, 69%), 558 ($[Ce\{C_5H_3(SiMe_3)_2\}_2]^+$, 44%), 418 ($[\{C_5H_3(SiMe_3)_2\}_2]^+$, 44%), 209 ($[C_5H_3(SiMe_3)_2]^+$, 55%), 73 ($[SiMe_3]^+$, 100%). Anal. Found: C, 51.6; H, 8.17. $C_{33}H_{63}CeSi_6$ Calc: C, 51.6; H, 8.21%.

3.2. Preparation of $[Ce\{\eta\text{-}C_5H_3{}^tBu_2\text{-}1,3\}_3]$ (6)

A mixture of $NaC_5H_3{}^tBu_2$ (3.25 g, 16.25 mmol) and $CeCl_3$ (1.09 g, 4.42 mmol) in suspension in THF (200 ml) was stirred at room temperature for 24 h, during which it gradually changed colour to yellow brown, the solvent removed in vacuo and toluene (300 ml) added to the residue. The mixture was heated under reflux for 48 h, the solvent removed in vacuo, hexane (300 ml) added and the solution filtered. Deep blue crystals of $[Ce\{\eta\text{-}C_5H_3Bu^t_2\text{-}1,3\}_3]$ (**6**) (2.64 g, 89%) were obtained from a concentrated solution in hexane at −22°C. ^1H NMR (C_6D_6, 298 K): δ 26.65 (br, 1H), 17.29 (br, 2H), −5.14 (s, 18H). MS: m/z 671 ($[M]^+$, 3%), 614 ($[M-{}^tBu]^+$, 18%), 494 ($[Ce\{C_5H_3{}^tBu_2\}_2]^+$, 60%), 479 ($[Ce\{C_5H_3{}^tBu_2\}_2-Me]^+$, 98%), 177 ($[C_5H_3{}^tBu_2]^+$, 20%), 57 ($[{}^tBu_2]^+$, 93%). Anal. Found: C, 69.7; H, 9.31. $C_{39}H_{63}Ce$ Calc.: C, 69.75; H, 9.39%.

3.3. Preparation of $[Nd\{\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}_3]$ (7)

A mixture of $KC_5H_3(SiMe_3)_2$ (6.27 g, 25.28 mmol) and $NdCl_3$ (2.11 g, 8.4 mmol) in suspension in THF (150 ml) was stirred for 16 h at room temperature, the THF removed in vacuo and toluene (200 ml) added to the residue. The mixture was heated under reflux for 48 h, the toluene removed in vacuo and the green residue stirred with hexane (200 ml) for 2h and the solution filtered. Rhombic green crystals of $[Nd\{\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}_3]$ (**7**) (6.16 g, 95%) were obtained from the concentrated filtrate at room temperature, m.p. 133–135°C. ^1H NMR (C_6D_6, 298 K): δ 34.86 (br, 1H), 15.47 (br, 2H), −7.88 (s, 18H). MS: m/z 771 ($[M]^+$, 2%), 756 ($[M-Me]^+$, 10%), 562 ($[Nd\{C_5H_3(SiMe_3)_2\}_2]^+$, 82%), 73 ($[SiMe_3]^+$, 100%). Anal. Found: C, 51.6; H, 8.18. $C_{33}H_{63}NdSi_6$ Calc. C, 51.4; H, 8.17%.

3.4. Preparation of $[Ce\{\eta^5\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}_2(\mu\text{-}OMe)]_2$ (1)

3.4.1. Method A

A solution of $[Ce\{\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}_3]$ (**5**) (1.08 g, 1.408 mmol) in DME (50 ml) was added to Li powder (0.02 g, 2.86 mmol) at −33°C. The mixture was stirred for 18 h at room temperature, during which the colour gradually changed from blue to deep violet and some gas was evolved. The mixture was then filtered and the filtrate concentrated in vacuo to ca. 25% of its volume. Some crystals separated from the dark solution at −22°C; these were washed with cold diethyl ether and dried in vacuo, yielding yellow microcrystals of **1** (0.76 g, 92%), m.p. 230–231°C. ^1H NMR (C_4D_8O, 298 K): δ 39.55 (s, 3H, μ-OMe), 7.19 (br, 4H, C_5H_3), −0.90 (br, 2H, C_5H_3), −1.06 (s, 36H, $SiMe_3$); ^1H NMR (C_4D_8O, 338 K): δ 33.79 (s., 3H, μ-OMe), 6.96 (br, 4H, C_5H_3), 0.98 (br, 2H, C_5H_3), −0.90 (s, 36H, $SiMe_3$). ^{29}Si NMR (C_4D_8O, 298 K): δ −19.15 s, MS: m/z 1178 ($[M]^+$, 1%), 969 ($[M-C_5H_3(SiMe_3)_2]^+$, 23%), 589 ($[M/2]^+$, 96%), 380 ($[Ce\{C_5H_3(SiMe_3)_2\}(OMe)]^+$, 100%), 73 ($[SiMe_3]^+$, 88%). Anal. Found: C, 46.7; H, 7.49. $C_{46}H_{90}Ce_2O_2Si_8$ Calc.: C, 46.9; H, 7.64%.

3.4.2. Method B

Complex **1** (0.66 g, 95%) was also obtained from the reaction between $[Ce\{\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}_3]$ (**5**) (0.91 g, 1.19 mmol) and potassium (0.12 g, 3.08 mmol) in DME (40 ml) for 10 h.

3.5. Preparation of $[\{Ce\{\eta^5\text{-}C_5H_3{}^tBu_2\text{-}1,3\}_2(\mu\text{-}OMe)\}_2]$ (2)

3.5.1. Method A

A solution of $[Ce\{\eta\text{-}C_5H_3{}^tBu_2\text{-}1,3\}_3]$ (**6**) (0.24 g, 0.357 mmol) in DME (35 ml) was stirred over a potassium mirror (0.04 g, 1.02 mmol) at −33°C for 10 h at room temperature, during which the colour changed from blue to deep violet and finally to yellow–brown and some gas was evolved. The mixture was then filtered and ca. two thirds of the solvent was removed in vacuo. Yellow crystals of **2** (0.26 g, 94.5%) were obtained from the concentrated solution in DME at −22°C, decomp. 245–248°C. ^{1}H NMR (C_4D_8O, 298 K): δ 37.03 (s, 3H, μ-OMe), 10.34 (br, 4H, C_5H_3), −1.57 (s, 36H, ^{t}Bu) −2.74 (br, 2H, C_5H_3). MS *m/z* 1004 ($[\mathrm{Ce}\{C_5H_3{}^tBu_2\}_2]_2(\mu\text{-}O))]^+$, 1%), 827 ($[\mathrm{Ce}_2\{C_5H_3{}^tBu_2\}_3(\mathrm{OMe}) - \mathrm{Me}]^+$, 13%), 525($[M/2]^+$, 50%), 494 ($[\mathrm{Ce}\{C_5H_3{}^tBu_2\}_2]^+$ 348($[\mathrm{Ce}\{C_5H_3{}^tBu_2\}(\mathrm{OMe})]^+$, 100%), 57 ($[{}^tBu]^+$, 92%). Anal. Found: C, 61.4; H, 8.29. $C_{54}H_{90}Ce_2O_2$ Calc.: C, 61.7; H, 8.57%.

3.5.2. *Method B*

Complex **2** (0.37 g, 88%) was also obtained by a similar procedure to method A for **1**, from $[\mathrm{Ce}\{\eta\text{-}C_5H_3{}^tBu_2\text{-}1,3\}_3]$ (**6**) (0.54 g, 0.080 mmol) and Li powder (0.02 g, 2.86 mmol) in DME (40 ml) for 24 h.

3.6. *Preparation of $[\{\mathrm{Nd}\{\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}_2(\mu\text{-}OMe)\}_2]$ (3)*

$[\mathrm{Nd}\{\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}_3]$ (**7**) (0.82 g, 1.06 mmol) was slowly added to a potassium mirror (0.11 g, 2.82 mmol) over DME (70 ml) at −33°C. The mixture was stirred for 10 h at room temperature, during which the colour changed from green to brown with some gas evolution. After stirring, ca. five sixths of the solvent was removed in vacuo and complex **3** (0.45 g, 71%) was obtained as light blue crystals from the concentrated solution at −22°C, m.p. 226–228°C. ^{1}H NMR (C_6D_6, 298 K): δ 23.98 (s, br, 2H, C_5H_3), 22.12 (br, 4H, C_5H_3), −4.32 (s, 36H, $SiMe_3$), −50.99 (s, 3H, μ-OMe). MS: *m/z* 977 ($[M - C_5H_3\ (SiMe_3)_2]^+$, 2%), 946 ($[\mathrm{Nd}_2\{C_5H_3(SiMe_3)_2\}_3(\mathrm{OMe})]^+$, 20%), 737 ($[\mathrm{Nd}_2\{C_5H_3(SiMe_3)_2\}_2(\mathrm{OMe})]^+$, 18%), 593 ($[M/2]^+$, 7%), 562 ($[\mathrm{Nd}\{C_5H_3(SiMe_3)_2\}_2]^+$, 19%), 384 ($[\mathrm{Nd}\{C_5H_3(SiMe_3)_2\}(\mathrm{OMe})]^+$, 27%), 209 ($[C_5H_3(SiMe_3)_2]^+$, 46%), 73 ($[SiMe_3]^+$, 100%). Anal. Found: C, 46.4; H, 7.44. $C_{46}H_{90}Nd_2O_2Si_8$ Calc.: C, 46.5; H, 7.59%.

3.7. *Preparation of $[\mathrm{Nd}\{\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}_2(\mu\text{-}OMe)_2Li(DME)]$ (4)*

$[\mathrm{Nd}\{\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}_3]$ (**7**) (1.06 g, 1.375 mmol) was added to metallic lithium (0.1 g, 14.28 mmol) over DME (80 ml) at −33°C. The colour of the mixture changed from green to deep brown and then to blue–green and some gas was evolved. After stirring for 18 h at room temperature, the supernatant liquor was decanted and ca. five sixths of the solvent was removed in vacuo. Light blue crystals of **4** (0.77 g, 78%) separated from the solution at −22°C. Crystals for the X-ray diffraction study were obtained in diethyl ether, decomp. 90–92°C. ^{1}H NMR (C_6D_6, 298 K): δ 5.88 (s br, 4H, C_5H_3), 4.68 (s, 6H, μ-OMe), 0.46 (s, 6H, OMe (DME)), −0.05 (s, 4H, CH_2–CH_2 (DME)), −2.84 (s, 36H, $SiMe_3$), −6.08 (s br, 2H, C_5H_3). ^{7}Li NMR (C_6D_6, 298 K): δ −7.77. (The NMR spectra of **4** changed after keeping the sample for 1 week, and some white precipitate appeared in the NMR tube.) MS: *m/z* 721 ($[M]^+$, 3%), 593 ($[\mathrm{Nd}\{C_5H_3(SiMe_3)_2\}_2(\mathrm{OMe})]^+$, 5%), 562 ($[\mathrm{Nd}\{C_5H_3(SiMe_3)_2\}_2]^+$, 14%), 384 ($[\mathrm{Nd}\{C_5H_3\text{-}(SiMe_3)_2\}(\mathrm{OMe})]^+$, 60%), 209 ($[C_5H_3(SiMe_3)_2]^+$, 57%), 73 ($[SiMe_3]^+$, 83%). Anal. Found: C, 46.3; H, 8.06. $C_{28}H_{58}LiNdO_4Si_4$ Calc.: C, 46.6; H, 8.04%.

3.8. *X-Ray structure determination for 2 and 4*

In both cases unique data sets were collected on an Enraf–Nonius CAD4 diffractometer with monochromated Mo Kα radiation. For **2** data were measured at

Table 5
X-ray crystal structure details for compounds 2 and 4

Parameter	$[\{\mathrm{Ce}\{\eta^5\text{-}C_5H_3{}^tBu_2\}_2(\mu\text{-}OMe)\}_2]$ (2)	$[\mathrm{Nd}\{\eta\text{-}C_5H_3(SiMe_3)_2\}_2(\mu\text{-}OMe)_2Li(DME)]$ (4)
Formula	$C_{54}H_{90}Ce_2O_2$	$C_{26}H_{58}LiNdO_4Si_4$
M	1051.5	698.3
Crystal system, space group	Monoclinic, $P2_1/n$	Orthorhombic *Pbcn*
a, *b*, *c* (Å)	12.547(3), 13.156(6), 17.423(3)	11.742(3), 18.102(4), 18.131(8)
β(°)	108.77(2)	90
U (Å^3), *Z*, D_C (g cm^{-1})	2723(2), 2, 1.28	3854(2), 4, 1.20
F(000)	1092	1460
μ(Mo Kα) (cm^{-1})	16.8	15.0
Crystal size (mm^3)	0.2 × 0.2 × 0.1	0.15 × 0.1 × 0.1
θ max for data (°)	30	25
Total unique reflections	8249	7354
Reflections with $I > 2\sigma(I)$	3907	3812
Number of variables	262	90
R (for $I > 2\sigma(I)$) [a]	0.057	0.060
Max parameter shift/e.s.d.	0.001	0.01
$(\Delta\rho)$ max, min (e Å^{-3})	+0.57, − 0.47	+0.68, − 0.43

[a] $R = [\Sigma(|F_o| - |F_c|)/\Sigma(|F_o|)]$.

room temperature using a crystal sealed in a capillary under argon. For **4** data were measured at 173 K using a crystal coated in oil. Data were corrected for Lorentz and polarization effects and for absorption using psi-scan data.

Both structures were solved by heavy atom methods using SHELXL-86 [29] and refined by full-matrix least-squares. For **2**, refinement was based on F^2 using SHELXL-93 [30] with all unique data and with non-H atoms anisotropic and H atoms in riding mode with U_{iso}(H) equal to $1.2U_{eq}$(C) or $1.5U_{eq}$(C) for methyl groups. The weighting scheme was that defined by the program. For **4** refinement was based on F using programs from the Enraf–Nonius Molen package with reflections with $I > 2\sigma(I)$, and with only Nd and Si atoms anisotropic and H atoms at fixed calculated positions and $U_{iso}(H) = 1.3U_{eq}(C)$, except for those on C(14) which were omitted. The weighting scheme was $w = \sigma^{-2}(F)$.

Further details are given in Table 5. Tables of atom positions and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

Acknowledgements

We thank the Royal Society for providing a fellowship to Yu. K. G. and EPSRC for other support and Professor J.L. Dye for useful information.

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