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Studies on organolanthanide complexes

XLVII *. Syntheses of bis(2-methoxyethylcyclopentadienyl)lanthanide tetrahydroborates (Ln = La, Pr, Nd, Sm or Gd); Crystal structures of bis(2-methoxyethylcyclopentadienyl) praseodymium and neodymium tetrahydroborates

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Abstract

Five new complexes, bis(2-methoxyethylcyclopentadienyl) lanthanide tetrahydroborates (Ln = La (**1**), Pr (**2**), Nd (**3**), Sm (**4**) or Gd (**5**)) have been synthesized with good yields by the reaction of bis(2-methoxyethylcyclopentadienyl)lanthanide chlorides with sodium borohydride in THF at room temperature. These complexes have been characterized by elemental analyses, MS, ^{1}H NMR and IR spectra. The X-ray structure analyses of **2** and **3** show both to be orthorhombic, with space group $P2_12_12_1$, $a = 11.081(3)$ Å, $b = 13.145(5)$ Å, $c = 12.080(3)$ Å, $D_{calc} = 1.518$ g cm^{-3} and $Z = 4$ for **2**, and space group $Pna2_1$, $a = 12.753(2)$ Å, $b = 11.207(2)$ Å, $c = 12.042(2)$ Å, $D_{calc} = 1.565$ g cm^{-3} and $Z = 4$ for **3**. The structures were solved from 2982 observed reflections with $F_o \geqslant 4\sigma(F_o)$ to a final R factor of 0.0610 for **2** and from 1149 observed reflections with $F_o \geqslant 4\sigma(F_o)$ to a final R factor of 0.0607 for **3**. The molecular structures show that they are monomers, and intramolecular coordination bonds between lanthanide metal and oxygen atom on ligand in the above tetrahydroborate complexes exist. The average Pr–O and Nd–O bond lengths are 2.605 Å and 2.560 Å respectively. The X-ray crystal structures also reveal that the Pr ··· B distance is 2.757(18) Å and the Nd ··· B distance is 2.664(25) Å and suggest the tridentate mode of BH_4^- bonding.

Key words: Lanthanum; Praseodymium; Neodymium; Samarium; Gadolinium; Crystal structure

1. Introduction

The chemistry of cyclopentadienyl tetrahydroborate with main group, transition metal and actinide elements has been extensively developed in the past two decades. However, the chemistry of lanthanide elements in this area has remained virtually untouched [2]. Although some syntheses of organolanthanum tetrahydroborates have been reported [3,4], the structural data on these complexes are still scarce in particular. More recently the molecular structure of cyclopentadienyl tetrahydroborates, such as $\{(\eta^5\text{-}C_5H_3\text{-}{}^tBu_2)_2Ce[\mu\text{:}\eta^4\text{-}(\mu_3\text{-}H)_2B(\mu_2\text{-}H)_2]\}_2$ and $\{(\eta^5\text{-}C_5H_3\text{-}{}^tBu_2)_2Sm[\mu\text{:}\eta^4\text{-}(\mu_3\text{-}H)_2B(\mu_2\text{-}H)_2]\}_2$ have been reported [5,6], but they are dimers.

Owing to the bulky cyclopentadienyl ligands, such as C_5Me_5, $C_5H_3(SiMe_3)_2$ and $C_5H_3{}^tBu_2$, which can efficiently satisfy the steric saturation of lanthanide ions, many organolanthanide derivatives with these ligands have successfully been synthesized. In other different approaches, we have chosen an ether-substituted cyclopentadienyl $MeOCH_2CH_2C_5H_4$ [7] as the ligand which can form the intramolecular coordination bond between the oxygen atom on the ligand and lanthanide metal. This ligand not only can stabilize the organolanthanide complexes but also can afford monomeric complexes which possess better solubility in (THF). It will

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be very useful for the study of the reactivity of these complexes. On the contrary, the $LnCl_3$–$NaBH_4$ systems [8–10] have been applied for the selective conversion of α,β-unsaturated ketones to allyl alcohols with good yields. When the new boron-reagent-containing bulky organic ligand is used, there is some possibility of improving the regioselectivity and stereoselectivity. Therefore we have chosen the ether-substituted cyclopentadienyl $MeOCH_2CH_2C_5H_4$ as a ligand and tried to obtain the stable solvent-free monomer of lanthanide tetrahydroborates.

In the present paper we describe the syntheses of monomeric derivatives of La^{III}, Pr^{III}, Nd^{III}, Sm^{III} and Gd^{III} tetrahydroborates with 2-methoxyethylcyclopentadienyl ligand and the structural characterization of $(MeOCH_2CH_2C_5H_4)_2Pr(BH_4)$ (**2**) and $(MeOCH_2CH_2C_5H_4)_2Nd(BH_4)$ (**3**).

2. Experimental details

All operations for these organolanthanide complexes were performed under pre-purified argon by use of the Schlenk technique or a glove-box. All solvents were refluxed and distilled over finely divided $LiAlH_4$ or blue sodium benzophenone under argon immediately before use. Bis(2-methoxyethylcyclopentadienyl)lanthanide chlorides were prepared by a published procedure [11]. Sodium borohydride was purchased from Aldrich (purity, 96% or higher). IR spectra were recorded in Nujol or Fluorolube mulls, in CsI disc on a Perkin–Elmer 983 instrument; the mulls were prepared in an argon-filled glove-box. Mass spectra were recorded on a Finnigan 4021 spectrometer. ^1H NMR spectra were obtained on a Varian XL-200 (200 MHz) spectrometer referenced to external Me_4Si. THF-d_8 was dried over an Na–K alloy and degassed by freeze–thaw cycles on a vacuum line.

The rare earth complexes were analysed by direct complexometric titration with disodium EDTA. Carbon and hydrogen analyses were carried out by the combustion method in an aluminium tube.

2.1. Preparation of the complexes

2.1.1. Bis(2-methoxyethylcyclopentadienyl)lanthanum tetrahydroborate (1)

A mixture containing $(MeOCH_2CH_2C_5H_4)_2LaCl$ (0.96 g, 2.28 mmol) and excess of $NaBH_4$ (0.172 g, 4.56 mmol) in THF (60 ml) was stirred at room temperature for about 2 days. The Schlenk flask was centrifuged to give a clear THF solution which was reduced in volume to about 10 ml. Addition of 2 ml of n-hexane gave the white precipitate ($NaBH_4$); this was then filtered to afford the clear THF–n-hexane solution which was allowed to stand overnight at room temperature (RT) to give colourless crystals (**1**) (0.82 g; yield, 90%; m.p., 169.5–171°C). Anal. Found: C, 48.05; H, 6.54; La, 34.94. $C_{16}H_{26}BO_2La$ calc.: C, 48.03; H, 6.55; La, 34.75%. MS (m/e, relative intensity): 400([M]$^+$, 30.52), 385 ([M–BH_4]$^+$, 100.00). IR: 247m, 374w, 773s, 829m, 991m, 1044s, 1068s, 1149s, 1376m, 1460m, 2207s, 2300w, 2421s, 2924s, 3002m, 3070m cm^{-1} ^1H NMR (THF-d_8, 25°C): 2.72 (t, 2H, OCH_2CH_2); 3.57(s, 3H, OCH_3); 4.01(t, 2H, OCH_2); 5.91(s, 2H, C_5H_4); 6.03(s, 2H, C_5H_4) ppm.

2.1.2. Bis(2-methoxyethylcyclopentadienyl)praseodymium tetrahydroborate (2)

The procedure followed was similar to that for **1**. Complex **2** was obtained as green crystals with a 68% yield (m.p., 170–172°C). Anal. Found: C, 47.73; H, 6.35; Pr, 35.62. $C_{16}H_{26}BO_2Pr$ calc.: C, 47.76; H, 6.47; Pr, 35.07%. MS (m/e, relative intensity): 402([M]$^+$, 13.30), 387([M–BH_4]$^+$, 100.00). IR: 243m, 374m, 774m, 827m, 992m, 1044s, 1065s, 1143m, 1376m, 1452m, 2190m, 2254m, 2404s, 2921s, 3092w, 3073 m cm^{-1}.

2.1.3. Bis(2-methoxyethylcyclopentadienyl)neodymium tetrahydroborate (3)

The procedure followed was similar to that for **1**. Complex **3** was obtained as blue crystals with a 77% yield (m.p., 170–172°C). Anal. Found: C, 47.43; H, 6.49; Nd, 36.53. $C_{16}H_{26}BO_2Nd$ calc.: C, 47.41; H, 6.42; Nd, 35.56%. MS (m/e, relative intensity): 405([M]$^+$, 1.47), 390([M–BH_4]$^+$, 21.92), 45([$MeOCH_2$]$^+$, 100.00). IR: 243m, 375m, 776m, 829m, 992m, 1044s, 1064s, 1143m, 1375m, 1457m, 2184m, 2260m, 2404s, 2913s, 3002w, 3073m cm^{-1}.

2.1.4. Bis(2-methoxyethylcyclopentadienyl)samarium tetrahydroborate (4)

The procedure followed was similar to that for **1**. Complex **4** was obtained as yellow crystals with a 71% yield (m.p., 169–171°C). Anal. Found: C, 46.79; H, 6.34; Sm, 36.48. $C_{16}H_{26}BO_2Sm$ calc.: C, 46.72; H, 6.33; Sm, 36.50%. MS (m/e, relative intensity): 411([M]$^+$, 1.32), 396([M–BH_4]$^+$, 2.72), 44([$MeOCH_2$–1]$^+$, 100.00). IR: 239m, 382m, 778m, 833m, 991m, 1042s, 1055s, 1154m, 1376m, 1454s, 2179m, 2200s, 2212m, 2364s, 2921s, 3002w, 3075m cm^{-1}.

2.1.5. Bis(2-methoxyethylcyclopentadienyl)gadolinium tetrahydroborate (5)

The procedure followed was similar to that for **1**. Complex **5** was obtained as colourless crystals with a 70% yield (m.p., 173–175°C). Anal. Found: C, 45.34; H, 6.31; Gd, 37.40. $C_{16}H_{26}BO_2Gd$ calc.: C, 45.82; H, 6.21; Gd, 37.56%. MS (m/e, relative intensity):

TABLE 1. Crystallographic data for $(MeOCH_2CH_2C_5H_4)_2Pr(BH_4)$ (**2**) and $(MeOCH_2CH_2C_5H_4)_2Nd(BH_4)$ (**3**)

	2	**3**
Formula	$C_{16}H_{26}BO_2Pr$	$C_{16}H_{26}BO_2Nd$
Molecular weight	402.1	405.4
Crystal system	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$Pna2_1$
Cell constants		
a (Å)	11.081(3)	12.753(2)
b (Å)	13.145(5)	11.207(2)
c (Å)	12.080(3)	12.042(2)
V (Å^3)	1759.6(9)	1721.1(6)
Z	4	4
D_{calc} (g cm^{-3})	1.518	1.565
Diffractometer	Siemens Rsm/V	Siemens Rsm/V
Radiation; wavelength (Å)	Mo Kα, 0.71073	Mo Kα, 0.71073
Monochromator	Highly oriented graphite	Highly oriented graphite
Data collected	$h, 0 \rightarrow 13$; $k, 0 \rightarrow 15$; $l, -14 \rightarrow 14$	$h, -15 \rightarrow 15$; $k, -13 \rightarrow 0$; $l, 0 \rightarrow 14$
Scan type	$\theta \rightarrow 2\theta$	$\theta \rightarrow 2\theta$
Scan width (°)	0.50 plus Kα separation	0.50 plus Kα separation
Scan speed (° min^{-1})	Variable	Variable
θ_{max} (°)	50.0	45.0
μ(Mo Kα) (mm^{-1})	2.758	3.027
Absolute correction	Semiempirical	Semiempirical
Number of reflections collected	3461	3555
Number of reflections with $F_o \geqslant 4.0\sigma(F_o)$	2982	1149
R_F (%); R_{wF} (%)	6.10; 7.89	6.07; 6.25
Goodness of fit	1.03	2.42

419([M]$^+$, 4.77), 404([M-BH$_4$]$^+$, 39.15), 45([MeO-CH$_2$]$^+$, 100.00). IR: 237m, 385m, 781m, 833m, 990m, 1041s, 1054s, 1153m, 1376m, 1456s, 2161m, 2186s, 2217m, 2364s, 2920s, 3002w, 3074m cm^{-1}.

2.2. Crystal structure determination for 2 and 3

A green crystal **2** of dimensions 0.40 mm × 0.30 mm × 0.15 mm was mounted in a thin-walled glass capillary on a Siemens Rsm/V four-circle X-ray

TABLE 2. Atomic coordinates of $(MeOCH_2CH_2C_5H_4)_2Pr(BH_4)$ (**2**)

Atom	x	y	z	U_{eq} [a]
Pr	1837(1)	2077(1)	2630(1)	41(1)
O(1)	3785(7)	3125(6)	2234(11)	75(3)
O(2)	−118(7)	1308(9)	3489(8)	74(3)
B	1525(15)	3514(14)	4268(14)	80(6)
C(11)	4009(10)	1053(9)	2743(13)	70(4)
C(12)	3333(14)	556(11)	1934(13)	87(5)
C(13)	2378(5)	12(8)	2444(17)	87(6)
C(14)	2482(12)	192(11)	3539(15)	80(5)
C(15)	3478(13)	841(11)	3748(13)	80(5)
C(16)	5095(12)	1749(13)	2648(27)	116(10)
C(17)	4912(12)	2612(16)	2100(19)	106(7)
C(18)	3801(15)	4155(10)	1968(20)	101(7)
C(21)	−215(12)	1996(15)	1304(12)	86(5)
C(22)	685(16)	1491(11)	720(12)	82(5)
C(23)	1533(15)	2170(13)	379(11)	88(6)
C(24)	1248(13)	3149(13)	717(13)	85(5)
C(25)	208(14)	3061(13)	1277(12)	84(5)
C(26)	−1269(16)	1568(26)	1859(21)	144(12)
C(27)	−1202(15)	1408(31)	2908(22)	168(15)
C(28)	−204(14)	1110(13)	4659(14)	88(6)

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

TABLE 3. Atomic coordinates of $(MeOCH_2CH_2C_5H_4)_2Nd(BH_4)$ (**3**)

Atom	x	y	z	U_{eq} [a]
Nd	2139(1)	4351(1)	2500	62(1)
B	3520(21)	3955(22)	882(19)	27(8)
O(1)	3308(10)	6154(11)	2881(14)	83(8)
O(2)	1413(17)	2454(14)	1587(14)	97(7)
C(11)	4406(14)	6019(21)	2930(24)	113(10)
C(12)	3007(20)	7214(24)	2343(49)	156(12)
C(13)	1920(13)	7543(18)	2816(18)	79(7)
C(14)	1231(13)	6519(14)	2403(22)	65(5)
C(15)	660(19)	5915(21)	3222(23)	91(9)
C(16)	31(16)	4980(17)	2794(14)	66(6)
C(17)	231(17)	5119(19)	1653(15)	69(7)
C(18)	912(19)	6060(20)	1385(20)	76(8)
C(21)	1162(45)	2244(44)	490(22)	253(32)
C(22)	1467(29)	1304(21)	1994(21)	122(12)
C(23)	2004(23)	1280(22)	3110(21)	95(9)
C(24)	2263(19)	2372(21)	3825(21)	90(8)
C(25)	1554(23)	3035(26)	4499(26)	117(10)
C(26)	2270(19)	3951(29)	4803(30)	131(12)
C(27)	3341(17)	4003(18)	4510(17)	47(6)
C(28)	3269(22)	2962(23)	3896(24)	134(12)

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

TABLE 4. Selected bond distances (Å) and angles (°) for $(MeOCH_2CH_2C_5H_4)_2Pr(BH_4)$ (**2**)

Bond distances			
Pr–O(1)	2.605(8)	C(11)–C(12)	1.394(21)
Pr–O(2)	2.605(8)	C(11)–C(15)	1.377(22)
Pr ··· B	2.757(18)	C(11)–C(16)	1.515(19)
Pr–C(11)	2.761(12)	C(12)–C(13)	1.418(22)
Pr–C(12)	2.730(15)	C(13)–C(14)	1.348(27)
Pr–C(13)	2.788(11)	C(14)–C(15)	1.417(20)
Pr–C(14)	2.802(15)	C(16)–C(17)	1.328(31)
Pr–C(15)	2.787(15)	Pr–cent(1)	2.509
O(1)–C(17)	1.429(17)	Pr–cent(2)	2.497
O(1)–C(18)	1.391(16)		
Bond angles			
O(1)–Pr–O(2)	165.3(3)	O(1)–C(17)–C(16)	118.7(16)
O(1)–Pr–B	82.7(4)	C(11)–C(16)–C(17)	115.6(14)
O(1)–Pr–cent(1)	88.6	C(15)–C(11)–C(16)	121.9(17)
O(1)–Pr–cent(2)	100.5	C(12)–C(11)–C(15)	107.0(12)
cent(1)–Pr–B	122.7	C(11)–C(12)–C(13)	109.4(14)
cent(2)–Pr–B	115.9	C(12)–C(13)–C(14)	105.9(14)
cent(1)–Pr–cent(2)	121.4	C(13)–C(14)–C(15)	110.3(14)
C(17)–O(1)–C(18)	115.0(12)	C(11)–C(15)–C(14)	107.3(13)

Cent(1) is the centroid of cyclopentadienyl ring defined by C(11)–C(15); cent(2) is the centroid of cyclopentadienyl ring defined by C(21)–C(25).

diffractometer at RT. Data were collected by use of the θ–2θ scan technique with Mo K radiation ($2\theta_{max} = 50°$). 3117 independent reflections were measured and 2982 reflections with $F_0 \geqslant 4.0\sigma(F_0)$ were used in the refinement ($R = 0.0610$). The intensities were corrected for Lorentz–polarization effects but not for absorption. The structure was solved by the direct method. The hydrogen atoms of the borohydride were not found in the Fourier map and were not included in the calculation. The remaining hydrogen atoms were calculated geometrically and were included in the refinement. All calculations were performed on a VMS computer using the Siemens SHELXTL PLUS program.

TABLE 5. Selected bond distances (Å) and angles (°) for $(MeOCH_2CH_2C_5H_4)_2Nd(BH_4)$ (**3**)

Bond lengths			
Nd–O(1)	2.553(13)	O(1)–C(12)	1.406(39)
Nd–O(2)	2.566(17)	C(12)–C(13)	1.544(37)
Nd ··· B	2.664(25)	C(13)–C(14)	1.529(26)
Nd–C(14)	2.694(16)	C(14)–C(15)	1.400(34)
Nd–C(15)	2.717(24)	C(15)–C(16)	1.416(31)
Nd–C(16)	2.801(21)	C(16)–C(17)	1.407(24)
Nd–C(17)	2.775(21)	C(17)–C(18)	1.404(31)
Nd–C(18)	2.814(23)	Nd–cent(1)	2.538
O(1)–C(11)	1.410(21)	Nd–cent(2)	2.545
Bond angles			
O(1)–Nd–O(2)	160.6(6)	C(11)–O(1)–C(12)	112.4(17)
O(1)–Nd–B	82.9(6)	O(1)–C(12)–C(13)	106.1(29)
O(1)–Nd–cent(1)	84.6	C(14)–C(15)–C(16)	113.3(22)
O(1)–Nd–cent(2)	108.8	C(15)–C(16)–C(17)	99.9(18)
Cent(1)–Nd–B	135.3	C(16)–C(17)–C(18)	114.8(19)
Cent(2)–Nd–B	114.4	C(17)–C(18)–C(14)	104.8(19)
Cent(1)–Nd–cent(2)	109.5	C(18)–C(14)–C(15)	106.9(18)

Cent(1) is the centroid of cyclopentadienyl ring defined by C(14)–C(18); cent(2) is the centroid of cyclopentadienyl ring defined by C(24)–C(28).

The solution of structure for **3** is similar to that of **2**. Further details of **2** and **3** are given in Table 1. The atomic coordinates of **2** and **3** are given in Tables 2 and 3, respectively. Selected bond lengths and angles are given in Tables 4 and 5.

3. Results and discussion

Lanthanide trichlorides react with sodium salt, $MeOCH_2CH_2C_5H_4Na$, in THF at RT to give the corresponding bis(2-methoxyethylcyclopentadienyl)-lanthanide chlorides. These chlorides react with excess of sodium borohydride in THF by Cl^-–BH_4^- displacement to yield the organolanthanocene tetrahydroborates **1–5** (eqns. (1) and (2)):

$$LnCl_3 + MeOCH_2CH_2C_5H_4Na \xrightarrow[RT]{THF} (MeOCH_2CH_2C_5H_4)_2LnCl + 2NaCl \quad (1)$$

$$(MeOCH_2CH_2C_5H_4)_2LnCl + NaBH_4 \xrightarrow[RT]{THF} (MeOCH_2CH_2C_5H_4)_2Ln(BH_4) + NaCl \quad (2)$$

Ln = La (**1**), Pr (**2**), Nd (**3**), Sm (**4**) or Gd (**5**);
yield, 70–90%

These compounds are soluble in THF but insoluble in hydrocarbons such as hexane at room temperature. These complexes are thermally stable; they all have definite melting point and can be sublimed at 160–180°C/10^{-4} mmHg, but are sensitive to air and moisture.

The MS of five new complexes show a parent molecular ion $[M]^+$ and related fragments, such as $[M-BH_4]^+$; no m/e greater than $[M]^+$ or equal to 72 or 71 was detected. The data indicate that the complexes are solvent free and monomeric, and that the Ln–BH_4 bond is first cleaved, giving very high relative intensity peaks of $[M-BH_4]^+$ which result from the intramolecular coordination bond.

The IR spectra of complexes **1–3** exhibit absorption peaks at about 2410 cm^{-1} (a sharp singlet $B(H_t)$, A_1) and at 2200 cm^{-1} (a strong broad band $B(H_b)_3$, A_1 and E), indicating that the BH_4^- is most probably the tridentate ligand to the early lanthanide metal [4,12]. The IR spectra of complexes **4** and **5**, however, show a strong band with a shoulder at around 2364 and 2286 cm^{-1} ($B(H_t)_2$, A_1 and B_1), and a strong doublet with 50–80 cm^{-1} splitting at about 2150 cm^{-1} ($B(H_b)_2$, A_1

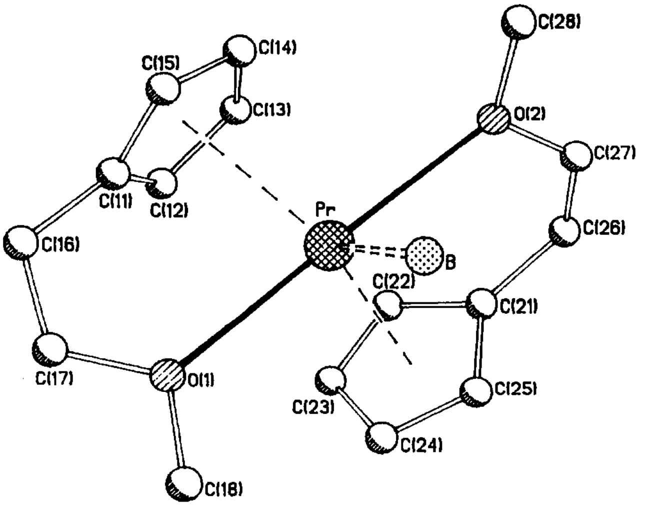

Fig. 1. X-Ray crystal structure of $(MeOCH_2CH_2C_5H_4)_2Pr(BH_4)$, 2.

and B_2). Therefore it appears to be in best agreement with bidentate as opposed to tridentate ligation geometry.

X-ray diffraction studies were carried out on complexes 2 and 3. The molecular structures of 2 and 3 are shown in Figs. 1 and 2 respectively. Since the hydride ligands cannot be located, the coordination environment about the central metal ion in 2 and 3 are difficult to describe. The Pr–C(η^5) bond lengths range from 2.730 to 2.802 Å, and the average Pr–C(η^5) distance of 2.77 Å is similar to those in other organopraseodymium (III) complexes, e.g. 2.82 Å in $(MeOCH_2CH_2C_5H_4)_3Pr$ [12] and 2.76 Å in $(Pr\{\eta\text{-}[C_5H_3(SiMe_3)_2]\}_2Cl)_2$ [13]. The ring(centroid)–Pr–ring(centroid) angle (121.4°) is comparable with 119.00(1)° in $(MeOCH_2CH_2C_5H_4)_3Pr$, and smaller than 130° in $(Pr\{\eta\text{-}[C_5H_3(SiMe_3)_2]\}_2Cl)_2$. The average Pr–O bond length is 2.605 Å, which is 0.19 Å shorter than that of $(MeOCH_2CH_2C_5H_4)_3Pr$ [12]. The bond angle of O(1)–Pr–O(2) is 165.3(3)°, which is smaller than that in the complex mentioned above: 174.8°.

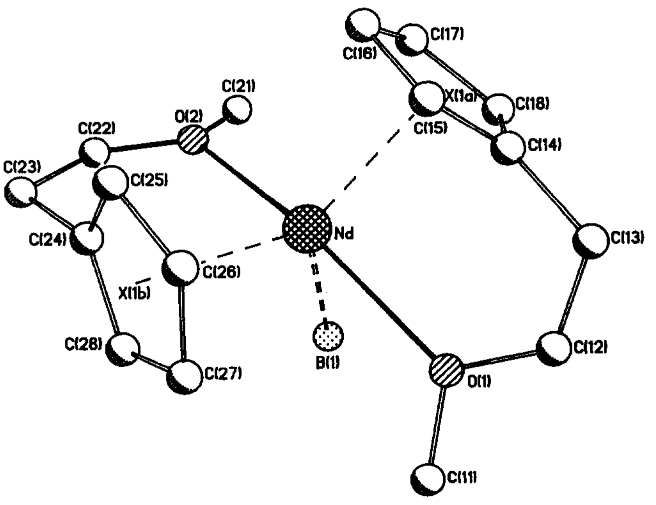

Fig. 2. X-Ray crystal structure of $(MeOCH_2CH_2C_5H_4)_2Nd(BH_4)$, 3.

TABLE 6. Comparison of structural parameters for $(MeOCH_2CH_2C_5H_4)_2Ln(BH_4)$ complexes

	Pr (2)	Nd (3)	Yb (6) [a]	Y (7) [a]
Ln^{3+} radius (Å)	1.319	1.303	1.182	1.215
Ln ··· B (Å)	2.757	2.664	2.800	2.773
Ln–C(η^5) (Å)	2.77	2.76	2.66	2.69
O(1)–Ln–O(2) (°)	165.3	160.6	148.7	152.2
Cent(1)–Ln–cent(2) (°)	121.4	109.5	120.6	122.9
Ln–O (average) (Å)	2.61	2.56	2.454	2.445

[a] Complexes 6 and 7; see ref. 14.

The most remarkable structural feature for complex 2 and 3 are the BH_4^- bonding modes. Some main structural parameters of $(MeOCH_2CH_2C_5H_4)_2Ln(BH_4)$ are shown in Table 6.

It has been observed [15] that the borohydrides in the structure having an Ln ··· B distance similar (±0.1 Å) to those of the two-site boron atom would be expected to have bidentate BH_4^-, and borohydrides with a much shorter Ln ··· B distance would then act as a tridentate ligand. In complexes 6 and 7, the bidentate coordination of BH_4^- are indicated by IR spectra [3]. On comparison between complexes 2 and 6, it is shown that the Ln ··· B separation for them are 2.757 Å and 2.800 Å respectively. After allowing 0.137 Å [16] for the difference between the metal radii, it seems that 2 probably has a different BH_4^- ligation from 6. Therefore we suggest that 2 has tridentate BH_4^- ligation.

The structure of the neodymium compound 3 is similar to that of the praseodymium compound 2, except for the fact that the bond distances involving the metal atom are slightly shorter for Nd than those for Pr. Complex 3 would also be expected to have tridentate BH_4^- ligation.

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