

*Journal of Organometallic Chemistry*, 413 (1991) 79–90  
 Elsevier Sequoia S.A., Lausanne  
 JOM 21943

## Organolanthanide hydroxides; the synthesis and crystal structures of the samarocene and ytterbocene hydroxides $[\{\text{SmCp}_2''(\mu\text{-OH})\}_2]$ and $[\{\text{YbCp}'_2(\mu\text{-OH})\}_2][\text{Cp}'' = \eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_{2-1,3}$ ; $\text{Cp}' = \eta^5\text{-C}_5\text{H}_4\text{SiMe}_3]$ \*.\*.\*

Peter B. Hitchcock, Michael F. Lappert and Sanjiv Prashar

*School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ (UK)*

(Received April 26th, 1991)

### Abstract

The organolanthanide(III) complexes  $[\{\text{SmCp}_2''(\mu\text{-OH})\}_2]$  (**1**) and  $[\{\text{YbCp}'_2(\mu\text{-OH})\}_2]$  (**2**) [ $\text{Cp}'' = \eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_{2-1,3}$ ;  $\text{Cp}' = \eta^5\text{-C}_5\text{H}_4\text{SiMe}_3$ ] were prepared from the appropriate lanthanocene(II) precursor  $[\text{SmCp}_2''(\text{THF})]$  (**3**) and  $[\text{YbCp}'_2(\text{OEt}_2)]$  (**4**), by treatment with water in an ethereal solution. The single crystal X-ray structures of **1** and **2** reveal that each complex is dimeric with bridging hydroxide groups, while NMR data indicate that these structures persist in aprotic media. The mean bond lengths Sm–O 2.40(2) and Sm–Cent(Cp'') 2.45 Å in crystalline **1** may be compared with Yb–O 2.29(2) and Yb–Cent(Cp') 2.33 Å in **2**; while the angle O–Sm–O' in **1** is 76.6(6) and O–Yb–O' in **2** is 77.9(7)° ("Cent" refers to the centroid of the  $\text{C}_5$  ring).

### Introduction

One of the most widely used ligands in *d*- and *f*-element organometallic chemistry is  $\text{C}_5\text{H}_5^-$  ( $\text{Cp}^-$ ), first discovered in 1951 in ferrocene [1]. Various substituted cyclopentadienyls have subsequently found a useful role, including  $\text{C}_5\text{Me}_5^-$ ,  $\text{C}_5\text{H}_4(\text{SiMe}_3)^-$  ( $\equiv \text{Cp}'^-$ ), and  $\text{C}_5\text{H}_3(\text{SiMe}_3)_{2-1,3}$  ( $\equiv \text{Cp}''^-$ ) [2].

The chemistry of organolanthanide (Ln) complexes in the ubiquitous 3+ oxidation state has been widely explored [3], yet no single organolanthanide(III) hydroxide has previously been reported in the literature, although a derivative of the prelanthanide element yttrium, namely  $[\{\text{Y}(\eta\text{-C}_5\text{H}_5)_2(\mu\text{-OH})\}_2(\text{PhC}\equiv\text{CPh})]$  is established [4]. The latter was prepared by partial hydrolysis of a mixture of  $[\text{Y}(\text{C}_5\text{H}_5)_2(\text{}^t\text{Bu})(\text{THF})]$  and  $\text{PhC}\equiv\text{CPh}$ , and was structurally characterised by X-ray crystallography (THF = tetrahydrofuran); a compound formulated as  $\text{Y}(\eta\text{-C}_5\text{H}_5)_2(\text{OH})(\text{THF})$  was obtained by treatment of  $[\text{Y}(\eta\text{-C}_5\text{H}_5)_3(\text{THF})]$  with NaOH in THF, but attempts to remove THF by sublimation led to decomposition.

\* Dedicated to Professor Peter Pauson, in recognition of his important contributions to organometallic chemistry and as a mark of friendship.

\*\* No reprints available.

A problem with such a synthesis relates to either (i) the tendency of organo-lanthanide complexes to undergo complete hydrolysis affording  $\text{Ln}(\text{OH})_3$ , or (ii) for a transient  $\text{LnCp}_2^x(\text{OH})$  complex to undergo associative dehydration to produce a  $\mu$ -oxo complex such as  $[(\text{LnCp}_2^x)_2(\mu\text{-O})]$  ( $\text{Cp}^x$  = an unsubstituted or substituted cyclopentadienyl).

The 2+ oxidation state for the lanthanides is less well developed, and is restricted to samarium ( $f^6$ ), europium ( $f^7$ ), and ytterbium ( $f^{14}$ ). The first X-ray characterised lanthanocene(II) derivatives were reported in 1980:  $[\text{YbCp}_2'(\text{THF})_2]$  [5],  $[\text{Yb}(\eta\text{-C}_5\text{H}_4\text{Me})_2(\text{THF})]$  [6], and  $[\text{Yb}(\eta\text{-C}_5\text{Me}_5)_2(\text{THF})] \cdot \frac{1}{2}\text{PhMe}$  [7]. The chemistry of lanthanide complexes in the 2+ oxidation state is dominated by their role as one-electron reducing agents [8]; however, abstraction of an OH radical from a substrate had not previously been observed.

The lanthanocene(II) starting materials used in the present study, namely  $[\text{SmCp}_2''(\text{THF})]$  (3) and  $[\text{YbCp}_2'(\text{OEt}_2)]$  (4) are new compounds.

## Experimental

### Materials and procedures

All manipulations were carried out under vacuum or argon by Schlenk techniques. Solvents were dried and distilled over potassium–sodium alloy under argon prior to use. The following compounds were prepared by published procedures:  $\text{SmI}_2(\text{THF})_2$  [8] and  $\text{YbI}_2$  [9], and  $\text{Cp}'\text{H}$  [10] and  $\text{Cp}''\text{H}$  [11]. Microanalyses were carried out in the micro-analytical department of the University of Sussex. NMR Spectra were recorded using Bruker WM360 or Bruker WM500 spectrometers. IR Spectra were examined using a Perkin–Elmer 1710 Fourier transform spectrometer.

### Preparation of $[(\text{SmCp}_2''(\mu\text{-OH}))_2]$ (1)

A standard solution of water (1  $\text{cm}^3$ , 55.56 mmol) in tetrahydrofuran (499  $\text{cm}^3$ ) was prepared. An aliquot of this solution (10  $\text{cm}^3$ , 1.11 mmol) was then further diluted by addition of tetrahydrofuran (100  $\text{cm}^3$ ) and was thoroughly degassed using the freeze-thaw method before being added to  $[\text{SmCp}_2''(\text{THF})]$  (3) (0.71 g, 1.11 mmol). The mixture was stirred for ca 1 h at ca 20 °C. The solvent was removed under reduced pressure and the residual yellow solid was extracted into toluene (40  $\text{cm}^3$ ). Cooling the toluene solution to –30 °C yielded yellow X-ray quality single crystals of the title complex 1 (0.53 g, 82%). Found: C, 45.0; H, 7.3.  $\text{C}_{44}\text{H}_{86}\text{O}_2\text{Si}_8\text{Sm}_2$  calc.: C, 45.1; H, 7.3%.

### Preparation of $[(\text{YbCp}_2'(\mu\text{-OH}))_2]$ (2)

A standard solution of water (1  $\text{cm}^3$ , 55.56 mmol) in diethyl ether (100  $\text{cm}^3$ ) was prepared. An aliquot (10  $\text{cm}^3$ , 1.11 mmol), further diluted by addition of diethyl ether (100  $\text{cm}^3$ ), was thoroughly degassed by the freeze-thaw method before being added to  $[\text{YbCp}_2'(\text{OEt}_2)]$  (4) (0.58 g, 1.11 mmol). The mixture was stirred for ca 1 h at ca 20 °C, then concentrated (to ca 40  $\text{cm}^3$ ) and cooled to –30 °C to yield yellow X-ray quality single crystals of the title complex 2 (0.42 g, 82%). Found: C, 41.0; H, 5.7.  $\text{C}_{32}\text{H}_{54}\text{O}_2\text{Si}_4\text{Yb}_2$  calc.: C, 41.4; H, 5.8%.

### Preparation of $[\text{SmCp}_2''(\text{THF})]$ (3)

A solution of  $[\text{SmI}_2(\text{THF})_2]$  (2.90 g, 5.29 mmol) in tetrahydrofuran (ca 100  $\text{cm}^3$ ) was added to a stirred solution of  $\text{KCp}''$  (5) (2.61 g, 10.51 mmol) in tetrahydrofuran

Table 1  
X-Ray crystal structure details

	[(SmCp <sub>2</sub> '(OH)) <sub>2</sub> ] (1)	[(YbCp <sub>2</sub> (OH)) <sub>2</sub> ] (2)
Formula	C <sub>44</sub> H <sub>86</sub> O <sub>2</sub> Si <sub>8</sub> Sm <sub>2</sub>	C <sub>32</sub> H <sub>54</sub> O <sub>2</sub> Si <sub>4</sub> Yb <sub>2</sub>
<i>M</i>	1172.5	929.2
Crystal system, space group	Triclinic, $\bar{P}1$	Monoclinic, $P2_1/c$
<i>a</i> , <i>b</i> , <i>c</i> (Å)	11.954(12), 12.964(15),	13.195(6), 23.819(19), 25.830(14)
$\alpha$ , $\beta$ , $\gamma$ (°)	11.606(13), 105.85(12),	90, 101.18(4), 90
	90.32(10), 117.02(10)	
<i>U</i> (Å <sup>3</sup> ), <i>Z</i> , <i>D<sub>c</sub></i> (g cm <sup>-3</sup> )	1523.6, 1, 1.28	7964.1, 8, 1.55
<i>F</i> (000)	602	3664
$\mu$ (Mo- <i>K<sub>α</sub></i> ) (cm <sup>-1</sup> )	21.0	48.0
Crystal size (mm <sup>3</sup> )	0.1 × 0.1 × 0.1	0.2 × 0.2 × 0.1
Total unique reflections, $\theta_{\max}$ (°)	2835, 20	7652, 20
Significant reflections,   <i>F</i> <sup>2</sup>   > 3σ  <i>F</i> <sup>2</sup>	1666	3911
Number of variables	253	696
<i>R</i> , <i>R'</i> <sup>a</sup>	0.071, 0.086	0.063, 0.072

$$^a R = \sum w(|F_o| - |F_c|) / (\sum w |F_o|); R' = [\sum w(|F_o| - |F_c|)^2 / (\sum w |F_o|^2)]^{1/2}.$$

Table 2

Fractional atomic coordinates ( $\times 10^4$ ) and equivalent isotropic thermal parameters (Å<sup>2</sup> × 10<sup>3</sup>) for [(SmCp<sub>2</sub>'(μ-OH))<sub>2</sub>] (1)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U<sub>eq</sub></i> <sup>a</sup>
Sm	1469.9(14)	1466.2(13)	88.8(14)	46(1)
Si(1)	1308(7)	3719(7)	3340(7)	63(3)
Si(2)	-290(8)	2960(7)	-1696(7)	71(3)
Si(3)	4908(7)	2368(7)	2131(7)	70(3)
Si(4)	3285(8)	1322(7)	-2938(7)	77(4)
O	327(13)	227(14)	1319(17)	68(8)
C(1)	1385(21)	3447(18)	1702(23)	53(10)
C(2)	318(24)	2897(20)	709(20)	57(11)
C(3)	781(25)	3110(17)	-331(22)	74(11)
C(4)	2148(21)	3716(22)	-126(20)	57(11)
C(5)	2415(21)	3879(19)	1046(23)	57(11)
C(6)	2378(27)	5405(28)	4055(29)	94(15)
C(7)	1834(32)	2860(29)	4025(26)	114(17)
C(8)	-286(29)	3340(29)	3663(26)	98(15)
C(9)	752(37)	4123(32)	-2434(30)	148(20)
C(10)	-1579(32)	3305(34)	-1121(43)	222(22)
C(11)	-1185(41)	1382(34)	-2795(35)	196(22)
C(12)	3726(22)	1604(17)	688(21)	48(10)
C(13)	3877(22)	2054(19)	-319(23)	55(11)
C(14)	3150(22)	1168(22)	-1381(23)	62(11)
C(15)	2540(22)	89(18)	-1047(22)	55(10)
C(16)	2879(23)	332(20)	76(18)	65(10)
C(17)	5327(34)	4010(32)	2754(31)	133(19)
C(18)	4259(33)	1575(31)	3273(25)	113(17)
C(19)	6388(32)	2236(35)	1761(40)	164(22)
C(20)	1672(38)	581(39)	-3841(33)	150(22)
C(21)	4055(51)	2913(33)	-2873(32)	176(26)
C(22)	4172(36)	597(36)	-3659(38)	242(22)

<sup>a</sup> *U<sub>eq</sub>* is defined as one third of the trace of the orthogonalised *U<sub>ij</sub>* tensor.

Table 3

Fractional atomic coordinates ( $\times 10^4$ ) and equivalent isotropic thermal parameters ( $\text{\AA}^2 \times 10^3$ ) for  $[\{\text{YbCp}_2(\mu\text{-OH})\}_2] (2)$

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}^a$
<i>Molecule 1</i>				
Yb(1)	8686.5(10)	8390.4(5)	579.7(5)	39(1)
Yb(2)	8678.3(10)	6906.0(5)	620.5(5)	42(1)
Si(1)	5778(7)	8891(4)	632(3)	53(5)
Si(2)	11594(7)	8853(4)	532(4)	57(5)
Si(3)	11265(7)	5998(4)	747(4)	74(6)
Si(4)	6064(7)	6003(4)	569(4)	71(6)
O(1)	9734(14)	7649(8)	953(8)	64(11)
O(2)	7730(16)	7637(8)	268(8)	71(11)
C(1)	7136(27)	8801(12)	974(14)	78(21)
C(2)	7840(23)	9254(12)	976(13)	62(19)
C(3)	8801(26)	9125(13)	1347(15)	85(23)
C(4)	8590(26)	8601(13)	1536(12)	72(19)
C(5)	7600(20)	8427(11)	1326(12)	49(17)
C(6)	5084(22)	9259(17)	1068(13)	91(24)
C(7)	5219(24)	8178(15)	558(14)	80(23)
C(8)	5680(30)	9187(18)	-27(15)	111(29)
C(9)	10197(19)	8761(10)	196(11)	39(15)
C(10)	9436(28)	9213(11)	105(14)	81(22)
C(11)	8587(19)	9020(15)	-252(12)	73(11) <sup>b</sup>
C(12)	8808(27)	8483(13)	-401(14)	81(22)
C(13)	9800(21)	8363(12)	-146(11)	53(17)
C(14)	12349(19)	9251(15)	103(13)	80(12) <sup>b</sup>
C(15)	12197(21)	8161(12)	650(13)	61(19)
C(16)	11686(21)	9194(17)	1165(12)	89(13) <sup>b</sup>
C(17)	10061(23)	6276(12)	296(11)	58(18)
C(18)	10055(29)	6788(13)	48(14)	82(22)
C(19)	9166(20)	6810(12)	-304(10)	49(17)
C(20)	8546(24)	6363(14)	-292(15)	80(22)
C(21)	9181(21)	5998(15)	120(14)	78(22)
C(22)	10926(33)	5370(15)	1068(19)	129(31)
C(23)	11916(35)	6457(17)	1230(18)	133(32)
C(24)	12170(33)	5814(28)	320(19)	204(44)
C(25)	7220(22)	6341(16)	992(13)	80(22)
C(26)	7310(22)	6911(12)	1214(13)	67(20)
C(27)	8250(25)	6940(13)	1552(13)	71(21)
C(28)	8784(18)	6456(13)	1548(12)	58(10) <sup>b</sup>
C(29)	8178(23)	6092(13)	1196(13)	69(20)
C(30)	6535(35)	5355(15)	290(21)	157(33)
C(31)	5408(27)	6448(20)	73(20)	142(33)
C(32)	5214(30)	5773(22)	991(17)	231(34)
<i>Molecule 2</i>				
Yb(3)	7621.6(9)	2650.8(6)	1770.4(5)	39(1)
Yb(4)	5017.6(9)	2601.6(5)	1960.6(5)	40(1)
Si(5)	3311(7)	3957(4)	2108(4)	66(6)
Si(6)	8480(8)	4267(4)	1935(4)	75(6)
Si(7)	8372(8)	1069(4)	1529(4)	64(6)
Si(8)	3567(8)	1131(4)	1982(4)	80(6)
O(3)	6536(15)	2097(14)	2158(9)	120(10) <sup>b</sup>
O(4)	6095(14)	3136(11)	1566(8)	101(15)

Table 3 (continued)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}^a$
C(33)	4178(20)	3365(11)	2447(12)	48(16)
C(34)	3893(24)	2856(12)	2651(12)	70(19)
C(35)	4757(24)	2610(13)	2943(11)	73(18)
C(36)	5596(23)	2947(14)	2923(12)	69(19)
C(37)	5287(20)	3443(13)	2649(10)	53(17)
C(38)	3165(32)	4497(14)	2574(15)	116(26)
C(39)	2014(23)	3670(17)	1828(18)	110(27)
C(40)	3857(29)	4232(18)	1583(16)	111(29)
C(41)	8598(24)	3543(12)	2214(12)	65(19)
C(42)	8108(19)	3287(14)	2612(11)	57(19)
C(43)	8590(26)	2783(13)	2762(13)	84(21)
C(44)	9320(21)	2694(13)	2450(12)	64(17)
C(45)	9339(23)	3159(12)	2143(12)	71(19)
C(46)	9539(30)	4682(16)	2296(18)	124(29)
C(47)	7287(35)	4554(13)	2012(22)	161(22) <sup>b</sup>
C(48)	8593(52)	4252(16)	1243(20)	200(44)
C(49)	8135(25)	1766(13)	1260(13)	69(20)
C(50)	7149(21)	1974(12)	925(12)	51(17)
C(51)	7324(24)	2509(10)	772(13)	62(19)
C(52)	8294(21)	2652(14)	922(13)	76(19)
C(53)	8849(29)	2230(14)	1206(12)	88(22)
C(54)	9386(27)	732(14)	1258(13)	83(22)
C(55)	8809(34)	1106(18)	2224(14)	117(29)
C(56)	7108(24)	675(12)	1390(14)	69(20)
C(57)	3788(26)	1748(12)	1571(12)	72(20)
C(58)	3192(20)	2247(16)	1508(12)	77(20)
C(59)	3553(25)	2559(13)	1148(14)	78(21)
C(60)	4383(22)	2327(15)	973(13)	76(20)
C(61)	4498(22)	1789(12)	1252(12)	56(18)
C(62)	3375(39)	510(14)	1557(17)	148(31)
C(63)	4706(47)	952(21)	2483(24)	249(45)
C(64)	2346(51)	1228(22)	2277(24)	316(47)

<sup>a</sup>  $U_{eq}$  is defined as one third of the trace of the orthogonalised  $U_{ij}$  tensor. <sup>b</sup>  $U_{iso}$ .

(ca 100 cm<sup>3</sup>). The resultant mixture was stirred at ca 20 °C for 20 h to give a purple suspension which was filtered. The volatiles were removed from the filtrate *in vacuo* to yield a green solid which was extracted into toluene (ca 100 cm<sup>3</sup>); the extract was filtered, concentrated to ca 50 cm<sup>3</sup>, and cooled to –30 °C to afford dark green crystals of the title complex **3** (2.57 g, 77%). Found: C, 48.4; H, 7.7. C<sub>26</sub>H<sub>50</sub>OSi<sub>4</sub>Sm calc.: C, 48.7; H, 7.9%.

#### Preparation of [YbCp<sub>2</sub>'(OEt<sub>2</sub>)] (**4**)

NaCp' (**6**) (1.56 g, 9.77 mmol) was added to a suspension of YbI<sub>2</sub> (2.19 g, 5.13 mmol) in diethyl ether (ca 200 cm<sup>3</sup>). The suspension was stirred for ca 20 h at ca 20 °C to give a dark red suspension, which was filtered. The volatiles were removed from the filtrate *in vacuo* to yield a green solid which was extracted into toluene (ca 50 cm<sup>3</sup>) and cooled to –30 °C to yield dark green crystals of the title complex **4** (1.78 g, 70%). Found: C, 48.3; H, 6.5. C<sub>20</sub>H<sub>36</sub>OSi<sub>2</sub>Yb calc.: C, 48.9; H, 6.9%.

### Preparation of $KCp''$ (5)

Bis-1,3-(trimethylsilyl)cyclopentadiene (8.75 g, 41.67 mmol) was added to a cooled ( $-50^{\circ}C$ ) stirred suspension of  $KH$  (2.08 g, 52.09 mmol) in tetrahydrofuran ( $300\text{ cm}^3$ ). The resultant mixture was allowed to stir for ca 12 h at ca  $20^{\circ}C$ , whereafter it was filtered. The solvent was removed from the filtrate in *vacuo* to give a white solid which was washed with two portions ( $100\text{ cm}^3$  each) of hexane and dried under vacuum to yield a free-flowing white powder of the title compound **5** (7.47 g, 12%). Found: C, 53.5; H, 8.4.  $C_{21}H_{27}KSi_2$  calc.: C, 53.2; H, 8.5%.

### Preparation of $NaCp'$ (6)

An excess of solid  $NaNH_2$  (3.4 g, 87.18 mmol) was added to a stirred solution of trimethylsilylcyclopentadiene (7.20 g, 52.14 mmol) in tetrahydrofuran ( $300\text{ cm}^3$ ). The resultant mixture was allowed to stir for ca 24 h at ca  $20^{\circ}C$ , whereafter it was filtered to remove unreacted  $NaNH_2$ . Solvent was removed from the brown filtrate in *vacuo* to yield a brown solid which was washed with two portions ( $100\text{ cm}^3$  each) of hexane and dried under vacuum to yield a free-flowing white powder of the title product **6** (4.01 g, 48%). Found: C, 59.4; H, 7.8.  $C_8H_{13}NaSi$  calc.: C, 60.0; H, 8.1%.

### X-Ray structure determinations for $[\{SmCp_2''(\mu-OH)\}_2]$ (1) and $[\{YbCp_2'(\mu-OH)\}_2]$ (2)

In both cases unique data were collected, using a crystal sealed in a capillary under argon on an Enraf-Nonius CAD4 diffractometer in the  $\theta$ - $2\theta$  mode with monochromated  $Mo-K_{\alpha}$  radiation ( $\lambda = 0.71069\text{ \AA}$ ). Two standard reflections monitored every hour showed no significant change. Data were corrected for Lorentz and polarisation effects and also for absorption using DIFABS [12] after isotropic refinement. Reflections with  $|F^2| > 3\sigma(F^2)$ , where  $\sigma(F^2) = \{\sigma^2(I) + (0.04I)^2\}^{1/2}/Lp$  were considered observed.

Both structures were solved using the heavy atom routines of SHELXS-86 [13]. For **2**, there are two independent molecules which have essentially the same geometry. Non-hydrogen atoms were refined with anisotropic thermal parameters by full-ma-

Table 4

Selected intramolecular distances ( $\text{\AA}$ ) and angles ( $^{\circ}$ ) with estimated standard deviations in parentheses for  $[\{SmCp_2''(\mu-OH)\}_2]$  (1) <sup>a</sup>

Bonds			
Sm-Cp1	2.46	Sm-Cp2	2.44
Sm-O	2.40(2)	Sm-O'	2.41(1)
Sm-C(1)	2.78(2)	Sm-C(2)	2.73(3)
Sm-C(3)	2.76(3)	Sm-C(4)	2.73(3)
Sm-C(5)	2.68(2)	Sm-C(12)	2.69(3)
Sm-C(13)	2.70(3)	Sm-C(14)	2.73(3)
Sm-C(15)	2.71(3)	Sm-C(16)	2.69(3)
Angles			
Cp1-Sm-Cp2	129.5	Cp1-Sm-O	132.0
Cp1-Sm-O'	114.6	Cp2-Sm-O	105.6
Cp2-Sm-O'	103.9	O-Sm-O'	76.6(6)

<sup>a</sup> Cp1 and Cp2 are the centroids of the cyclopentadienyl rings C(1) to C(5) and C(12) to C(16), respectively. Symmetry element ' is  $-x, -y, -z$ .

trix least-squares using programs from the Enraf–Nonius SDP-PLUS package. In 2, five carbon atoms, for which the thermal parameters became non-positive definite, were re-set to isotropic. Hydrogen atoms from the hydroxyl groups could not be

Table 5

Selected intramolecular distances (Å) and angles (°) with estimated standard deviations in parentheses for  $\{[\text{YbCp}_2(\mu\text{-OH})]_2\}$  (2) <sup>a</sup>

<i>Bonds</i>			
Yb(1)–O(1)	2.33(2)	Yb(1)–O(2)	2.25(2)
Yb(1)–C(1)	2.64(4)	Yb(1)–C(2)	2.64(3)
Yb(1)–C(3)	2.63(4)	Yb(1)–C(4)	2.55(3)
Yb(1)–C(5)	2.62(3)	Yb(1)–C(9)	2.55(3)
Yb(1)–C(10)	2.60(3)	Yb(1)–C(11)	2.60(3)
Yb(1)–C(12)	2.58(4)	Yb(1)–C(13)	2.60(3)
Yb(1)–Cp1	2.33	Yb(1)–Cp2	2.30
Yb(2)–O(1)	2.31(2)	Yb(2)–O(2)	2.23(2)
Yb(2)–C(17)	2.62(3)	Yb(2)–C(18)	2.57(4)
Yb(2)–C(19)	2.60(3)	Yb(2)–C(20)	2.66(4)
Yb(2)–C(21)	2.67(4)	Yb(2)–C(25)	2.67(3)
Yb(2)–C(26)	2.58(3)	Yb(2)–C(27)	2.58(3)
Yb(2)–C(28)	2.60(3)	Yb(2)–C(29)	2.61(3)
Yb(2)–Cp3	2.35	Yb(2)–Cp4	2.32
Yb(3)–O(3)	2.31(3)	Yb(3)–O(4)	2.29(2)
Yb(3)–C(41)	2.63(3)	Yb(3)–C(42)	2.62(3)
Yb(3)–C(43)	2.65(3)	Yb(3)–C(44)	2.57(3)
Yb(3)–C(45)	2.58(3)	Yb(3)–C(49)	2.64(3)
Yb(3)–C(50)	2.69(3)	Yb(3)–C(51)	2.55(3)
Yb(3)–C(52)	2.52(4)	Yb(3)–C(53)	2.58(4)
Yb(3)–Cp6	2.33	Yb(3)–Cp7	2.31
Yb(4)–O(3)	2.31(2)	Yb(4)–O(4)	2.29(2)
Yb(4)–C(33)	2.58(3)	Yb(4)–C(34)	2.60(3)
Yb(4)–C(35)	2.62(3)	Yb(4)–C(36)	2.59(3)
Yb(4)–C(37)	2.66(3)	Yb(4)–C(57)	2.67(3)
Yb(4)–C(58)	2.61(3)	Yb(4)–C(59)	2.56(3)
Yb(4)–C(60)	2.61(3)	Yb(4)–C(61)	2.66(3)
Yb(4)–Cp5	2.32	Yb(4)–Cp8	2.34
<i>Angles</i>			
O(1)–Yb(1)–O(2)	77.9(7)	O(1)–Yb(1)–Cp1	109.5
O(1)–Yb(1)–Cp2	108.9	O(2)–Yb(1)–Cp1	110.8
O(2)–Yb(1)–Cp2	108.2	Cp1–Yb(1)–Cp2	129.6
O(1)–Yb(2)–O(2)	78.7(7)	O(1)–Yb(2)–Cp3	108.8
O(1)–Yb(2)–Cp4	108.0	O(2)–Yb(2)–Cp3	110.2
O(2)–Yb(2)–Cp4	108.2	Cp3–Yb(2)–Cp4	130.7
Yb(1)–O(1)–Yb(2)	99.2(7)	Yb(1)–O(2)–Yb(2)	104.1(7)
O(3)–Yb(3)–O(4)	78.3(9)	O(3)–Yb(3)–Cp6	108.4
O(3)–Yb(3)–Cp7	110.4	O(4)–Yb(3)–Cp6	111.6
O(4)–Yb(3)–Cp7	109.1	Cp6–Yb(3)–Cp7	128.0
O(3)–Yb(4)–O(4)	78.5(9)	O(3)–Yb(4)–Cp5	108.7
O(3)–Yb(4)–Cp8	108.6	O(4)–Yb(4)–Cp5	109.7
O(4)–Yb(4)–Cp8	107.4	Cp5–Yb(4)–Cp8	131.3
Yb(3)–O(3)–Yb(4)	101(1)	Yb(3)–O(4)–Yb(4)	102(1)

<sup>a</sup> Cp1, Cp2, Cp3, Cp4, Cp5, Cp6, Cp7, and Cp8 are the centroids of the cyclopentadienyl rings C(1) to C(5), C(9) to C(13), C(17) to C(21), C(25) to C(29), C(33) to C(37), C(41) to C(45), C(49) to C(53), and C(57) to C(61), respectively.

located and were omitted. Other hydrogen atoms were held fixed at calculated positions with  $U_{iso} = 1.3 U_{eq}$  for the parent atom. Further details are given in Table 1. Atom positions are listed in Tables 2 and 3, and selected bond lengths and angles are given in Tables 4 and 5. Tables of complete bonds and angles, H atom positions, thermal parameters, and structure factors are available from one of the authors (P.B.H.).

## Results and discussion

### 1. Synthesis of $[\{SmCp_2''(\mu-OH)\}_2]$ (1) and $[\{YbCp_2'(\mu-OH)\}_2]$ (2)

The hydrolysis of  $[SmCp_2''(THF)]$  (3) in tetrahydrofuran and  $[YbCp_2'(OEt_2)]$  (4) in diethyl ether afforded  $[\{SmCp_2''(\mu-OH)\}_2]$  (1) and  $[\{YbCp_2'(\mu-OH)\}_2]$  (2), respectively, as shown in Scheme 1 (for 1 and 3:  $R = SiMe_3 = R'$ ; for 2 and 4:  $R = SiMe_3$  and  $R' = H$ ).

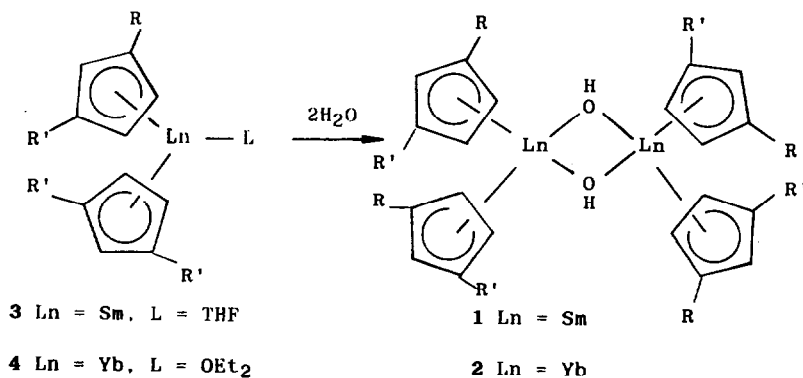
It was necessary to prepare a solution of water in a large volume of either diethyl ether or tetrahydrofuran in order to add the small amount of water required quite accurately, thus avoiding excess hydrolysis which would have led to decomposition of 1 or 2.

X-Ray quality single crystals were obtained by recrystallisation: for  $[\{SmCp_2''(\mu-OH)\}_2]$  (1) from toluene, and for  $[\{YbCp_2'(\mu-OH)\}_2]$  (2) from diethyl ether. The hydroxyl hydrogen atoms were not located in either 1 or 2 in the X-ray diffraction study, but their presence was confirmed both by IR [ $\nu(OH)$  at 3175 and 3250  $cm^{-1}$  in 1, and 2, respectively] and for 2 by  $^1H$  NMR spectroscopy ( $\delta$  31.1, in toluene- $d_8$  at 300 K).

The synthesis of the organolanthanide(III) hydroxide complexes 1 and 2 evidently proceeded via the unprecedented oxidative addition of the OH radical to the appropriate organolanthanide(II) metallocene complex 3 and 4.

### 2. Synthesis of $[SmCp_2''(THF)]$ (3) and $[YbCp_2'(OEt_2)]$ (4)

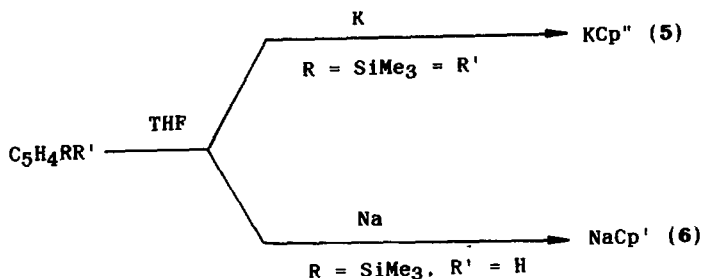
The solvated metallocene complexes  $[SmCp_2''(THF)]$  (3) and  $[YbCp_2'(OEt_2)]$  (4) were prepared in a manner similar to that for the known metallocene complexes of the divalent lanthanides incorporating the pentamethylcyclopentadienyl ligand [14], using as substrate the appropriate lanthanide(II) iodide and alkali-metal cyclopentadienyl in an ethereal solution as shown in Scheme 2.



Scheme 1







Scheme 3

and Yb(3)–O(3)–Yb(4)–O(4) bridging units are planar, as are the YbCYb'C' and YbCIYb'Cl' units in the cited bridged methyl and chloride. The bent metallocene arrangement also in complexes **1** and **2** is unexceptional with the Cent–Ln–Cent' bond angle being about 130 compared with 128.2 for **8** [17] and 130° for **9** [18]. [for **1** Cent(1)–Sm–Cent(2), 129.5; for **2a** Cent(1)–Yb(1)–Cent(2), 129.6; Cent(3)–Yb(2)–Cent(4), 130.7; for **2b** Cent(6)–Yb(3)–Cent(7), 128.0; Cent(5)–Yb(4)–Cent(8) 131.3°].

The mean Sm–O bond length of 2.40(2) Å in **1** is as expected (lanthanide contraction) longer than the mean Yb–O bond length of 2.29(2) Å in **2**. This may be compared with the corresponding Y–O distance of 2.34(2) Å in [Y(Cp)<sub>2</sub>(μ-

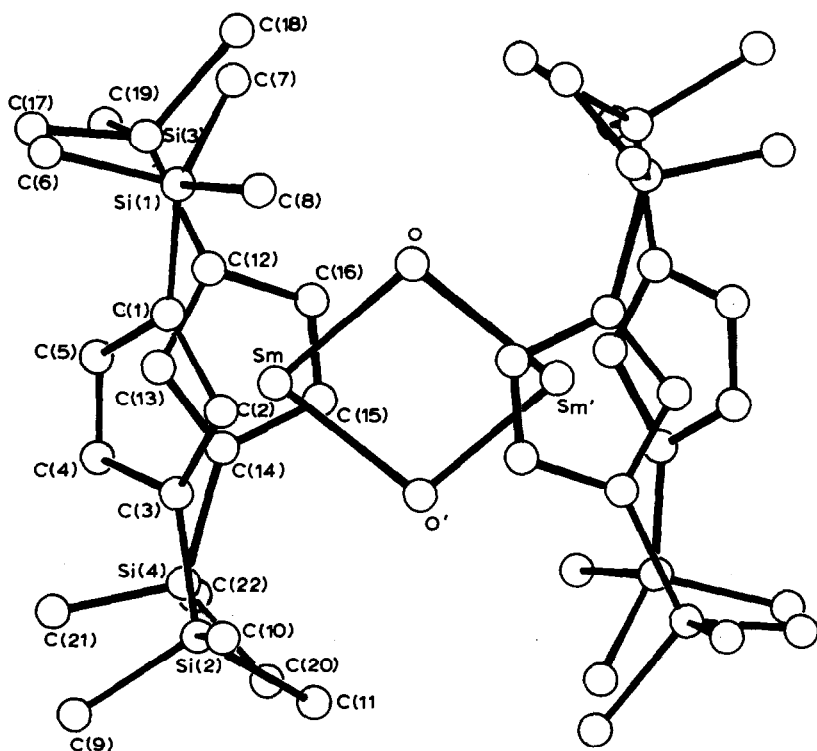


Fig. 1

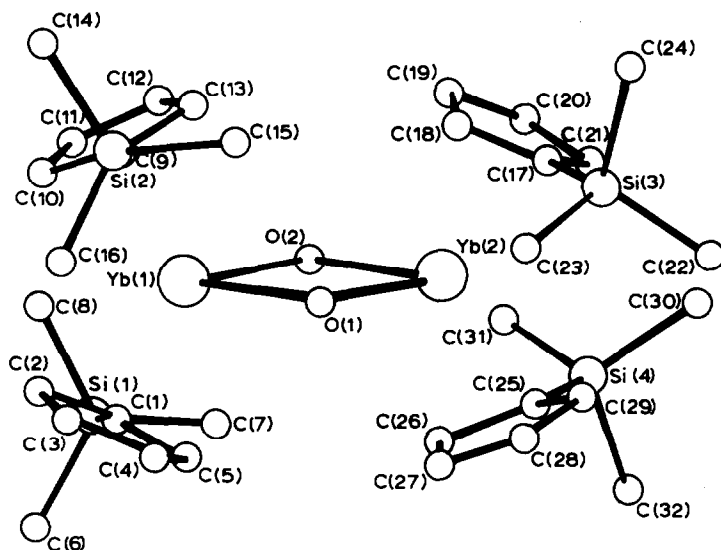


Fig. 2.

$\text{OH})_2(\text{PhC}\equiv\text{CPh})$  [4]. The only hydroxolanthanide(III) complexes to have been previously X-ray characterised are  $[\text{Yb}(\text{paphy})(\text{OH})_2(\text{OH})_2]\text{Cl}_4 \cdot 4\text{H}_2\text{O}$  for which  $\text{Yb}-\text{OH}$  is 2.19(1) Å (paphy = pyridine-2-carboxaldehyde-2'-pyridylhydrazone) [19], and  $[(\text{Pr}(15\text{-crown-5}))_2(\mu\text{-OH})(\mu\text{-OCOCF}_3)_3][\text{Pr}_2(\text{OCOCF}_3)_8]$  for which  $\text{Pr}-\text{OH}$  is 2.31(1) Å [20]. In the four-membered  $\text{Ln}-\text{O}-\text{Ln}'-\text{O}'$  rings of **1** and **2** the angles at Ln are appreciably smaller (76.6(6) in **1** and 77.9(7)° in **2** than at O; this compares with 93.4(5) for  $\text{C}-\text{Yb}-\text{C}'$  in **8** [17] and 80° for  $\text{Cl}-\text{Yb}-\text{Cl}'$  in **9** [18].

## Acknowledgements

We thank Johnson–Matthey for the samarium and ytterbium metals, and for a C.A.S.E. award for S.P., and S.E.R.C. for support. We acknowledge a useful discussion with Professor W.J. Evans, who also informed us of his independent synthesis of  $\text{SmCp}_2''(\text{THF})$  (**3**).

## References

- 1 T.J. Keely and P.L. Pauson, *Nature*, 168 (1951) 1039; S.A. Miller, J.A. Tebboth and J.F. Tremaine, *J. Chem. Soc.*, (1952) 632.
- 2 cf., M.F. Lappert and A. Singh, *Inorg. Synth.*, 27 (1990) 168, and references therein.
- 3 T.J. Marks and R.D. Ernst, in G. Wilkinson, F.G.A. Stone and E.W. Abel (Eds.), *Comprehensive Organometallic Chemistry*, Vol. 3, Pergamon, Oxford, 1982, p. 173; H. Schumann, *Angew. Chem., Int. Ed. Engl.*, 23 (1984) 474; W.J. Evans, *Polyhedron*, 6 (1987) 803.
- 4 W.J. Evans, M.A. Hozbor, S.G. Bott, G.H. Robinson and J.L. Atwood, *Inorg. Chem.*, 27 (1988) 1990.
- 5 M.F. Lappert, P.I.W. Yarrow, J.L. Atwood, R. Shakir and J. Holton, *J. Chem. Soc., Chem. Commun.*, (1980) 987.
- 6 H.A. Zinnen, J.J. Pluth, and W.J. Evans, *J. Chem. Soc., Chem. Commun.*, (1980) 810.
- 7 T.D. Tilley, R.A. Andersen, B. Spencer, H. Ruben, A. Zalkin and D.H. Templeton, *Inorg. Chem.*, 19 (1980) 2999.

- 8 P. Girard, J.L. Namy and H.B. Kagan, *J. Am. Chem. Soc.*, 102 (1980) 2693; J.L. Namy, P. Girard and H.B. Kagan, *Nouv. J. Chim.*, 5 (1981) 479; P.L. Watson, T.H. Tulip and I. Williams, *Organometallics*, 9 (1990) 1999.
- 9 T.D. Tilley, J. M. Boncella, D.J. Berg, C.J. Burns and R.A. Andersen, *Inorg. Synth.*, 27 (1990) 146.
- 10 C.S. Kraihanzel and M.L. Lossee, *J. Am. Chem. Soc.*, 90 (1968) 4701.
- 11 E.W. Abel and S. Moorhouse, *J. Organomet. Chem.*, 19 (1971) 227.
- 12 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 39 (1983) 158.
- 13 G.M. Sheldrick in G.M. Sheldrick, C. Krüger and R. Goddard (Eds.), *Crystallographic Computing 3*, Oxford Univ. Press, 1985, p. 175–189.
- 14 W.J. Evans, J.W. Grate, H.W. Choi, I. Bloom, W.E. Hunter and J.L. Atwood, *J. Am. Chem. Soc.*, 107 (1985) 941.
- 15 M.F. Lappert and S. Prashar, unpublished results.
- 16 W.J. Evans and T.A. Ullibbarri, *Polyhedron*, 8 (1989) 1007.
- 17 J. Holton, M.F. Lappert, D.G.H. Ballard, R. Pearce, J.L. Atwood and W.E. Hunter, *J. Chem. Soc., Dalton Trans.*, (1979) 54.
- 18 M.F. Lappert, A. Singh, J.L. Atwood and W.E. Hunter, *J. Chem. Soc., Chem. Commun.*, (1981) 1190.
- 19 E. Baraniak, R.St.L. Bruce, H.C. Freeman, N.J. Hair and J. James, *Inorg. Chem.*, 15 (1976) 2226.
- 20 D. Harrison, A. Giorgetti, and J.-C.G. Bünzli, *J. Chem. Soc., Dalton Trans.*, (1985) 885.