

JOM 23628

## Studies on organolanthanoid complexes

# LI \*. Syntheses of bis- and tris(2-methoxyethylcyclopentadienyl)lanthanoid complexes and crystal structures of bis(2-methoxyethylcyclopentadienyl)ytterbium iodide and tris(2-methoxyethylcyclopentadienyl)samarium

Daoli Deng, Changtao Qian, Fuquan Song<sup>1</sup>, Zhaoyu Wang<sup>1</sup>, Guang Wu<sup>2</sup>, Peiju Zheng<sup>2</sup>, Songchun Jin<sup>3</sup> and Yonghua Lin<sup>3</sup>

Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032 (China)

(Received December 3, 1992; in revised form February 25, 1993)

### Abstract

Reactions of lanthanoid triiodides ( $L_n = \text{Sm, Yb}$ ) with two or three equivalents of 2-methoxyethylcyclopentadienyl potassium salt in tetrahydrofuran afford bis(2-methoxyethylcyclopentadienyl)lanthanoid iodide complex  $\text{Cp}'_2\text{YbI}$  (I) ( $\text{Cp}' = \text{MeOCH}_2\text{CH}_2\text{C}_5\text{H}_4$ ), tris(2-methoxyethylcyclopentadienyl)lanthanoid complexes  $\text{Cp}'_3\text{Sm}$  (II) and  $\text{Cp}'_3\text{Yb}$  (III), respectively. The compound  $\text{Cp}'_2\text{YbI}$  (I) crystallizes from THF/hexane in orthorhombic space group  $P2_12_12_1$  with cell dimensions  $a = 10.892(2)$ ,  $b = 12.278(3)$ ,  $c = 12.805(5)$  Å,  $V = 1712.4$  Å<sup>3</sup> and  $D_{\text{calcd}} = 2.118$  g cm<sup>-3</sup> for  $Z = 4$ . The central metal Yb is coordinated by two  $\text{Cp}'$  ring centroids, one iodine atom and two oxygen atoms of  $\text{Cp}'$  forming a distorted trigonal bipyramid. The crystal of  $\text{Cp}'_3\text{Sm}$  (II) belongs to the monoclinic crystal system, space group  $P2_1/n$  with  $a = 8.415(7)$ ,  $b = 20.439(3)$ ,  $c = 12.926(2)$  Å,  $\beta = 90.34(3)^\circ$ ,  $V = 2223.2$  Å<sup>3</sup>,  $D_{\text{calcd}} = 1.562$  g cm<sup>-3</sup> and  $Z = 4$ . The three  $\text{Cp}'$  ring centroids and two oxygen atoms of  $\text{Cp}'$  describe a trigonal bipyramid around the central ion of samarium. Complexes I, II and III are all unsolvated monomeric molecules with higher coordination number.

### 1. Introduction

In recent years, studies on organometallic compounds of the lanthanoid metals have shown them to be active in such important processes as C–H activation [2], alkene and alkyne reduction [3–5], alkene polymerization [4–6], carbonyl activation [7–8], C–C, C=C and C–heteroatom bond formation [9–12], C=C isomerization [11], deoxygenation of organoheteroatom oxides [13] and catalytic dehalogenation of aryl and vinyl halides [14]. So the synthesis of metallocene and organolanthanoid halides is of fundamental impor-

tance and their structural parameters might provide clear benchmarks upon which to evaluate more complex systems.

The chemistry of cationic compounds of the early transition metals and actinide elements has developed rapidly within the last five years. This interest arises from suggestions that such cationic species play a major role in the polymerization of olefins by Ziegler-Natta and Kaminsky type catalyst systems. Cationic compounds of the early lanthanide have only recently been prepared. It has been shown that the lanthanide iodides are useful precursors for syntheses of cationic compounds [15,16].

In the previous work, we used the ether-substituted cyclopentadienyl  $\text{MeOCH}_2\text{CH}_2\text{C}_5\text{H}_4$  as ligand and synthesized a series of organolanthanoid derivatives [17–21]. In order to extend the application of  $\text{MeOCH}_2\text{CH}_2\text{C}_5\text{H}_4$  in organolanthanide chemistry and to develop a new synthetic method for metallocenes

Correspondence to: Dr. C. Qian.

\* For part L, see ref. 1.

<sup>1</sup> Hebei Normal University.

<sup>2</sup> Fudan University.

<sup>3</sup> Changchun Institute of Applied Chemistry, Chinese Academy of Sciences.

and organolanthanide iodides, we report the syntheses of (2-methoxyethylcyclopentadienyl)lanthanoid complexes Cp<sub>2</sub>'YbI (I), Cp<sub>3</sub>'Sm (II) and Cp<sub>3</sub>'Yb (III) as well as structural studies on complexes I and II.

## 2. Experimental section

The complexes described below are extremely air- and moisture-sensitive. Therefore, both the syntheses and subsequent manipulations of these compounds were conducted under argon with rigorous exclusion of air and water by using Schlenk, vacuum-line, and glovebox techniques. Tetrahydrofuran and hexane were predried with LiAlH<sub>4</sub> and freshly distilled from blue sodium benzophenone under argon immediately prior to use. THF-d<sub>8</sub> was dried over Na/K alloy and was degassed by freeze-thaw cycles on the vacuum line. Mass spectra were recorded on a Finnigan 4021 spectrometer. <sup>13</sup>C NMR spectra were obtained on an FX-90Q (90 MHz) spectrometer. Samarium and ytterbium were analysed by direct complexometric titration with disodium EDTA. Carbon and hydrogen analyses were carried out by the combustion method in an aluminium tube. Melting points were determined in sealed argon filled capillaries and were uncorrected.

### 2.1. MeOCH<sub>2</sub>CH<sub>2</sub>C<sub>5</sub>H<sub>4</sub>K (Cp'K)

2-methoxyethylcyclopentadiene (11 g, 0.089 mol) [22] was added dropwise to the stirred mixture of KH-THF (4 g, 0.1 mol; 100 ml) for 1 h at 5°C and then the reaction mixture was stirred for 12 h at room temperature. The solvent was removed *in vacuo* after taking out the sediment. The crude Cp'K was washed twice with the mixed solvent THF-hexane (5 ml:30 ml) and dried *in vacuo* to give Cp'K 12.9 g (yield 86%).

### 2.2. SmI<sub>3</sub>

The mixture of Sm powder (40 mesh, 0.484 g, 3.22 mmol), and iodine (1.227 g, 4.83 mmol) in 40 ml of THF, was stirred with refluxing over a period of 12 h under argon. A yellow suspension of SmI<sub>3</sub> in THF was obtained and used during the following syntheses.

### 2.3. YbI<sub>3</sub>

The procedure followed was similar to that of the preparation of SmI<sub>3</sub>.

### 2.4. (MeOCH<sub>2</sub>CH<sub>2</sub>C<sub>5</sub>H<sub>4</sub>)<sub>2</sub>YbI (I)

Cp'K (13.44 ml, 2.8 mmol) was added to a suspension of YbI<sub>3</sub> (1.4 mmol) in 30 ml of THF. The suspension was stirred for 5 h at room temperature. The mixture was centrifuged to remove KI, and the solvent was reduced by vacuum to 1/5 volume. The product was obtained as deep red crystals after adding 5 ml of

hexane in 65% yield (496 mg). M.p. 162–164°C. Anal. Calcd for C<sub>16</sub>H<sub>22</sub>O<sub>2</sub>YbI: Yb, 31.68; C, 35.16; H, 4.03. Found: Yb, 31.62; C, 35.41; H, 4.21%. Mass spectrum: *m/z* (rel. int.): 420 ([M – I]<sup>+</sup>, 100.00), 124(14.57), 91(30.15). Crystals suitable for X-ray diffraction were obtained from a mixture of THF/hexane.

### 2.5. (MeOCH<sub>2</sub>CH<sub>2</sub>C<sub>5</sub>H<sub>4</sub>)<sub>3</sub>Sm (II)

A solution of Cp'K (1.56 g, 9.6 mmol) in 32 ml of THF was added dropwise to a stirred suspension of SmI<sub>3</sub> (60 ml, 3.22 mmol) in THF. The mixture was stirred for 5 h at room temperature to give a light yellow suspension. The solvent was removed by vacuum to give a yellow solid which was extracted in 120 ml of hexane. The extract was concentrated to form yellow needle crystals in 80% yield (1.34 g). M.p. 64–65°C. Anal. Calcd for C<sub>24</sub>H<sub>33</sub>SmO<sub>3</sub>: Sm, 29.04; C, 55.38; H, 6.35. Found: Sm, 29.26; C, 55.29; H, 6.42%. Mass spectrum: *m/z* (rel. int.) 398 ([M – Cp']<sup>+</sup>, 75.40). <sup>13</sup>C NMR (d<sub>8</sub>-THF): 56.72 (CH<sub>3</sub>-O-); 58.40 (-O-CH<sub>2</sub>-); 37.84 (-CH<sub>2</sub>-Cp'); 118.30, 104.10, 100.77 (C<sub>5</sub>H<sub>4</sub>). Crystals suitable for X-ray diffraction were obtained from hexane.

### 2.6. (MeOCH<sub>2</sub>CH<sub>2</sub>C<sub>5</sub>H<sub>4</sub>)<sub>3</sub>Yb (III)

The procedure followed was similar to that for II. Complex III was obtained as dark green crystals in 91% yield. M.p. 60–62°C. Anal. Calcd. for C<sub>24</sub>H<sub>33</sub>YbO<sub>3</sub>: Yb, 31.92; C, 53.14; H, 6.09. Found: Yb, 31.61; C, 52.62; H, 6.06%. Mass spectrum: *m/z* (rel. int.) 420 ([M – Cp']<sup>+</sup>, 2.02).

## 2.7. X-ray crystallography

### 2.7.1. (MeOCH<sub>2</sub>CH<sub>2</sub>C<sub>5</sub>H<sub>4</sub>)<sub>2</sub>YbI (I)

A single crystal measuring 0.20 × 0.34 × 0.12 mm was sealed under argon in a thin-walled glass capillary. Intensity data were collected at 20°C with a Nicolet R3M/E diffractometer using graphite monochromated Mo K $\alpha$  radiation. 2335 unique reflections were measured in the range 3° < 2 $\theta$  < 56° with 0 ≤ h ≤ 15, 0 ≤ k ≤ 17, 0 ≤ l ≤ 17. The correction of Lp and absorption was applied to the reflection data. The Yb atom was located by the Patterson method and the other non-H atoms were carried out by difference Fourier synthesis. All positional parameters and anisotropic thermal parameters for non-H atoms were refined by full-matrix least squares technique. Final *R*, *R<sub>w</sub>* values were 0.040, 0.042, respectively for 1608 observed reflections (*F* > 3 $\sigma$ (*F*)). All calculations were performed on an Eclipse S/140 computer with SHELXTL programs. Scattering factors were taken from International Tables for X-ray crystallography (Vol. 4, Pages 55, 99 and 149). Table 1 lists the crystal data for I.

TABLE 1. Crystallographic data for (MeOCH<sub>2</sub>CH<sub>2</sub>C<sub>5</sub>H<sub>4</sub>)<sub>2</sub>YbI (I) and (MeOCH<sub>2</sub>CH<sub>2</sub>C<sub>5</sub>H<sub>4</sub>)<sub>3</sub>Sm (II)

Compound	I	II
Chemical formula	C <sub>16</sub> H <sub>22</sub> O <sub>2</sub> IYb	C <sub>24</sub> H <sub>33</sub> O <sub>3</sub> Sm
Crystal system	Orthorhombic	monoclinic
Mol wt	546.2	522.9
Crystal size, mm	0.20 × 0.34 × 0.12	0.23 × 0.20 × 0.37
Cell dimensions		
<i>a</i> , Å	10.892(2)	8.415(7)
<i>b</i> , Å	12.278(3)	20.439(3)
<i>c</i> , Å	12.805(5)	12.926(2)
β, deg		90.34(3)
<i>V</i> , Å <sup>3</sup>	1712.4	2223.2
Scan range 2θ, deg	3–56	0–50
Number of reflections for   <i>F</i> <sub>o</sub>   > 3.0σ(  <i>F</i> <sub>o</sub>  )	2335	3897
Space group	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>z</i>	4	4
<i>D</i> , g cm <sup>-3</sup>	2.118	1.562
<i>R</i>	0.040	0.031
<i>R</i> <sub>w</sub>	0.042	0.039
<i>F</i> (000)	1028	1052

### 2.7.2. (MeOCH<sub>2</sub>CH<sub>2</sub>C<sub>5</sub>H<sub>4</sub>)<sub>3</sub>Sm (II)

A single crystal measuring 0.23 × 0.20 × 0.37 mm was sealed under argon in a thin-walled glass capillary. Intensity data were collected at 20°C with an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo Kα radiation. 3897 unique reflections were measured in the range 0° < 2θ < 50° with 0 ≤ *h* ≤ 10, 0 ≤ *k* ≤ 24, -15 ≤ *l* ≤ 15. The correction of *Lp* and absorption was applied to the reflection data. The Sm atom was located by Patterson method and the other non-H atoms were carried out by difference Fourier synthesis. All positional parameters and anisotropic thermal parameters for non-H atoms were refined by full-matrix least square technique. Final *R*, *R*<sub>w</sub> and *S* values were 0.031, 0.039, 2.39 respectively for 3276 observed reflections (*F* > 3σ(*F*)). All calculations were performed on a Microvax II computer with SDP and ORTEP programs. Scattering factors were taken from the International Tables for X-ray crystallography (1974). Table 1 lists the crystal data for II.

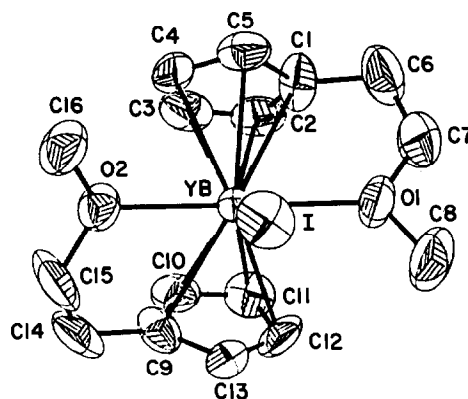
## 3. Results and discussion

### 3.1. Synthesis

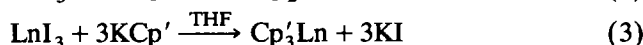
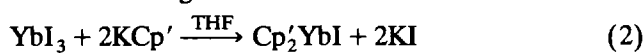
Lanthanoid triiodides can easily be synthesized by using the stoichiometric reaction between metal and iodine in THF solution as depicted in eqn. (1).



Reaction between lanthanide triiodide (Ln = Sm, Yb) and 2-methoxyethylcyclopentadienyl potassium in THF gave bis- and tris cyclopentadienyl organolanthanide

Fig. 1. Perspective diagram of the molecule of Cp<sub>2</sub>'YbI.

derivatives in accordance with the respective 1:2 and 1:3 ratios of agents.



Ln = Sm (II), Yb (III)

The products of reactions (2) and (3) have been characterized by elemental analyses, mass spectroscopy, <sup>13</sup>C NMR spectroscopy and X-ray crystal analyses.

### 3.2. Structure

#### 3.2.1. (MeOCH<sub>2</sub>CH<sub>2</sub>C<sub>5</sub>H<sub>4</sub>)<sub>2</sub>YbI (I)

The structure of I is shown in Fig. 1, the final fractional coordinates for I are given in Table 2, and

TABLE 2(a). Atomic coordinates (×10<sup>4</sup>) and isotropic thermal parameters (Å<sup>2</sup> × 10<sup>3</sup>) for I

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sup>a</sup>
Yb	9400(1)	4890(1)	4535(1)	40(1)
I	5924(1)	3272(1)	1114(1)	71(1)
O(1)	11133(11)	4645(12)	5715(9)	74(5)
O(2)	7586(10)	5890(8)	3899(10)	60(4)
C(1)	11547(14)	5066(18)	3670(12)	69(6)
C(2)	10964(19)	4228(16)	3157(15)	77(8)
C(3)	10023(23)	4608(22)	2557(16)	92(9)
C(4)	9979(19)	5728(21)	2722(14)	82(9)
C(5)	10952(18)	6017(16)	3392(15)	72(7)
C(6)	12629(17)	5026(27)	4419(16)	101(9)
C(7)	12320(18)	4761(28)	5437(18)	118(12)
C(8)	11113(23)	4518(26)	6816(14)	112(11)
C(9)	7344(16)	3800(14)	4711(17)	67(7)
C(10)	8047(18)	3226(15)	4062(18)	82(8)
C(11)	9057(19)	2801(13)	4627(16)	79(7)
C(12)	8884(19)	3089(15)	5601(15)	79(7)
C(13)	7874(16)	3777(16)	5728(14)	66(6)
C(14)	6230(17)	4462(19)	4358(26)	115(12)
C(15)	6414(16)	5491(19)	4139(31)	132(14)
C(16)	7586(18)	7028(15)	3658(17)	76(8)

<sup>a</sup> Equivalent isotropic *U* defined as one third of the trace of the orthogonalized *U*<sub>*ij*</sub> tensor.

TABLE 2(b). Positional parameters and their estimated standard deviations for II

Atom	x	y	z	B (Å <sup>2</sup> ) <sup>a</sup>
Sm	0.25371(3)	0.15511(2)	0.14667(2)	2.354(1)
O(1)	0.1812(6)	0.2826(3)	0.990(4)	2.4(1)
O(2)	0.975(6)	0.741(3)	-0.3125(4)	3.2(1)
O(3)	0.3318(6)	0.226(3)	0.2148(4)	3.3(1)
C(1)	-0.629(7)	0.1926(4)	0.1488(5)	3.6(1)
C(2)	-0.469(7)	0.1506(4)	0.627(5)	3.6(1)
C(3)	-0.196(8)	0.862(4)	0.989(6)	4.1(2)
C(4)	-0.173(8)	0.883(4)	0.2093(6)	4.4(2)
C(5)	-0.452(7)	0.1550(4)	0.2392(5)	3.8(1)
C(6)	0.912(9)	0.2654(4)	0.1468(7)	4.7(2)
C(7)	0.185(9)	0.3002(4)	0.746(7)	4.9(2)
C(8)	0.2890(1)	0.3298(4)	0.563(7)	5.9(2)
C(9)	0.2946(7)	0.1221(3)	-0.666(5)	2.9(1)
C(10)	0.3596(9)	0.1852(4)	-0.536(5)	4.5(2)
C(11)	0.4957(9)	0.1786(5)	0.112(5)	5.4(2)
C(12)	0.5123(8)	0.1130(5)	0.397(5)	5.1(2)
C(13)	0.3873(8)	0.774(4)	-0.91(5)	3.8(1)
C(14)	0.1602(8)	0.1048(4)	-0.1400(5)	4.0(2)
C(15)	0.2255(8)	0.792(4)	-0.2407(5)	3.9(1)
C(16)	0.6460(1)	0.4479(5)	0.898(6)	6.0(2)
C(17)	0.4345(8)	0.1353(4)	0.3246(5)	4.0(1)
C(18)	0.2892(8)	0.1635(4)	0.3578(5)	4.0(1)
C(19)	0.2836(9)	0.2288(4)	0.3246(5)	4.2(1)
C(20)	0.4253(9)	0.2422(4)	0.2700(5)	4.6(2)
C(21)	0.5192(8)	0.1849(4)	0.2708(5)	4.4(2)
C(22)	0.4990(1)	0.670(5)	0.3456(7)	6.1(2)
C(23)	0.3810(1)	0.148(5)	0.3201(7)	6.0(2)
C(24)	0.2620(1)	0.376(5)	0.1759(8)	6.4(2)
Cp1	0.384	0.1345	0.1518	
Cp2	0.4099	0.1353	-0.157	
Cp3	0.3903	0.1909	0.3096	

<sup>a</sup> Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as:  $(4/3) \cdot (a^2 \cdot B_{1,1} + b^2 \cdot B_{2,2} + c^2 \cdot B_{3,3} + ab(\cos \gamma) \cdot B_{1,2} + ac(\cos \beta) \cdot B_{1,3} + bc(\cos \alpha) \cdot B_{2,3})$ .

TABLE 3(a). Selected bond lengths (Å) for I

Yb-O(1)	2.436(12)	O(2)-C(15)	1.401(22)
Yb-O(2)	2.464(11)	O(2)-C(16)	1.431(21)
Yb-I	3.049(1)	Yb-Cp1	2.334
O(1)-C(7)	1.349(24)	Yb-Cp2	2.345
O(1)-C(8)	1.419(21)		

Cp1 = centroid of C1-C5 ring  
Cp2 = centroid of C9-C13 ring

TABLE 3(b). Selected bond lengths (Å) for II

Sm-O(1)	2.744(3)	O(3)-C(23)	1.429(6)
Sm-O(3)	2.923(4)	O(3)-C(24)	1.451(6)
O(1)-C(7)	1.449(6)	Sm-Cp1	2.495
O(1)-C(8)	1.440(6)	Sm-Cp2	2.516
O(2)-C(15)	1.422(5)	Sm-Cp3	2.503
O(2)-C(16)	1.403(6)		

Cp1 = centroid of C1-C5 ring  
Cp2 = centroid of C9-C13 ring  
Cp3 = centroid of C17-C21 ring

TABLE 4(a). Selected bond angles (°) for I

I-Yb-Cp1	119.9	Cp2-Yb-O(2)	92.7
I-Yb-Cp2	113.0	O(1)-Yb-O(2)	152.6(4)
Cp1-Yb-Cp2	127.1	Yb-O(1)-C(7)	124.5(12)
I-Yb-O(1)	76.7(3)	C(7)-O(1)-C(8)	106.8(16)
Cp1-Yb-O(1)	92.1	Yb-O(2)-C(16)	123.9(10)
Cp2-Yb-O(1)	100.2	Yb-O(1)-C(8)	128.1(12)
I-Yb-O(2)	76.0(3)	Yb-O(2)-C(15)	118.9(13)
Cp1-Yb-O(2)	99.3	C(15)-O(2)-C(16)	112.9(14)

Cp1 = centroid of C1-C5 ring  
Cp2 = centroid of C9-C13 ring

selected bond distances and angles are listed in Table 3(a) and Table 4(a). The molecular structure of I has the usual bent metallocene configuration with two oxygen atoms and one iodine atom attached to the central metal. The metal Yb lies nearly on the centre of trigonal-planar geometry described by two ring centroids and one iodine atom. Two oxygen atoms are attached to the metal on either side of the plane to form a distorted trigonal bipyramidal coordination geometry. I is five-coordinated compound and the coordination number of the central metal is nine. It is to our knowledge the first example of a solvent-free monomeric organolanthanide halide complex. The molecular structure of compound I is similar to that of Cp<sub>2</sub>SmI [1] except the radius of metal and corresponding bond distances are shorter for Yb than for Sm.

### 3.2.2. (MeOCH<sub>2</sub>CH<sub>2</sub>C<sub>5</sub>H<sub>4</sub>)<sub>3</sub>Sm (II)

The structure of II is shown in Fig. 2, the final fractional coordinates for II are given in Table 2(b), and selected bond distances and angles are shown in Tables 3(b) and 4(b). In II, the three Cp' ring centroids and the two oxygen atoms form pseudohexahedral coordination geometry around samarium. The central metal Sm<sup>3+</sup> is coordinated by two oxygen atom of the substituents together with three cyclopentadienyl rings in η<sup>5</sup>-bonded fashion and the third oxygen atom of substituents has drifted away. Therefore, complex II is

TABLE 4(b). Selected bond angles (°) for II

O(1)-Sm-O(3)	175.4(1)	Cp1-Sm-Cp2	121.0
O(1)-Sm-Cp1	87.0	Cp1-Sm-Cp3	118.4
O(1)-Sm-Cp2	94.8	Cp2-Sm-Cp3	120.6
O(1)-Sm-Cp3	90.7	O(1)-C(7)-C(6)	109.4(4)
O(3)-Sm-Cp1	93.2	O(2)-C(15)-C(14)	108.1(4)
O(3)-Sm-Cp2	89.1	O(3)-C(23)-C(22)	108.5(5)
O(3)-Sm-Cp3	85.2		

Cp1 = centroid of C1-C5 ring  
Cp2 = centroid of C9-C13 ring  
Cp3 = centroid of C17-C21 ring

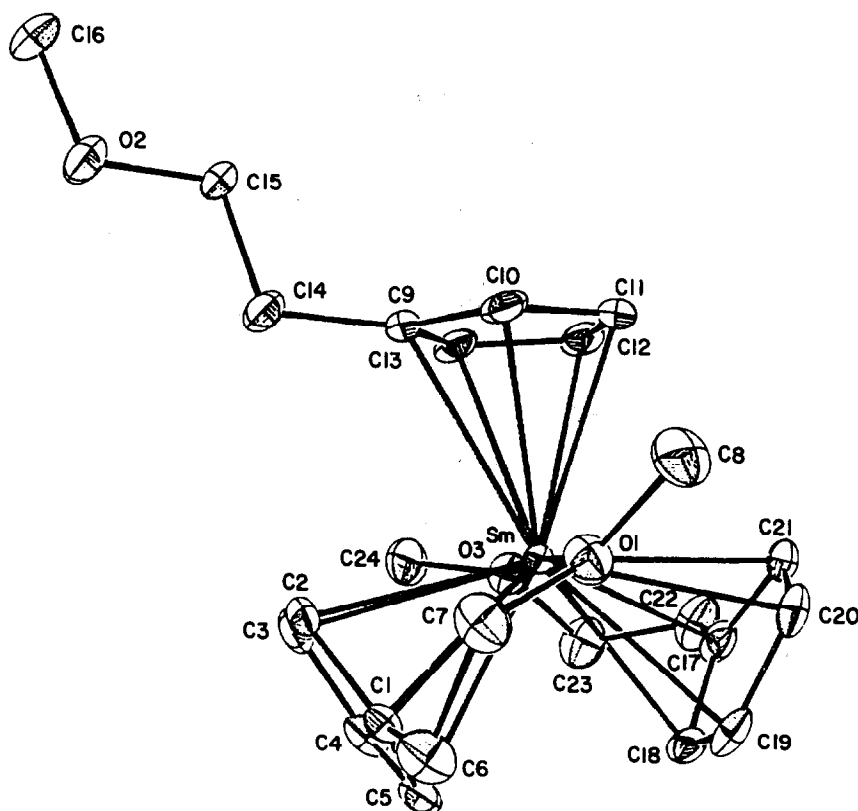


Fig. 2. Perspective diagram of the molecule of  $\text{Cp}_3\text{Sm}$ .

also a five-coordinated compound, but the coordination number of the central metal is eleven. Three of the centroid–Sm–centroid angles are nearly equal: 121.0, 118.4, and 120.6°. Because the coordination environment around samarium shows considerable steric crowding, the three bond distances centroid–Sm and the corresponding angles are all different. The O(2) of the second ring does not coordinate to samarium and the centroid–Sm distance of the second ring is greatest, indicating that the Cp'(2)–Sm bond is the weakest. Compound **II** has a molecular structure analogous to that of  $\text{Cp}'_3\text{Pr}$  [17]; the radius of  $\text{Sm}^{3+}$  is 0.049 Å shorter than that of  $\text{Pr}^{3+}$ . The Sm–centroid bond length is on average 0.054 Å shorter than that of Pr–centroid. However, the bond length of Sm–O is 0.045 Å longer than that of Pr–O, demonstrating that there is larger steric hindrance in **II** causing the longer Sm–O bond distance. The bond angles centroid–Sm–centroid in complex **II** are 118.4–121.0° and are in accordance with those in other complexes, such as  $[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_3\text{Sm}$  (119.97, 120.1, 120°) [23],  $(\text{C}_9\text{H}_7)_3\text{Sm}$  (120, 121, 116°) [24] and  $(\text{C}_5\text{Me}_5)_3\text{Sm}$  (120°) [25]. However, they are obviously different from those in compound  $(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{C}_5\text{H}_5)$  (127, 116.9, 116.2°) [26].

## Acknowledgments

The authors thank the Chinese National Foundation of Natural Science and Laboratory of Rare Earth Chemistry and Physics, Changchun Institute of Applied Chemistry, and Chinese Academy of Sciences for financial support.

## References

- 1 D. Deng, C. Qian, F. Song and Z. Wang, submitted to *Science in China, Ser. B*.
- 2 (a) P.L. Watson, *J. Chem. Soc., Chem. Commun.*, (1983) 276; (b) P.L. Watson, *J. Am. Chem. Soc.*, 105 (1983) 6491; (c) W.J. Evans, T.A. Ulibarri and J.W. Ziller, *Organometallics*, 10 (1991) 134; (d) M. Booi, A. Meetsma and J.H. Teuben, *Organometallics*, 10 (1991) 3246.
- 3 H. Mauer mann, P.N. Swebston and T.J. Marks, *Organometallics*, 4 (1985) 200.
- 4 (a) T. Jeske, H. Lauke, H. Mauer mann, H. Schumann and T.J. Marks, *J. Am. Chem. Soc.*, 107 (1985) 8091; (b) J. Jeske, L.E. Schook, P.N. Swebston, H. Schumann and T.J. Marks, *J. Am. Chem. Soc.*, 107 (1985) 8103; (c) J. Jeske, H. Lauke, H. Mauer mann, P.N. Swebston, H. Schumann and T.J. Marks, *J. Am. Chem. Soc.*, 107 (1985) 8111.
- 5 (a) W.J. Evans, I. Bloom, W.E. Hunter and J.L. Atwood, *J. Am. Chem. Soc.*, 103 (1981) 6507; (b) W.J. Evans, I. Bloom, W.E.

- Hunter and J.L. Atwood, *J. Am. Chem. Soc.*, 105 (1983) 1401; (c) W.J. Evans, *J. Organomet. Chem.*, 250 (1983) 1401; (d) W.J. Evans, J.H. Meadows, W.E. Hunter and J.L. Atwood, *J. Am. Chem. Soc.*, 106 (1984) 1291; (e) Z. Xie, C. Qian and Y. Huang, *J. Organomet. Chem.*, 412 (1991) 61.
- 6 P.L. Watson, *J. Am. Chem. Soc.*, 104 (1982) 337.
- 7 W.J. Evans, J.W. Grate and R.J. Doedens, *J. Am. Chem. Soc.*, 107 (1985) 1671.
- 8 (a) T.D. Tilley and R.A. Anderson, *J. Am. Chem. Soc.*, 104 (1982) 1; (b) J.M. Boncella and R.A. Anderson, *Inorg. Chem.*, 23 (1984) 432.
- 9 (a) Y. Huang, Y. Hill and B. Freiser, *J. Am. Chem. Soc.*, 113 (1991); (b) H.J. Heeres and J.H. Teuben, *Organometallics*, 10 (1991) 180; (c) C. Qian, D. Zhu and Y. Gu, *J. Organomet. Chem.*, 401 (1991) 23; (d) S. Matsubara, H. Onishi and K. Utimoto, *Tetrahedron Lett.* 31 (1990) 6209.
- 10 C. Qian, A. Qiu, Y. Huang and W. Chen, *J. Organomet. Chem.*, 412 (1991) 53.
- 11 C. Qian, D. Zhu and D. Li, *J. Organomet. Chem.*, 430 (1992) 175.
- 12 T. Sakakura, H. Lautenschlager and M. Tanaka, *J. Chem. Soc., Chem. Commun.*, (1991) 40.
- 13 C. Qian and D. Zhu, *Synlett.*, (1990) 417.
- 14 C. Qian and D. Zhu, *J. Mol. Catal.*, 63 (1990) L1.
- 15 P.N. Nazin, J.W. Brown and G.K. Schulte, *Organometallics*, 9 (1990) 416.
- 16 M.J. Heeres and J.H. Teuben, *J. Organomet. Chem.*, 414 (1991) 351.
- 17 C. Qian, B. Wang and D. Deng, *J. Organomet. Chem.*, 427 (1992) C29.
- 18 D. Deng, C. Qian, G. Wu and P. Zheng, *J. Chem. Soc., Chem. Commun.*, (1990) 880.
- 19 D. Deng, Y. Jiang and C. Qian, *Chinese Science Bulletin*, 37 (1992) 348.
- 20 D. Deng, X. Zheng, C. Qian, S. Jin and Y. Lin, *Acta Chim. Sinica*, 50 (1992) 1024.
- 21 D. Deng, C. Qian, F. Song, Z. Wang, G. Wu and P. Zheng, *J. Organomet. Chem.*, 443 (1993) 79.
- 22 Q. Huang, Y. Qian and G. Li, *Transition Met. Chem.*, 15 (1990) 483.
- 23 W.J. Evans, R.A. Keyer and W. Ziller, *J. Organomet. Chem.*, 197 (1990) 87.
- 24 J.L. Atwood, J.H. Burns and P.G. Lauberau, *J. Am. Chem. Soc.*, 95 (1973) 1830.
- 25 W.J. Evans, S.L. Gonzales and J.W. Ziller, *J. Am. Chem. Soc.*, 113 (1991) 7423.
- 26 W.J. Evans and T.A. Ulibarri, *J. Am. Chem. Soc.*, 106 (1987) 4292.