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Synthesis and crystal structures of tris(2-methoxyethylcyclopentadienyl)-lanthanide complexes †

Changtao Qian,[*,a] **Bing Wang,**[a] **Daoli Deng,**[a] **Jie Sun,**[a] **F. Ekkehardt Hahn,**[b] **Jian Chen**[c] **and Peiju Zheng**[c]

[a] *Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Lu, Shanghai 200032, China*

[b] *Institut für Anorganische and Analytische Chemie, Freie Universität Berlin, Fabeckstrasse 34–36, D-14195 Berlin, Germany*

[c] *Center of Analysis and Measurement, Fudan University, Shanghai 200433, China*

The tris(2-methoxyethylcyclopentadienyl)lanthanide complexes $[Ln(C_5H_4CH_2CH_2OMe)_3]$ (Ln = La, Pr, Nd, Gd or Y) were synthesized by the reaction of sodium 2-methoxyethylcyclopentadienide with the corresponding $LnCl_3$ and the products were characterized by elemental analyses, mass, IR and ^1H NMR spectroscopy. Crystal structure determinations revealed the complexes to be unsolvated monomeric metallocenes with lanthanide centres co-ordinated by three cyclopentadienyl rings and two oxygen atoms of the three 2-methoxyethyl moieties present; the third oxygen is not co-ordinated. The distances Ln–C (η^5) and Ln–O(1) (co-ordinated oxygen) decrease as the ionic radius decreases; however, Ln–O(3) (co-ordinated oxygen) increases.

Since tris(cyclopentadienyl)lanthanide metallocenes, $Ln(C_5H_5)_3$, were first synthesized by Birmingham and Wilkinson[2] in 1956, many molecular structures of trivalent lanthanide metallocenes have been reported. The results suggested that the solid-state structures are dependent on the size of the substituents of the cyclopentadienyl rings as well as the lanthanide metals. For example, $La(C_5H_5)_3$[3] and $Nd(C_5H_5)_3$[4] are zigzag polymers, in which each metal ion is η^5 co-ordinated to three $C_5H_5^-$ ligands and η^2 co-ordinated to a fourth bridging $C_5H_5^-$. However, $La(C_5H_4Me)_3$[5] and $Nd(C_5H_4Me)_3$[6] are tetramers, in which each metal ion is η^5 co-ordinated to three $C_5H_5^-$ and η^1 co-ordinated to a fourth bridging $C_5H_5^-$, and $Yb(C_5H_4Me)_3$ is a monomer.[7]

There has been considerable interest in the synthesis of very sterically encumbered metallocene derivatives of the 4f elements. Recently, Evans *et al.*[8] have shown that, under appropriate conditions, the permethylated compound $[Sm(C_5Me_5)_3]$ can be prepared, while Schumann *et al.*[9] used tetramethylcyclopentadienyl to synthesize $Ln(C_5HMe_4)_3$ (Ln = La or Sm). Moreover, another type of very sterically congested metallocenes show high co-ordination numbers, such as $[Ln(C_5H_5)_3(NCMe)_2]$ (Ln = La, Ce or Pr),[10] $[Ln(C_5H_5)_3(NCEt)_2]$[11] and $[Ln(C_5H_4CH_2CH_2NMe_2)_3]$ (Ln = La or Nd).[12]

In order to study further the synthesis of very sterically encumbered metallocenes, and the effect of lanthanide metal centres on the structure of these compounds, we have recently investigated the synthesis and crystal structure of $[Ln(C_5H_4CH_2CH_2OMe)_3]$, containing large and small lanthanide cations. Some of this work has been communicated previously.[13]

Results and Discussion

Synthesis of tris(2-methoxyethylcyclopentadienyl)lanthanide metallocenes 1–5

Five new complexes **1**–**5** were prepared in high yield by treating the corresponding anhydrous $LnCl_3$ with an excess of $Na(C_5H_4CH_2CH_2OMe)$ at room temperature (r.t.) [equation (1)]. After crystallization from hexane, crystals were obtained having different colours depending on the lanthanide metal used. These crystals are moderately soluble in hexane, but dissolve readily in more polar solvents such as benzene and tetrahydrofuran (thf).

$$LnCl_3 + 3Na(C_5H_4CH_2CH_2OMe) \xrightarrow[\text{r.t.}]{\text{thf}} [Ln(C_5H_4CH_2CH_2OMe)_3] + 3NaCl \quad (1)$$

Ln = La **1**, Pr **2**, Nd **3**, Gd **4** or Y **5**

The new metallocenes have been extensively characterized by elemental analysis, IR, mass and low-temperature ^1H NMR spectroscopy and X-ray structural analyses. The compounds $Ln(C_5H_4CH_2CH_2OMe)_3$ (Ln = Sm or Yb) were previously synthesized by the reaction of potassium 2-methoxyethylcyclopentadienide and the corresponding lanthanide triiodides.[14]

The electron impact (EI) mass spectra of the complexes $Ln(C_5H_4CH_2CH_2OMe)_3$ (Ln = La, Pr, Nd, Gd or Y) are all very similar. All showed a parent molecular ion, M^+, and related fragments; no m/z value greater than that of M^+ was detected, which suggests that the complexes may be monomers in the solid and/or vapour phase. The infrared spectra (4000–180 cm^{-1} Nujol mulls, between CsI discs) are also very similar. Characteristic peaks of the cyclopentadienyl group are apparent. The strong peak due to the asymmetric stretching vibration ν(C–O–C) occurs at $\approx$1045 cm^{-1}. When compared with the corresponding sodium salt (1080 cm^{-1}),[15] this signal has shifted by $\Delta\nu \approx 35$ cm^{-1}, probably as a consequence of significant oxygen atom co-ordination, in accord with our previous observations for the complexes $[LnO(C_5H_4CH_2CH_2)_2Cl]$,[16] $[Ln(C_5H_4CH_2CH_2OMe)_2Cl]$,[15] $[Ln(C_5H_4CH_2CH_2OMe)_2I]$[17] and $[Ln(C_5H_5)_2(C_5H_4CH_2CH_2OMe)]$.[18]

The ^1H NMR spectra of complexes **1**, **5** and the precursor sodium salt were measured using $[^2H_8]$thf as solvent. The results are shown in Table 1. Compared with the sodium salt, the signals of OMe and OCH_2 are shifted to lower field with $\Delta\delta$ = 0.28, 0.27 ppm for **1** and 0.15, 0.20 for **5**, respectively. These shifts indicate the presence of an intramolecular co-ordinated oxygen bond.[15–17] Moreover, in the low-temperature ^1H NMR spectrum, the resonances of the CH_2, OCH_2 and

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† Studies on Organolanthanide Complexes. Part 59.[1]

OMe groups are each split into two. For example, the three OMe groups appeared at δ 3.15 (s, 3 H) and 3.45 (s, 6 H) (Table 1). This indicated that two oxygen atoms of three substituents co-ordinate to the lanthanum ion, the third is free. This result was confirmed by X-ray structural analysis.

Crystal structures of complexes 1–4

Suitable single crystals of complexes 1–4 were obtained by crystallization from hexane. Selected bond distances and angles are listed in Table 2, crystallographic data in Table 3 and atomic coordinates in Tables 4–7.

As is evident from the unit-cell parameters and atomic coordinates, complexes 1–4 are isomorphous and isostructural. Each consists of a Ln atom surrounded by three cyclopentadienyl rings and two oxygen atoms from three substituents, the co-ordination can be described as a distorted trigonal bipyramid if a cyclopentadienyl is regarded as occupying a single polyhedral vertex. The co-ordination number of the central metal ion is 11. The structure of $[Gd(C_5H_4CH_2CH_2OMe)_3]$ **4** is shown in Fig. 1. It is noteworthy that the co-ordination number of Gd^{3+} is the highest of all cyclopentadienyllanthanide complexes investigated so far by X-ray diffraction.

The distance La–C (η^5) in complex **1** (Fig. 2) ranges from 2.805(12) to 2.917(10) Å (average 2.860 Å), similar to the 2.836 Å in $[\{La(C_5H_4CH_2CH_2OMe)_2Cl\}_2]$,[15] 2.805 Å in $[La(C_5H_4CH_2CH_2OMe)_2I]$,[17] 2.85(8) Å in $[La(C_5H_5)_3]_\infty$,[3] 2.843(3) Å in $[\{La(C_5H_4Me)_3\}_4]$,[5] 2.82(4) Å in $[La(C_5H_5)_3(thf)]$,[20] 2.830(5) Å in $[La(C_5H_5)_3(NCMe)]$,[10] 2.86(1) Å in $[La(C_5H_5)_3(NCEt)_2]$[11] and 2.82 Å in $[La(C_5H_4CH_2CH_2NMe_2)_3]$.[12] The La–O(1) and La–O(3) distances in **1** are 2.752(7) and 2.806(6) Å, respectively, significantly longer than those observed in other lanthanum complexes, such as 2.583(11) and 2.584(11) Å in $[La(C_5H_4CH_2CH_2OMe)_2I]$,[17] 2.665(2) and 2.775(2) Å in $[\{La(C_5H_4CH_2CH_2OMe)_2Cl\}_2]$[15] and 2.57 Å in $[La(C_5H_5)_3(thf)]$.[20]

The average Nd–C (η^5) distance in complex **3** (Fig. 3) is 2.807 Å which is comparable with those in analogous cyclopentadienylneodymium complexes, such as 2.79 Å in $[Nd(C_5H_5)_3(thf)]$,[21] 2.795 Å in $[Nd(C_5H_4Bu^t)_3(thf)]$[22] and 2.79 Å in $[Nd(C_5H_4CH_2CH_2NMe_2)_3]$.[12] However, it is slightly longer than that of $[Nd(C_5H_4CH_2CH_2NMe_2)_2]$[22] (2.769 Å) and $[Nd(C_5H_4CH_2CH_2OMe)_2(BH_4)]$ (2.76 Å).[23] The mean Nd–O distance (2.782 Å) in **3** is significantly longer than Nd–O (thf) (2.56 Å) in $[Nd(C_5H_5)_3(thf)]$,[21] Nd–O (thf) (2.536 Å) in $[Nd(C_5H_4Bu^t)_3(thf)]$[22] and Nd–O (2.605 Å) in $[Nd(C_5H_4CH_2CH_2OMe)_2(BH_4)]$.[23] The average Pr–C ($\eta^5$) distance in complex **2** (Fig. 4) is 2.825 Å which is in the expected range and in good agreement with values for analogous praseodymium derivatives.[13] The average Gd–C (η^5) distance in complex **4** is 2.75 Å which is in agreement with Gd–C (η^5) (2.74 Å) in $[Gd(C_5H_5)_3(thf)]$.[24]

From Table 2 it can be seen that the Ln–C (η^5) and Ln–O(1) distances follow the trends expected on the basis of radial size. However, the Ln–O(3) distances do not follow this trend, increasing as the ion radius decreases. This fact reveals that the complexes become co-ordinatively oversaturated as the ionic radius further decreases. The lanthanide would therefore tend to form one intramolecular co-ordination bond, and it is possible that ten-co-ordinated complexes will be formed for the heavier lanthanides. We could not obtain the structure and

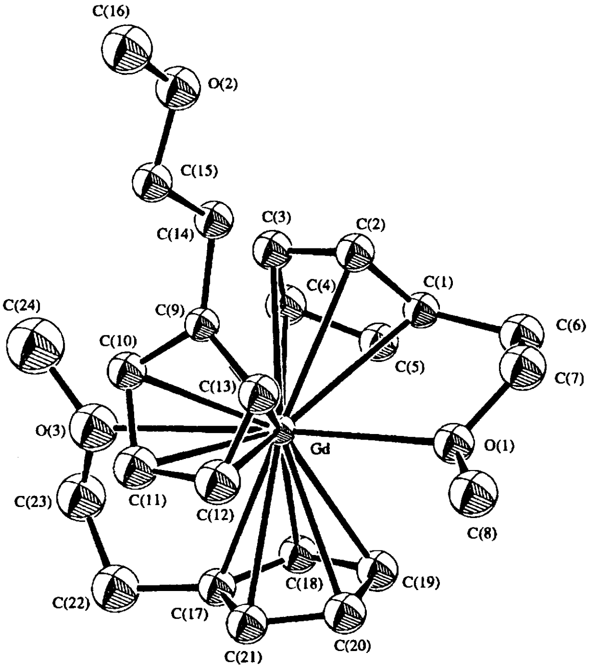

Fig. 1 An ORTEP[19] plot of $[Gd(C_5H_4CH_2CH_2OMe)_3]$ **4** showing the numbering scheme employed

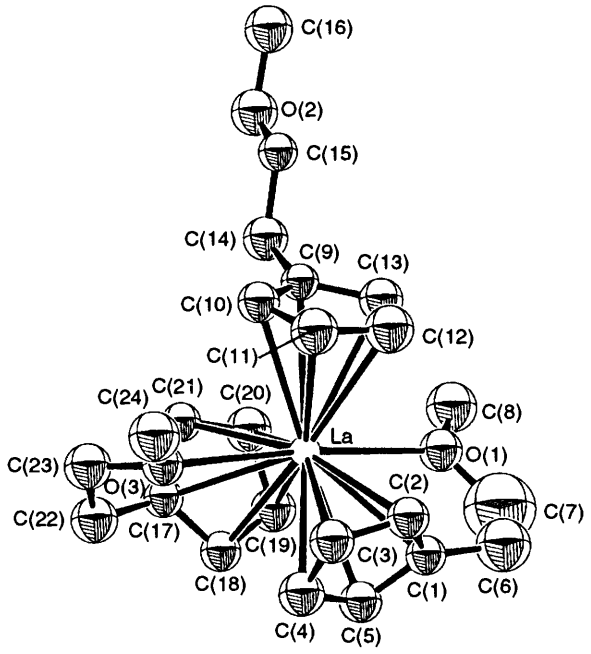

Fig. 2 An ORTEP plot of $[La(C_5H_4CH_2CH_2OMe)_3]$ **1** showing the numbering scheme employed

Table 1 Proton NMR data in $[^2H_8]$thf

		δ			
Complex	T/°C	C_5H_4	CH_2	CH_2O	CH_3
$Na(C_5H_4CH_2CH_2OMe)$	25	5.18 (t) 5.31 (t)	2.50 (t)	3.05 (t)	3.28 (s)
$[Y(C_5H_4CH_2CH_2OMe)_3]$	25	5.64 (s)	2.56 (t)	3.48 (t)	3.20 (s)
$[La(C_5H_4CH_2CH_2OMe)_3]$	25	5.59 (s)	2.53 (t)	3.55 (t)	3.33 (s)
	−112	5.51– 5.66 (m)	2.45 (s) 2.63 (s)	3.76 (s) 3.08 (s)	3.45 (s) 3.15 (s)

Table 2 Important structural data for complexes $[Ln(C_5H_4CH_2CH_2OMe)_3]$ (Ln = La, Pr, Nd, Sm or Gd)

	1 (La)	**2** (Pr)	**3** (Nd)	Sm[14]	**4** (Gd)
Ion radius/Å	1.216	1.179	1.163	1.132	1.107
Ln–O(1)/Å	2.752(7)	2.740(3)	2.724(3)	2.744(3)	2.701(4)
Ln–O(3)/Å	2.806(6)	2.836(3)	2.839(3)	2.923(4)	2.985(5)
Ln–O (average)/Å	2.779	2.788	2.782	2.834	2.843
Ln–C (average)/Å	2.860	2.825	2.807	2.779	2.750
Ln–Cent(1)/Å	2.588	2.540	2.526	2.495	2.473
Ln–Cent(3)/Å	2.610	2.548	2.534	2.503	2.487
Ln–Cent(2)/Å	2.622	2.569	2.552	2.516	2.492
Cent(1)–Ln–Cent(2)/°	119.0	119.28	121.61	121.0	120.7
Cent(1)–Ln–Cent(3)/°	119.0	119.00	118.90	118.4	118.3
Cent(2)–Ln–Cent(3)/°	122.0	121.67	119.45	120.6	120.6
Cent(1)–Ln–O(1)/°	85.7	86.4	86.8	87.0	87.7
Cent(1)–Ln–O(3)/°	91.2	90.4	90.2	93.2	92.7
Cent(3)–Ln–O(1)/°	92.5	93.4	93.2	90.7	92.0
Cent(3)–Ln–O(3)/°	84.6	84.6	84.9	85.2	84.2
O(1)–Ln–O(3)/°	174.0(2)	174.8(1)	175.0(2)	175.4(1)	175.9(1)

Cent = Centroid of cyclopentadienyl ring.

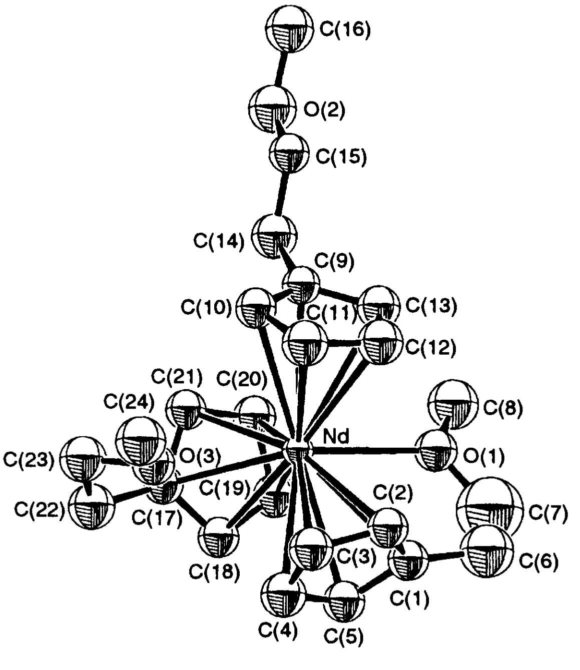

Fig. 3 An ORTEP plot of $[Nd(C_5H_4CH_2CH_2OMe)_3]$ **3** showing the numbering scheme employed

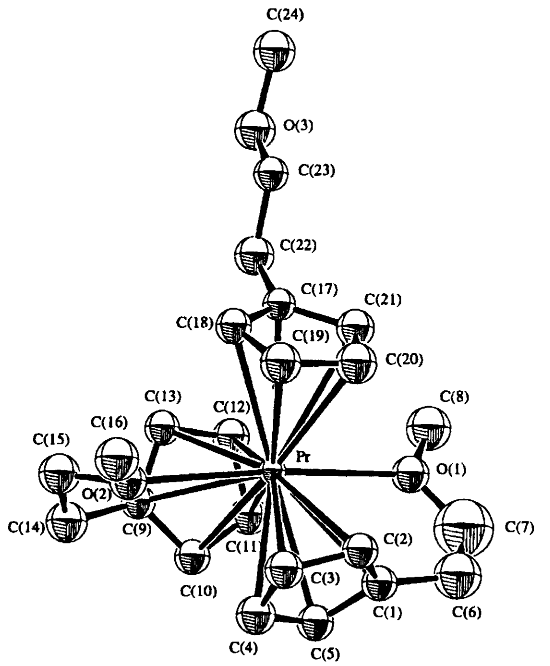

Fig. 4 An ORTEP plot of $[Pr(C_5H_4CH_2CH_2OMe)_3]$ **2** showing the numbering scheme employed

low-temperature ^1H NMR data for complex $[Y(C_5H_4CH_2CH_2OMe)_3]$ **5**. However, the ten-co-ordinated complex $[Y(C_5H_5)_2(C_5H_4CH_2CH_2OMe)]$ which could easily be synthesized by treating anhydrous yttrium trichloride with sodium 2-methoxyethylcyclopentadienide and sodium cyclopentadienide, was structurally characterized previously.[18] The Y–O distance [2.414(13) Å] is in good agreement with that in $Y(C_5H_5)_3{\cdot}thf$[20] [2.418(4) Å], but significantly shorter than the mean Ln–O distances in complexes **1**–**4**. Recently Herrmann and co-workers[12] reported the eleven-co-ordinated complex $[La(C_5H_4CH_2CH_2NMe_2)_3]$ in which two nitrogen atoms are co-ordinated with La–N distances of 2.898(6) and 3.688(5) Å. In the analogous neodymium complex one nitrogen atom was co-ordinated while the other two remained free. This reduced co-ordination number may arise from the greater congestion around the lanthanide metal ions.

Experimental

All operations were performed under purified argon by using Schlenk techniques. Solvents were refluxed and distilled either over finely divided $LiAlH_4$ or blue sodium–benzophenone under argon immediately before use. Sodium cyclopentadienide was prepared by the usual method and sodium 2-methoxyethylcyclopentadienide by our previous method.[15] The IR spectra were recorded on Perkin-Elmer 983 and Digilab FTIS-20/E Fourier-transform spectrometers with Nujol and Fluorolube mulls and were examined between disc-shaped CsI crystals; the mulls were prepared in an argon-filled glove-box. Proton NMR spectra were obtained on a FX-90Q (90 MHz) spectrometer referenced to external $SiMe_4$ in $[^2H_8]$thf. The solvent (E. Merck for NMR spectroscopy) was dried over a Na–K alloy and degassed by freeze–thaw cycles on a vacuum line. Mass spectra were recorded on a Finnigan 4201 spectrometer at 50–300 °C and 1.3 kV. Metal analyses for the complexes were accomplished using a direct complexometric titration with disodium ethylenediaminetetraacetate. Carbon and hydrogen analyses were obtained by the combustion method in an aluminium tube.

Table 3 Crystallographic data for complexes [Ln($C_5H_4CH_2CH_2OMe$)$_3$] (Ln = La **1**, Pr **2**, Nd **3** or Gd **4**)*

	1	**2**	**3**	**4**
Formula	$C_{24}H_{33}LaO_3$	$C_{24}H_{33}O_3Pr$	$C_{24}H_{33}NdO_3$	$C_{24}H_{33}GdO_3$
M	508.4	510.44	513.8	526.8
T/K	298	293	293	293
Crystal size/mm	0.3 × 0.2 × 0.1	0.30 × 0.20 × 0.4	0.3 × 0.2 × 0.4	0.50 × 0.35 × 0.30
a/Å	8.590(4)	8.517(2)	8.501(2)	8.391(2)
b/Å	24.554(9)	24.422(2)	24.405(3)	20.455(5)
c/Å	11.113(6)	11.132(1)	11.133(2)	12.904(2)
β/°	95.82(4)	95.73(1)	95.74(4)	90.40(2)
U/Å^3	2332(2)	2303(9)	2298.3(2)	2215(2)
D_c/g cm^{-3}	1.448	1.471	1.458	1.580
μ/cm^{-1}	18.57	21.26	22.87	30.3
2θ Range/°	3.0–45	0–50	0–45	2–45
Independent reflections	3067	4156	3926	2891
No. observed data	2471 [$F > 4.0\sigma(F)$]	3054 [$F_o^2 \geqslant 3\sigma(F_o^2)$]	3290 [$F_o^2 \geqslant 3\sigma(F_o^2)$]	2338 [$F_o^2 \geqslant 3\sigma(F_o^2)$]
F(000)	1032	1040	1044	1072
R, R'	0.039, 0.053	0.030, 0.036	0.031, 0.037	0.025, 0.032
Goodness of fit	1.22		2.00	1.18
Weighting scheme, w	$[\sigma^2(F_o) + 0.0012F_o^2]^{-1}$	1	1	$[\sigma(F)^2]^{-1}$

* Details in common: monoclinic, space group $P2_1/n$; $Z = 4$; data collected h, k, $\pm l$.

Table 4 Atomic coordinates (× 10^4) for complex **1**

Atom	x	y	z
La	5 637(1)	1 325(1)	7 772(1)
O(1)	6 165(9)	1 412(3)	5 378(6)
O(2)	4 441(7)	3 867(3)	7 528(7)
O(3)	4 936(7)	1 134(3)	10 148(5)
C(1)	7 351(12)	486(4)	6 736(9)
C(2)	8 292(11)	628(4)	7 743(11)
C(3)	7 593(14)	465(4)	8 742(10)
C(4)	6 194(14)	211(4)	8 345(12)
C(5)	6 039(11)	224(4)	7 100(11)
C(6)	7 672(18)	604(6)	5 464(11)
C(7)	6 934(27)	1 021(8)	4 837(13)
C(8)	5 495(14)	1 811(5)	4 587(10)
C(9)	6 150(10)	2 502(3)	8 081(9)
C(10)	6 548(12)	2 256(4)	9 209(9)
C(11)	7 880(13)	1 949(4)	9 169(13)
C(12)	8 363(11)	2 001(4)	8 043(15)
C(13)	7 281(13)	2 336(4)	7 352(11)
C(14)	4 920(12)	2 921(3)	7 787(11)
C(15)	5 522(10)	3 487(4)	7 929(9)
C(16)	4 991(14)	4 402(4)	7 588(11)
C(17)	2 446(9)	1 194(4)	8 247(10)
C(18)	2 578(10)	862(4)	7 252(10)
C(19)	2 739(11)	1 195(5)	6 272(11)
C(20)	2 725(10)	1 725(5)	6 632(11)
C(21)	2 540(9)	1 739(4)	7 876(9)
C(22)	2 244(11)	999(5)	9 520(10)
C(23)	3 438(13)	1 239(5)	10 493(10)
C(24)	6 061(14)	1 168(5)	11 159(9)

Table 5 Positional parameters for complex **2**

Atom	x	y	z
Pr	0.061 54(3)	0.132 91(1)	0.776 51(3)
O(1)	0.115 2(6)	0.143 1(2)	0.538 9(4)
O(2)	−0.005 8(6)	0.112 8(2)	1.017 0(4)
O(3)	0.445 5(6)	0.112 4(2)	1.255 2(6)
C(1)	0.231 5(8)	0.050 1(3)	0.671 8(7)
C(2)	0.327 6(8)	0.063 8(3)	0.776 4(7)
C(3)	0.252 8(9)	0.046 6(3)	0.876 1(7)
C(4)	0.108(1)	0.021 8(3)	0.832 0(8)
C(5)	0.096 0(9)	0.024 5(3)	0.705 4(7)
C(6)	0.271(1)	0.062 0(4)	0.544 8(8)
C(7)	0.189(2)	0.104 14(5)	0.480 5(9)
C(8)	0.042(1)	0.184 6(4)	0.457 2(8)
C(9)	−0.254 5(7)	0.119 8(3)	0.828 6(6)
C(10)	−0.241 9(7)	0.085 5(3)	0.726 7(7)
C(11)	−0.225 2(7)	0.121 2(4)	0.627 7(7)
C(12)	−0.223 6(7)	0.176 0(3)	0.669 3(7)
C(13)	−0.241 5(6)	0.175 5(3)	0.794 7(7)
C(14)	−0.277 1(8)	0.098 2(4)	0.953 4(7)
C(15)	−0.160 6(9)	0.122 7(4)	1.049 8(7)
C(16)	0.113(1)	0.117 9(4)	1.120 9(7)
C(17)	0.111 7(7)	0.249 5(3)	0.807 7(7)
C(18)	0.148 8(9)	0.225 1(3)	0.921 6(7)
C(19)	0.285 6(9)	0.193 1(3)	0.917 8(8)
C(20)	0.335 5(8)	0.198 2(3)	0.801 3(9)
C(21)	0.225 8(9)	0.232 3(3)	0.731 2(8)
C(22)	−0.014 2(9)	0.292 5(3)	0.775 3(9)
C(23)	0.057 5(8)	0.348 3(2)	0.796 1(7)
C(24)	0.006(1)	0.442 6(3)	0.762 6(9)

Preparation of tris(2-methoxyethylcyclopentadienyl)lanthanum complexes

[La($C_5H_4CH_2CH_2OMe$)$_3$] 1. A thf solution (10 cm^3) of 1.10 mol dm^{-3} 2-methoxyethylcyclopentadienylsodium was added slowly to a suspension of $LaCl_3$ (0.87 g, 3.5 mmol) in thf (10 cm^3) at room temperature. After stirring for 30 h, the Schlenk flask was centrifuged and the precipitate was separated from the solution, then the solvent was removed. The solid was extracted with hexane (2 × 20 cm^3) and the solvent evaporated until solid appeared. The solid was dissolved by heating and the clear solution was cooled at 0 °C to give 1.10 g of colourless crystals of the product (65%) (Found: C, 56.50; H, 6.35; La, 27.45. $C_{24}H_{33}LaO_3$ requires C, 56.70; H, 6.55; La, 27.30%). IR (cm^{-1}): 3067s, 2925s, 2829s, 1476s, 1450s, 1082s, 1046s, 972vs, 762vs, 662m, 593m and 326w. Mass spectrum: m/z 507 ($M^+ - 1$), 387 ($M - CH_3OCH_2CH_2C_5H_4$) and 124 ($CH_3OCH_2CH_2C_5H_5$).

[Pr($C_5H_4CH_2CH_2OMe$)$_3$] 2. This compound was prepared from $PrCl_3$ (0.87 g, 3.5 mmol) and a solution (18 cm^3) of 0.63 mol dm^{-3} 2-methoxyethylcyclopentadienylsodium in thf (20 cm^3) using the procedure described above. Pale yellow crystals were obtained: yield 1.34 g, 75% (Found: C, 57.40; H, 6.55; Pr, 28.50. $C_{24}H_{33}O_3Pr$ requires C, 56.50; H, 6.50; Pr, 27.45%). IR (cm^{-1}): 3066s, 2919s, 2830s, 1457s, 1086s, 1074s, 1047s, 1032s, 974m, 765vs, 676m and 319w. Mass spectrum: m/z 509 ($M^+ - 1$), 387 ($M - CH_3OCH_2CH_2C_5H_4$) and 124 ($CH_3OCH_2CH_2C_5H_5$).

[Nd($C_5H_4CH_2CH_2OMe$)$_3$] 3. This compound was prepared from $NdCl_3$ (0.51 g, 2.0 mmol) and a solution (10 cm^3) of 0.63 mol dm^{-3} 2-methoxyethylcyclopentadienylsodium in thf (20 cm^3) using the procedure described above. Violet-red crystals were obtained: yield 0.71 g, 70% (Found: C, 56.05; H, 6.25; Nd, 28.30. $C_{24}H_{33}NdO_3$ requires C, 56.10; H, 6.45; Nd, 28.10%). IR (cm^{-1}): 3068s, 2924s, 2829s, 1475s, 1450s, 1080s,

Table 6 Positional parameters for complex **3**

Atom	*x*	*y*	*z*
Nd	0.060 54(3)	0.133 22(1)	0.276 15(3)
O(1)	0.112 7(6)	0.143 8(2)	0.039 1(4)
O(2)	−0.053 2(6)	0.388 1(2)	0.256 4(6)
O(3)	−0.004 8(6)	0.112 9(2)	0.517 9(4)
C(1)	0.230 0(8)	0.051 0(3)	0.171 2(6)
C(2)	0.326 3(8)	0.064 3(3)	0.277 1(7)
C(3)	0.249 2(9)	0.047 1(3)	0.375 9(7)
C(4)	0.103(1)	0.022 8(3)	0.331 0(8)
C(5)	0.094 2(8)	0.025 2(3)	0.205 1(7)
C(6)	0.272(1)	0.062 8(4)	0.045 2(8)
C(7)	0.181(2)	0.100 6(5)	−0.021 8(9)
C(8)	0.041(1)	0.185 2(4)	−0.042 1(8)
C(9)	0.110 6(7)	0.249 1(2)	0.306 9(7)
C(10)	0.146 2(8)	0.224 7(3)	0.420 5(7)
C(11)	0.286 0(9)	0.192 9(3)	0.417 2(8)
C(12)	0.333 5(8)	0.198 1(3)	0.300 5(9)
C(13)	0.223 6(8)	0.232 3(3)	0.230 0(8)
C(14)	−0.014 6(8)	0.292 2(3)	0.276 4(9)
C(15)	0.057 6(8)	0.348 3(2)	0.297 3(7)
C(16)	0.007(1)	0.442 9(3)	0.264 6(9)
C(17)	−0.253 7(6)	0.119 8(3)	0.329 2(6)
C(18)	−0.243 0(7)	0.086 7(3)	0.226 4(7)
C(19)	−0.225 2(7)	0.121 6(3)	0.127 4(7)
C(20)	−0.223 9(7)	0.176 4(3)	0.170 6(7)
C(21)	−0.240 4(6)	0.175 7(3)	0.295 5(7)
C(22)	−0.275 8(8)	0.098 0(4)	0.455 1(7)
C(23)	−0.160 4(9)	0.121 9(4)	0.551 1(7)
C(24)	0.111(1)	0.118 5(4)	0.621 9(7)

Table 7 Positional parameters for complex **4**

Atom	*x*	*y*	*z*
Gd	0.752 63(2)	0.343 57(1)	0.145 67(2)
O(1)	0.680 8(4)	0.218 4(2)	0.099 7(3)
O(2)	0.597 6(5)	0.426 0(2)	−0.313 2(3)
O(3)	0.834 4(5)	0.478 9(2)	0.214 6(3)
C(1)	0.437 6(5)	0.308 5(3)	0.147 2(4)
C(2)	0.454 2(6)	0.350 4(3)	0.063 3(4)
C(3)	0.483 3(6)	0.412 7(3)	0.100 4(4)
C(4)	0.484 5(6)	0.410 5(3)	0.207 0(4)
C(5)	0.455 2(6)	0.345 7(3)	0.236 9(4)
C(6)	0.409 1(7)	0.235 6(3)	0.144 1(5)
C(7)	0.518 5(7)	0.201 6(3)	0.073 8(5)
C(8)	0.787 9(8)	0.172 5(3)	0.055 5(6)
C(9)	0.794 3(6)	0.378 4(2)	−0.066 2(4)
C(10)	0.884 4(6)	0.421 2(3)	−0.006 2(4)
C(11)	1.007 8(6)	0.378 8(3)	0.041 2(4)
C(12)	0.993 5(7)	0.323 0(3)	0.012 3(4)
C(13)	0.861 9(7)	0.317 0(3)	−0.053 0(4)
C(14)	0.663 3(7)	0.395 2(3)	−0.140 1(4)
C(15)	0.723 8(7)	0.421 1(3)	−0.241 6(4)
C(16)	0.643 3(9)	0.447 5(3)	−0.409 2(5)
C(17)	0.933 3(6)	0.364 8(3)	0.323 6(4)
C(18)	0.790 3(7)	0.337 4(3)	0.355 5(4)
C(19)	0.784 3(7)	0.272 8(3)	0.323 8(4)
C(20)	0.923 5(7)	0.260 0(3)	0.270 9(4)
C(21)	1.015 8(6)	0.315 9(3)	0.270 9(4)
C(22)	0.995 8(8)	0.432 4(3)	0.344 2(5)
C(23)	0.883 7(8)	0.485 3(3)	0.318 1(5)
C(24)	0.765 6(8)	0.539 3(4)	0.177 9(6)

1045s, 970m, 760vs, 662m, 593m and 326w. Mass spectrum: *m*/*z* 510 (M^+ − 1), 388 (M − $CH_3OCH_2CH_2C_5H_4$) and 124 ($CH_3OCH_2CH_2C_5H_5$).

[$Gd(C_5H_4CH_2CH_2OMe)_3$] 4. This compound was prepared from $GdCl_3$ (0.81 g, 3.07 mmol) and a solution (10 cm^3) of 0.96 mol dm^{-3} 2-methoxyethylcyclopentadienylsodium in thf (20 cm^3) using the procedure described above. Colourless crystals were obtained: yield 1.01 g, 62% (Found: C, 54.60; H, 6.20; Gd, 29.55. $C_{24}H_{33}GdO_3$ requires C, 54.70; H, 6.30; Gd, 29.80%). IR (cm^{-1}): 3067s, 2925s, 2829s, 1476s, 1450s, 1082s, 1046s, 972vs, 762vs, 662m, 593m and 326w. Mass spectrum: *m*/*z* 526 (M^+ − 1), 403 (M − $CH_3OCH_2CH_2C_5H_4$) and 124 ($CH_3OCH_2CH_2C_5H_5$).

[$Y(C_5H_4CH_2CH_2OMe)_3$] 5. This compound was prepared from YCl_3 (0.62 g, 3.21 mmol) and a solution (12 cm^3) of 0.82 mol dm^{-3} 2-methoxyethylcyclopentadienylsodium in thf (20 cm^3) using the procedure described above. Colourless crystals were obtained: yield 0.86 g, 60% (Found: C, 62.55; H, 7.15; Y, 20.05. $C_{24}H_{33}O_3Y$ requires C, 62.90; H, 7.25; Y, 19.40%). IR (cm^{-1}): 3083s, 2890s, 2830s, 1469s, 1452s, 1079s, 1057s, 1049s, 1029s, 969m, 766vs, 681m and 312w. Mass spectrum: *m*/*z* 458 (M^+ − 1), 336 (M − $CH_3OCH_2CH_2C_5H_4$) and 124 ($CH_3OCH_2CH_2C_5H_5$).

Crystal structure determinations of complexes 1–4

Suitable single crystals were sealed under argon in thin-walled glass capillaries. Intensity data were collected on a Siemens R3m/V diffractometer for complex **1** and on an Enraf-Nonius CAD4 diffractometer for **2**–**4**, using graphite-monochromated Mo-Kα radiation (λ = 0.7107 Å) in the 2θ–θ scan mode for **1** and the ω–2θ scan mode for **2**–**4**. Final lattice parameters were obtained by least-squares refinement of the 2θ values of 25 reflections. The crystal data and the data collection parameters are listed in Table 3. The intensities were corrected for Lorentz and polarization effects, but not for absorption for complex **1** and for Lorentz, polarization and absorption effects for **2**–**4**.

The metal atoms were located by the Patterson method and other non-hydrogen atoms by Fourier-difference synthesis. All positional parameters and anisotropic thermal parameters for non-hydrogen atoms were refined by the full-matrix least-squares technique. All hydrogen atoms were introduced in calculated positions. All calculations for complex **1** were performed on a Micro Vax-II computer with Siemens SHELXTL PLUS (VMS)[25] programs and all calculations for **2**–**4** on a Micro Vax-II computer with SDP[26] plus ORTEP programs.

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

Acknowledgements

Financial support of this project by the National Nature Science Foundation of China is gratefully acknowledged. C. Qian and J. Sun thank the National Laboratory for Structural Chemistry of Unstable and Stable Species for financial support.

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Received 3rd *October* 1995; *Paper* 5/06526