Inorganica Chimica Acta, *170* (1990) 109–113

Monocyclopentadienyl Lanthanide(III) Complexes. The Synthesis and Crystallographic Characterization of the Organosamarium(III) Complex: $(\eta^5\text{-}C_5H_5)SmCl(THF)_2(\mu\text{-}Cl)_2SmCl_2(THF)_3$ *

GIOVANNI DEPAOLI**, PIERLUIGI ZANONATO

Dipartimento di Chimica Inorganica Metallorganica ed Analitica, Università degli Studi di Padova, Via L. Loredan 4, 35100 Padua (Italy)

and GIOVANNI VALLE

Centro Studi sui Biopolimeri del CNR, Via Marzolo 1, 35141 Padua (Italy)

(Received September 11, 1989; revised November 6, 1989)

Abstract

$(\eta^5\text{-}C_5H_5)SmCl(THF)_2(\mu\text{-}Cl)_2SmCl_2(THF)_3$ was obtained by reacting $SmCl_3$ and $Na(C_5H_5)$ in tetrahydrofuran at room temperature (molar ratio NaCp/$SmCl_3$ = 0.6). The compound crystallizes in the space group $P2_1/c$ with $a = 16.615(3)$, $b = 17.766(3)$, $c = 13.440(2)$ Å, $\beta = 104.0(2)°$, $V = 3849.4$ Å^3 and $Z = 4$. Least-squares refinement led to a value for the conventional R index of 0.066 for 3268 reflections having $I \geqslant 3\sigma(I)$.

The molecular structure consists of dinuclear units in which two samarium atoms are bridged by two chlorine atoms. The samarium atoms differ in coordination and the whole molecule can be described by a distorted octahedron connected to a pentagonal bipyramid through two chlorine atoms.

Introduction

So far, only monomeric monocyclopentadienyl lanthanide(III) halides of the type $(\eta^5\text{-}C_5H_5)LnX_2(THF)_n$ (Ln = lanthanide(III) ion, THF = tetrahydrofuran, X = Cl, Br and n = 2, 3, or 4) have been reported [1–3.] Complexes with n = 3 have been studied in the solid state for europium(III) [4], erbium(III) [5] and ytterbium(III) [6]. They are isostructural and the crystal structure consists of lanthanide(III) ions coordinated by two halogen atoms, three THF oxygen atoms and an η^5-bonded cyclopentadienyl ligand. Although the coordination number of the lanthanide(III) ions is formally eight, a pseudo octahedral coordination geometry results, if the $\eta^5\text{-}C_5H_5$ ligand is regarded as occupying a single polyhedral vertex, the THF oxygen atoms having a *mer* configuration and the chlorine ions being in *trans* positions.

In the course of a series of experiments carried out for checking the influence of the unsubstituted cyclopentadienyl ligand on the coordination number and geometry of the lanthanide(III) ions in the 'gadolinium break' region of the lanthanide series, we have isolated a new samarium(III) monocyclopentadienide. This represents hitherto the first example of a monocyclopentadienyl complex of the lanthanides in a dinuclear form as shown by the crystal and molecular structure presented here.

Experimental

Preparation

The samarium(III) complex is extremely sensitive to air and moisture, therefore both the syntheses and subsequent manipulations were conducted with rigorous exclusion of air and water using the glove box techniques. The solvents (tetrahydrofuran and pentane) were purified by standard methods and distilled under nitrogen from potassium benzophenone ketyl immediately prior to use.

Anhydrous $SmCl_3$ and sodium cyclopentadienide were prepared according to reported methods [7, 8]. The solution of cyclopentadienyl sodium in THF was standardized and used directly in the synthesis.

The reaction of $SmCl_3$ with NaCp was carried out at room temperature in THF using a molar ratio NaCp/$SmCl_3$ = 0.6. The mixture was stirred for two days, filtered and concentrated under reduced pressure. The precipitated yellow solid was dried and analyzed. A molar ratio Cl/Sm = 2.95 resulted. Since this result was difficult to explain, the analyzed compound was crystallized in THF and a few drops of pentane were added to the THF solution. Pale

---

*Paper presented at the XIII International Conference on Organometallic Chemistry, Torino, Italy, Sept. 4–9, 1988.

**Author to whom correspondence should be addressed.

0020-1693/90/$3.50

yellow–green crystals suitable for X-ray data collection precipitated in a day.

Anal. Calc. for $Sm_2Cl_5O_5C_{25}H_{45}$: Sm, 33.24; Cl, 19.61. Found: Sm, 33.13; Cl, 19.25%.

Structural Investigation

Single crystals of this air-sensitive compound were sealed under nitrogen in thin-walled glass capillaries filled with degassed and dried paraffin oil.

A summary of the crystal data as determined from a least-squares refinement for 25 reflections in the range of $8° < \theta < 14°$ is given in Table 1, as well as details concerning crystal size, unit cell, density and number of reflections.

The data were collected on a Philips PW1100 diffractometer using the $\theta/2\theta$ scan mode. Calculations were carried out with the SHELX76 system of computer programs [9]. The positions of samarium atoms were revealed by a Patterson synthesis and the subsequent difference Fourier map showed the positions of all the non-hydrogen atoms.

The cyclopentadienyl ring was refined isotropically as a rigid group (C–C, 1.42 Å) [9]. The samarium, chlorine and THF oxygen atoms were dealt with anisotropically, while all other carbon atoms were treated with isotropic thermal parameters. The hydrogen atoms were calculated and not refined. The final agreement factor is $R = 0.066$.

Scattering factors for the samarium atom were taken from the International Tables of Crystallography [10].

TABLE 1. Crystal data and structure refinement parameters for $(\eta^5\text{-}C_5H_5)SmCl(THF)_2(\mu\text{-}Cl)_2Sm(Cl)_2(THF)_3$

Compound	$Sm_2Cl_5O_5C_{25}H_{45}$
Molecular weight	903.7
Space group	$P2_1/c$
a (Å)	16.615(3)
b (Å)	17.766(3)
c (Å)	13.440(2)
β (°)	104.0(2)
V (Å^3)	3849.4
Z	4
D_c (g cm^{-3})	1.56
μ_{calc} (cm^{-1})	32.68
Radiation	Mo Kα
Crystal size (mm)	0.30 × 0.50 × 0.60
Scan width (°)	1.2
No. reflections	7077
No. unique reflections	6778
No. reflections in refinements	3268 ($I \geq 3\sigma(I)$)
Decay of standards	10%
No. parameters varied	209
GOF	1.54
R	0.066
R_w	0.073

$w = 1/\sigma^2(F) + 0.003F^2$).

Results and Discussion

The interaction of LnX_3 with one, two or three equivalents of MC_5H_5 (Ln = lanthanide metal, X = halogen, M = Li, Na or K) has been extensively investigated [11]. Less attention has been paid to the reaction between MC_5H_5 and the lanthanide halide using a fractional molar ratio (MC_5H_5/LnX_3 = non-integer number). In our investigation this ratio was fixed at 0.6 and our interest was focused on the lanthanide elements able to give a variety of cyclopentadienyls (Sm–Lu). In this approach the larger lanthanides (Ce–Lu) which generally form only tricyclopentadienyl complexes were not considered.

Using a molar ratio $MCp/LnX_3 = 0.6$ (Ln = Sm or Eu) different kinds of complexes have been obtained. Europium(III) forms a monomeric cyclopentadienyl compound [4] of the type $CpEuCl_2(THF)_3$, which is isostructural with the erbium(III) and ytterbium(III) analogous [5, 6]. Samarium(III), however, forms in the solid state a dimeric complex whose positional parameters are given in Table 2.

Due to a certain degree of disorder of the tetrahydrofuran and cyclopentadienyl group and to the fact that in the course of the X-ray data collection some decrease of intensity of the reflections was observed, the discussion of this structure mainly concerns bond lengths and angles between the coordinated atoms and the samarium(III) ions (see Table 3).

The molecular structure of the title compound is illustrated in Fig. 1. It consists of two samarium atoms connected by two chlorine bridges. The samarium atoms differ in coordination: Sm(1) is surrounded by four chlorine atoms and three THF oxygen atoms, Sm(2) is coordinated by three chlorine atoms, two THF oxygens and a penta-hapto-C_5H_5 ligand. This structure can be compared with the dimeric biscyclopentadienyl complex of samarium(II), $[(C_5Me_5)Sm(\mu\text{-}I)(THF)_2]_2$ [12]. In this molecule the $Sm(\mu\text{-}I)_2Sm$ unit is perfectly planar, the C_5Me_5 ring is on one side of the plane, and the two THF molecules on the other. The samarium atoms have a symmetric environment with respect to the plane containing the iodine atoms, perpendicular to the $Sm(\mu\text{-}I)_2Sm$ unit.

In the title compound the distribution of the ligands around each samarium atom is different as far as their number and type are concerned. If one considers the η^5-bonded C_5H_5 ligand as occupying a single vertex, the coordination polyhedra around the samarium atoms can be described as follows. Sm(1) is located at the center of a distorted pentagonal bipyramid having two chlorine atoms (Cl(1) and Cl(2)) on the apical positions almost equidistant from Sm(1) forming an angle Cl(1)–Sm(1)–Cl(2) of 179°. The five atoms in the equatorial plane (O(1), O(2), O(3), Cl(3) and Cl(4) are coplanar (Fig. 2). The six-coordinated donor atoms on Sm(2) are arranged

TABLE 2. Positional parameters for $(\eta^5\text{-}C_5H_5)SmCl(THF)_2(\mu\text{-}Cl)_2SmCl_2(THF)_3$[a]

Atom	x	y	z	$U_{iso/eq}$
Sm(1)	0.80003(5)	0.37965(5)	0.68156(6)	0.0520(3)
Sm(2)	0.72737(6)	0.62071(5)	0.64889(8)	0.0664(4)
Cl(1)	0.8607(3)	0.3879(3)	0.8796(3)	0.079(2)
Cl(2)	0.7416(4)	0.3517(3)	0.4853(4)	0.088(2)
Cl(3)	0.6703(3)	0.4796(3)	0.6920(4)	0.074(2)
Cl(4)	0.8551(3)	0.5197(2)	0.6372(4)	0.076(2)
Cl(5)	0.8297(4)	0.7167(3)	0.5938(6)	0.123(3)
O(1)	0.8398(8)	0.2442(6)	0.7002(9)	0.082(6)
C(1)*	0.836(2)	0.192(2)	0.625(3)	0.17(1)
C(2)*	0.862(2)	0.116(2)	0.667(3)	0.15(1)
C(3)*	0.895(2)	0.130(2)	0.772(3)	0.15(1)
C(4)*	0.881(2)	0.208(2)	0.787(3)	0.16(1)
O(2)	0.9423(7)	0.3646(7)	0.6601(9)	0.072(5)
C(5)*	1.017(2)	0.380(1)	0.741(2)	0.108(7)
C(6)*	1.084(2)	0.391(2)	0.686(2)	0.13(1)
C(7)*	1.042(2)	0.400(2)	0.574(3)	0.15(1)
C(8)*	0.963(1)	0.367(1)	0.559(2)	0.100(7)
O(3)	0.6875(8)	0.3058(8)	0.713(1)	0.096(7)
C(9)*	0.613(2)	0.290(2)	0.636(3)	0.15(1)
C(10)*	0.573(3)	0.255(3)	0.704(5)	0.29(3)
C(11)*	0.596(4)	0.278(3)	0.800(5)	0.31(2)
C(12)*	0.671(2)	0.302(2)	0.815(3)	0.18(1)
O(4)	0.6726(8)	0.5765(7)	0.471(1)	0.089(6)
C(13)*	0.595(1)	0.535(1)	0.429(2)	0.108(7)
C(14)*	0.595(2)	0.511(2)	0.327(2)	0.13(1)
C(15)*	0.668(2)	0.544(2)	0.306(3)	0.15(1)
C(16)*	0.726(2)	0.575(2)	0.396(2)	0.124(9)
O(5)	0.8069(9)	0.6201(9)	0.828(1)	0.101(7)
C(17)*	0.782(2)	0.594(2)	0.909(3)	0.13(1)
C(18)*	0.854(2)	0.585(2)	0.996(2)	0.14(1)
C(19)*	0.923(3)	0.607(2)	0.958(2)	0.20(2)
C(20)*	0.901(2)	0.638(2)	0.856(3)	0.16(1)
C(21)*	0.564(1)	0.653(1)	0.631(2)	0.103(7)
C(22)*	0.595(2)	0.658(1)	0.726(2)	0.114(8)
C(23)*	0.655(2)	0.721(2)	0.747(2)	0.121(9)
C(24)*	0.658(2)	0.752(2)	0.660(2)	0.132(9)
C(25)*	0.601(2)	0.715(1)	0.584(2)	0.117(8)

[a] Starred atoms were refined isotropically. Temperature factors of anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $U_{eq} = \frac{1}{3}\Sigma_i \Sigma_j U_{ij} a^*_i a^*_j \mathbf{a}_i \mathbf{a}_j$.

in a pseudo octahedral configuration, in which two chlorine and two oxygen atoms in *trans* position are coplanar, the center of gravity (Cg) of the carbon ring of the cyclopentadienyl ligand occupies an apical position, the opposite one being occupied by another chlorine atom. In Table 4 a comparison of selected distances and angles of this polyhedron with those observed in the monocyclopentadienyl complexes of europium(III), erbium(III) and ytterbium(III) is reported. With the exception of the Cg–Ln–Y angle which is slightly smaller than that found in the latter compounds, the other figures are comparable.

TABLE 3. Bond lengths (Å) polyhedral edge lengths (Å) and bond angles (°) of $(\eta^5\text{-}C_5H_5)SmCl(THF)_2(\mu\text{-}Cl)_2Sm(Cl)_2(THF)_3$

Sm(1)–Cl(1)	2.612(5)
Sm(1)–Cl(2)	2.628(5)
Sm(1)–Cl(3)	2.822(5)
Sm(1)–Cl(4)	2.766(5)
Sm(1)–O(1)	2.49(1)
Sm(1)–O(2)	2.46(1)
Sm(1)–O(3)	2.40(2)
Sm(2)–Cl(3)	2.790(5)
Sm(2)–Cl(4)	2.812(5)
Sm(2)–Cl(5)	2.637(7)
Sm(2)–O(4)	2.471(1)
Sm(2)–O(5)	2.451(1)
Sm(2)–C(21)	2.72(2)
Sm(2)–C(22)	2.73(3)
Sm(2)–C(23)	2.66(3)
Sm(2)–C(24)	2.62(3)
Sm(2)–C(25)	2.67(3)
Sm(1)–Sm(2)	4.441(1)
Cg–Sm(2)	2.411(3)
Cg...Cl(3)	4.02(2)
Cg...Cl(5)	3.954(4)
Cg...O(4)	3.76(5)
Cg...O(5)	3.67(5)
Cl(4)...Cl(3)	3.40(1)
Cl(4)...Cl(5)	3.56(1)
Cl(4)...O(4)	3.45(3)
Cl(4)...O(5)	3.37(2)
Cl(3)...O(3)	3.11(3)
O(3)...O(1)	2.80(5)
O(1)...O(2)	2.87(6)
O(2)...Cl(4)	3.09(1)
Cl(2)...Cl(3)	3.985(5)
Cl(2)...Cl(4)	3.84(2)
Cl(2)...O(3)	3.48(7)
Cl(2)...O(1)	3.52(6)
Cl(2)...O(2)	3.59(7)
Cl(1)...O(1)	3.47(5)
Cl(1)...O(2)	3.56(6)
Cl(1)...O(3)	3.51(5)
Cl(1)...Cl(3)	3.89(2)
Cl(1)...Cl(4)	4.00(1)
O(2)–Sm(1)–O(1)	70.6(4)
O(1)–Sm(1)–O(3)	69.7(5)
O(3)–Sm(1)–Cl(3)	72.3(3)
Cl(3)–Sm(1)–Cl(4)	75.0(1)
Cl(4)–Sm(1)–O(2)	72.3(3)
Cl(1)–Sm(1)–O(1)	85.7(3)
Cl(1)–Sm(1)–O(2)	88.9(3)
Cl(1)–Sm(1)–O(3)	88.8(4)
Cl(1)–Sm(1)–Cl(3)	91.4(2)
Cl(1)–Sm(1)–Cl(4)	95.9(2)
Cl(2)–Sm(1)–O(1)	86.7(3)
Cl(2)–Sm(1)–O(2)	98.6(3)
Cl(2)–Sm(1)–O(3)	87.5(4)

(continued)

TABLE 3. *(continued)*

Cl(2)–Sm(1)–Cl(3)	93.9(2)
Cl(2)–Sm(1)–Cl(4)	90.8(2)
O(1)–O(2)–Cl(4)	113.5(4)
O(1)–O(3)–Cl(3)	116.7(3)
O(2)–Cl(4)–Cl(3)	102.6(2)
Cl(4)–Cl(3)–O(3)	99.1(3)
Cl(3)–O(3)–O(1)	116.7(2)
Cg–Sm(2)–Cl(4)	175.1(2)
Cg–Sm(2)–Cl(3)	100.9(3)
Cg–Sm(2)–Cl(5)	103.0(4)
Cg–Sm(2)–O(4)	100.5(6)
Cg–Sm(2)–(5)	98.1(5)
Cl(3)–Sm(2)–Cl(5)	156.0(2)
O(4)–Sm(2)–O(5)	159.0(5)
Cl(3)–Sm(2)–O(4)	81.5(3)
O(4)–Sm(2)–Cl(5)	92.6(4)
Cl(5)–Sm(2)–O(5)	92.7(4)
O(5)–Sm(2)–Cl(3)	85.5(4)
Cl(4)–Sm(2)–O(4)	81.3(3)
Cl(4)–Sm(2)–O(5)	81.4(2)
Cl(4)–Sm(2)–Cl(3)	74.8(1)
Cl(4)–Sm(2)–Cl(5)	79.4(4)
Sm(1)–Cl(3)–Sm(2)	104.6(4)
Sm(1)–Cl(4)–Sm(2)	105.5(6)

Cg = center of gravity of the cyclopentadienyl ligand.

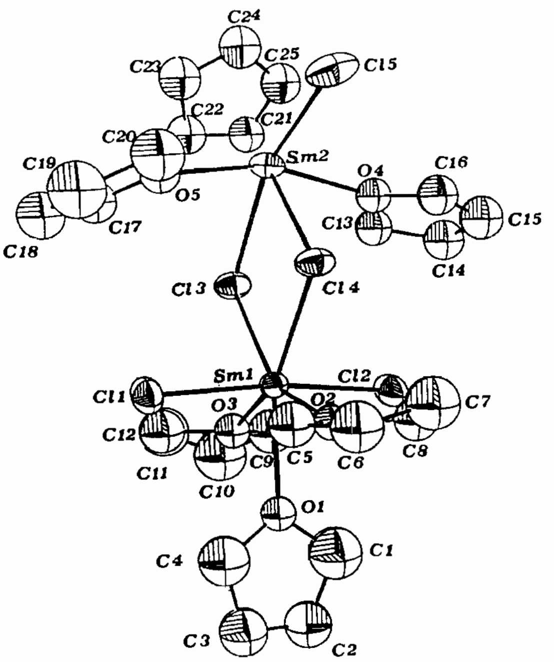


Fig. 1. ORTEP drawing with the numbering scheme. Thermal ellipsoids scaled at 30% probability level.

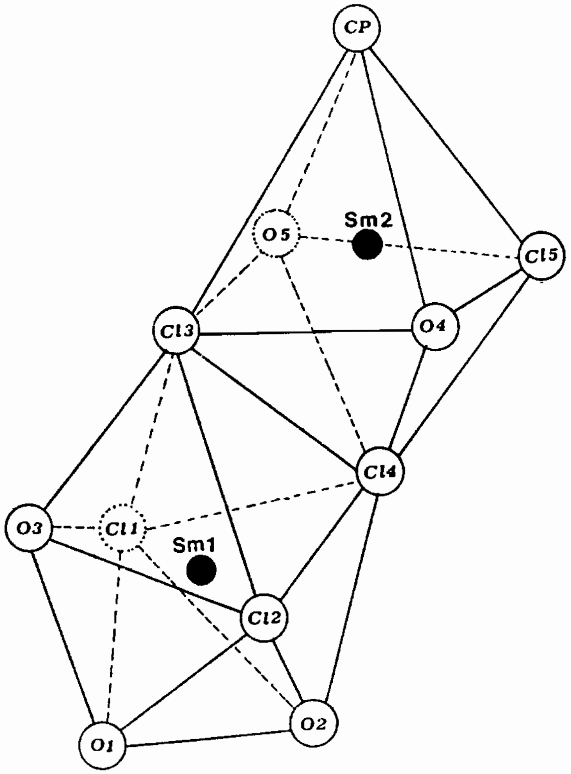


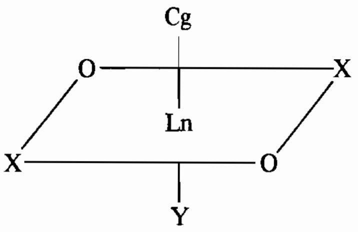
Fig. 2. The idealized coordination polyhedron of $(\eta^5\text{-}C_5H_5)SmCl(THF)_2(\mu\text{-}Cl)_2SmCl_2(THF)_3$.

If one considers the $Sm(\mu\text{-}Cl)_2Sm$ unit the crystallographic results show that the atoms Sm(1), Cl(3), Cl(4), Sm(2) are on the same plane ($\sigma = 0.006$ Å) as in the case of the samarium(II) dimer [12] and this plane in turn virtually coincides with that of the pentagonal base of the polyhedron containing Sm(1).

A comparison of the bond angles in the central unit $M(\mu\text{-}X)_2M$ (M = Gd, Dy, Er, Yb; X = Cl, Br) [13–16] of biscyclopentadienyl complexes of some lanthanide(III) ions with those of the title complex, shows that in the latter the angles X–M–X and M–X–M are about 10° smaller and 10° larger respectively. This more pronounced stretching in the direction of the Sm–Sm axes can be due to the equatorial five coordination of Sm(1). The whole molecule can therefore be represented by the combination of the described polyhedra as shown in Fig. 2. The resulting polyhedron is quite different from that so far known for bis(cyclopentadienyl) lanthanide(III) complexes. In fact, in these compounds the coordination framework can generally be illustrated by two tetrahedra connected through an edge (halogen bridge).

It is nevertheless evident that, except for the Cp group on Sm(2) and the corresponding two THF molecules on Sm(1), the vertex positions of the two polyhedra still retain a pseudo mirror symmetry

TABLE 4. Selected distances (A) and angles (°) in the pseudo octahedral (η^5-C_5H_5)$LnX_2(THF)_3$ (Ln = Eu, Er, Yb; X = Cl or Br) complexes compared with those of the pseudo octahedral configuration around Sm(2) in the title compound



Metal	Cg–Ln	O(THF)–Ln	X–Ln	Cg–Ln–Y	Reference
Eu (X = Cl, Y = O)	2.44(2)	2.43(2)	2.67(1)	179.5(4)	4
Er (X = Cl, Y = O)	2.389(3)	2.36(1)	2.617(3)	179.3(1)	5
Yb (X = Br, Y = O)	2.358(16)	2.34(1)	2.775(4)	179.0(2)	6
Sm (X = Y = Cl)	2.411(3)	2.46(2)	2.71(1)	175.1(2)	this work

(Fig. 1). In both coordination polyhedra the (Sm–Cl) distances of the terminal chloride are shorter than the bridging ones as pointed out by Evans *et al.* [17].

Supplementary Material

Further details of the structure determination are available on request from the authors.

Acknowledgement

The authors thank Dr A. Polo for the elaboration of the ORTEP drawing of the molecule.

References

1 S. Manastyrskyj, R. E. Maggin and M. Dubeck, *Inorg. Chem.*, *2* (1963) 904.

2 G. Z. Suleimanov, T. Kh. Urbanov, Ya. A. Nuriev, L. F. Rybaova and I. P. Beletskaya, *Dokl. Acad. Nauk SSSR*, *265* (1982) 896; *Proc. Acad. Sci. USSR*, *265* (1982) 254.

3 G. Z. Suleimanov, T. Kh. Kurbanov, Ya. A. Nuriev, L. F. Rybaova, I. P. Beletskaya, *Izv. Akad. Nauk SSSR*, (1982) 1671; *Bull. Akad. Sci. USSR*, (1982) 1490.

4 G. Depaoli, results to be published.

5 C. S. Day, V. W. Day, R. D. Ernst and S. H. Vollmer, *Organometallics*, *1* (1982) 998.

6 G. B. Deacon, G. D. Fallon and D. L. Wilkinson, *J. Organomet. Chem.*, *293* (1985) 45.

7 M. D. Taylor and C. P. Carter, *J. Inorg. Nucl. Chem.*, *24* (1962) 387.

8 R. B. King and F. G. A. Stone, *Inorg. Synth.*, *7* (1963) 99.

9 G. M. Sheldrick, *SHELX 76*, a system for computer programs for X-ray structure determination, 1976.

10 D. T. Cromer and J. T. Waber, *International Tables for X-ray Crystallography*, Vol. IV, Kynoch Press, Birmingham, 1974.

11 H. Schumann, Organolanthanides: Review and new developments, in T. J. Marks and I. L. Fragala (eds.), *element Chemistry*, D. Reidel, Dordrecht, 1985, pp. 1–48.

12 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.

13 W. Lamberts, H. Lueken and U. Elsenhans, *Inorg. Chim. Acta*, *121* (1986) 81.

14 H. Lueken, W. Lamberts and P. Hannibal, *Inorg. Chim. Acta*, *132* (1987) 111.

15 W. Lamberts, H. Lueken and B. Hessner, *Inorg. Chim. Acta*, *134* (1987) 155.

16 H. Lueken, J. Schmitz, W. Lamberts, P. Hannibal and K. Handrick, *Inorg. Chim. Acta*, *156* (1989) 119.

17 W. J. Evans, T. T. Peterson, M. D. Rausch, W. E. Hunter, H. M. Zhang and J. L. Atwood, *Organometallics*, *4* (1985) 554.