Journal of Organometallic Chemistry, 349 (1988) 103–115
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Organometallic compounds of the lanthanides

XLIV *. Bis(cyclopentadienyl)lutetium alkoxides, thiolates and selenolates. Crystal structures of $(C_5Me_5)_2Lu(\mu\text{-}S^tC_4H_9)_2Li(THF)_2$ and $(C_5H_5)_2Lu(\mu\text{-}SeC_6H_5)_2Li(THF)_2$

Herbert Schumann *, Ilse Albrecht, Michael Gallagher, Ekkehardt Hahn, Christine Muchmore and Joachim Pickardt

Institut für Anorganische und Analytische Chemie der Technischen Universität Berlin, D-1000 Berlin 12, (B.R. Deutschland)

(Received January 12th, 1988)

Abstract

Bis(tetrahydrofuran)lithium dimethylbis(cyclopentadienyl)lutetate(III) have been shown to react with t-butyl alcohol, t-butyl hydrosulfide, and phenyl hydroselenide in ether at −78°C to give the complexes $(C_5H_5)_2Lu(OC_4H_9\text{-t})(THF)$, $(C_5H_5)_2Lu(SC_4H_9\text{-t})_2Li(THF)_2$, and $(C_5H_5)_2Lu(SeC_6H_5)_2Li(THF)_2$, respectively. The analogous pentamethylcyclopentadienyl complexes $(C_5Me_5)_2Lu(OC_4H_9\text{-t})(THF)$, and $(C_5Me_5)_2Lu(SC_4H_9\text{-t})_2Li(THF)_2$ have been prepared from $(C_5Me_5)_2Lu(\mu\text{-}CH_3)_2Li(THF)_2$ and $t\text{-}C_4H_9OH$ or $t\text{-}C_4H_9SH$, respectively. The new compounds have been characterized by elemental analysis and ^1H and ^{13}C NMR spectroscopy. The structures of the complexes $(C_5Me_5)_2Lu(SC_4H_9\text{-t})_2Li(THF)_2$ (**7**) and $(C_5H_5)_2Lu(SeC_6H_5)_2Li(THF)_2$ (**8**) have been determined by X-ray diffraction. The crystals of **7** are monoclinic with a 19.016(7), b 17.206(6), c 11.899(4) Å, β 101.82(3)°, space group $P2_1/n$, $Z = 4$, $R = 0.052$, and 4228 observed ($I \geqslant 2\sigma(I)$) reflections. The crystals of **8** are monoclinic with a 21.60(3), b 13.98(1), c 11.43(1) Å, β 120.68(7)°, space group $P2_1/a$, $Z = 4$, $R = 0.066$, and 2615 observed ($I \geqslant 3\sigma(I)$) reflections.

Introduction

Organolanthanides of the type $(C_5H_5)_3Ln$, as well as organolanthanide chlorides, $(C_5H_5)_2LnCl$, have been synthesized for all lanthanide metals and for scandium,

---

* For part XLIII see ref. 1.

0022-328X/88/$03.50

yttrium and lanthanum [2]. In contrast, very few organolanthanide alkoxides [3] and even fewer organometallic compounds of the "hard" electropositive lanthanides with bonds to "soft" atoms such as sulfur, selenium, phosphorus or silicon have been reported. Such compounds are, however, of special interest as reagents for organic synthesis because of their very reactive Ln–X bonds. To our knowledge only two organolanthanide-sulfur compounds, $(C_5Me_5)_2LnS_2CNEt_2$ with Ln = Nd, Yb [4], have so far been characterized, and no organolanthanide-selenium compounds are known [5*]. In addition, several dicyclopentadienyllanthanide phosphane [6], silyl [7], germanyl [8] and stannyl [8] compounds have been reported. Only five of these complexes have been definitively characterized by single crystal X-ray analyses, $(C_5Me_5)_2SmOC_6HMe_4$ [3d], the cluster compound $(C_5H_5)_5Y_5(\mu\text{-}OCH_3)_4(\mu_3\text{-}OCH_3)_4(\mu_5\text{-}O)$ [3e], one sulfur derivative, $(C_5Me_5)_2YbS_2CNEt_2$ [4], $(C_5H_5)_2Lu(\mu\text{-}PPh_2)_2Li(tmed)$ [6e], and $[Li(dme)_3][(C_5H_5)_2Sm(SiMe_3)_2]$ [7].

We have now investigated a simple, versatile route to this interesting class of compounds, and have succeeded in isolating and characterizing stable dicyclopentadienyllutetium-t-butoxide, t-butyl sulfide and phenyl selenide complexes, as well as the corresponding bis(pentamethylcyclopentadienyl) derivatives [9]. The structures of the complexes $(C_5Me_5)_2Lu(\mu\text{-}S\text{-}t\text{-}Bu)_2Li(THF)_2$ [9] and $(C_5H_5)_2Lu(\mu\text{-}SePh)_2Li(THF)_2$ have been determined by single crystal X-ray diffraction.

Results and discussion

Synthesis of dicyclopentadienyllutetium t-butylates, t-butylthiolates and phenylselenolate

Dicyclopentadienyllutetium chloride reacts in tetrahydrofuran with t-butyllithium at −78°C to form t-butyldicyclopentadienyllutetium-tetrahydrofuran (**1**). This compound, in turn, reacts with t-butyl alcohol to give t-butoxycyclopentadienyllutetium-tetrahydrofuran (**3**). Better yields of **3** are obtained by treating bis(tetrahydrofuran)lithium dimethylcyclopentadienyllutetate(III) (**2**), with t-butyl alcohol under the same conditions (eq. 1 to 3).

$$(C_5H_5)_2LuCl(THF) + LiC(CH_3)_3 \xrightarrow{THF} \underset{(\mathbf{1})}{(C_5H_5)_2Lu(C(CH_3)_3)(THF)} + LiCl \quad (1)$$

$$\underset{(\mathbf{1})}{(C_5H_5)_2Lu(C(CH_3)_3)(THF)} + (CH_3)_3COH \xrightarrow{THF} \underset{(\mathbf{3})}{(C_5H_5)_2Lu(OC(CH_3)_3)(THF)} + (CH_3)_3CH \quad (2)$$

$$\underset{(\mathbf{2})}{(C_5H_5)_2Lu(\mu\text{-}CH_3)_2Li(THF)_2} + 2(CH_3)_3COH \xrightarrow{THF} \underset{(\mathbf{3})}{(C_5H_5)_2Lu(OC(CH_3)_3)(THF)} + LiOC(CH_3)_3 + 2\ CH_4 \quad (3)$$

The corresponding pentamethylcyclopentadienyl derivative **5** is produced when bis(tetrahydrofuran)lithium dimethylbis(pentamethylcyclopentadienyl)lutetate(III)

---

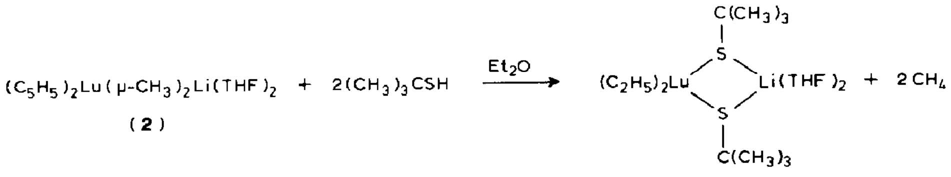
* Reference number with asterisk indicates a note in the list of references.

(4) reacts in ether with t-butylalcohol at −78 °C (eq. 4).

$$\underset{(4)}{(C_5Me_5)_2Lu(\mu\text{-}CH_3)_2Li(THF)_2} + 2\,(CH_3)_3COH \xrightarrow{Et_2O}$$

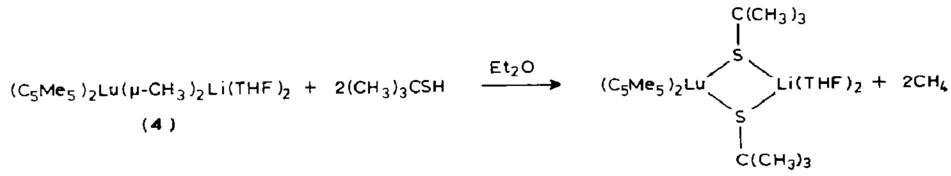
$$\underset{(5)}{(C_5Me_5)_2Lu(OC(CH_3)_3)(THF)} + LiOC(CH_3)_3 + 2\,CH_4 \quad (4)$$

The reaction of **1** with t-butyl thiol in tetrahydrofuran did not yield the expected dicyclopentadienyllutetium thiolate. After 1 h at room temperature only the starting materials could be detected by ^1H NMR spectroscopy. Refluxing of the reaction mixture led only to decomposition products, as evidenced by the large number of signals in ^1H NMR spectrum. Attempts to isolate a pure organolutetium complex from the dark brown solution were unsuccessful, but when **2** was used as the starting material it was possible to synthesize the first organolutetium thiolate, bis(tetrahydrofuran)lithium-di(t-butylthio)dicyclopentadienyllutetate(III) (**6**). Similarly **4** reacts with t-butyl thiol to give the bis(pentamethylcyclopentadienyl)lutetium complex **7** (eq. 5 and 6).



(6)

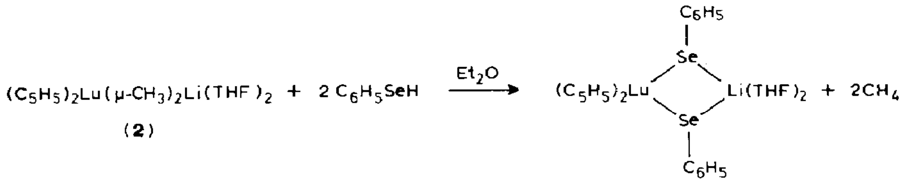
(5)



(7)

(6)

Bis(tetrahydrofuran)lithium-di(phenylseleno)dicyclopentadienyllutetate(III) (**8**), the first organolanthanide derivative with a lanthanide metal to selenium bond, is produced by reaction of **2** with phenylselenol in ether at room temperature (eq. 7).



(8)

(7)

All the compounds prepared are air-sensitive and colorless, and were obtained as crystalline powders after extraction with toluene and subsequent crystallization from ether. They are soluble in benzene, toluene and tetrahydrofuran but insoluble in saturated hydrocarbons. All the complexes are stable at room temperature, but decompose with loss of the coordinated THF above 124 °C for **6** and above 260 °C for the surprisingly stable complex **7**. The selenium derivative **8**, is also light sensitive, and darkens on exposure to light with formation of diphenyl diselenide.

The alkoxides **3** and **5** seem to be monomers, with terminal t-butoxy groups and one THF molecule coordinated to the lutetium atom. The ^1H and ^{13}C NMR spectra show the expected signals, while integration of the proton spectrum gives the expected ratio for this formulation. Complexes **6**, **7** and **8**, on the other hand, appear to have a bridged structure, derived from a 1/1 complex between the dicyclopentadienyllutetium thiolate or selenolate unit and a lithium thiolate or selenolate, respectively, as indicated by the ^1H and ^{13}C NMR spectra. Single crystal X-ray diffraction studies of **7** and **8** confirmed this structure, in which both of the metals, lithium and lutetium, are tetrahedrally coordinated, lutetium by the two centroids of the cyclopentadienyl ligands and the two chalcogen atoms, and lithium by the two chalcogen atoms and two oxygen atoms of two THF ligands. This bridged structure is also observed in analogous dicyclopentadienyllanthanide phosphine [6e] and arsine complexes [1], as well as in $C_5Me_5Lu(XC(CH_3)_3)_3Li(tmed)$ with X = O and S [9] in for which there is rapid exchange between the terminal and the bridging $XC(CH_3)_3$ groups.

Molecular structure of $(C_5Me_5)_2Lu(\mu\text{-}S^tC_4H_9)_2Li(THF)_2$ *(7) and* $(C_5H_5)_2Lu(\mu\text{-}SeC_6H_5)_2Li(THF)_2$ *(8)*

The structure of $(C_5Me_5)_2Lu(\mu\text{-}S^tC_4H_9)_2Li(THF)_2$ is shown in Fig. 1. Selected bond lengths and angles are listed in Tables 1 and 2. The structure shows a bis(t-butylthio)bridged, dinuclear lutetium-lithium complex. The lutetium atom is in a distorted tetrahedral environment consisting of the centroids of two cyclopentadienyl rings and the two bridging sulfur atoms, whereas the two sulfur atoms, and the oxygen atoms of two THF molecules form the coordination sphere of the lithium. In the dicyclopentadienyllanthanide complexes so far investigated by X-ray crystallography, $[Cp_2Ln(\mu\text{-}X)_2Li(B)_{1-2}]$, Cp = C_5Me_5, Ln = Yb, B = Et_2O, X = Cl, I [10], Cp = C_5H_5, B = tmed, X = CH_3, Ln = Er [11], Lu [12] a planar four-atom unit $Ln(\mu\text{-}X)_2Li$ was observed. In **7**, on the other hand, there is a dihedral angle of 168.1(7)° between the S(1)–Lu–S(2) and S(1)–Li–S(2) planes. Such a puckered $Ln(\mu\text{-}X)_2Li$ unit with two Cp ligands on the Ln atom is also found in the P- and

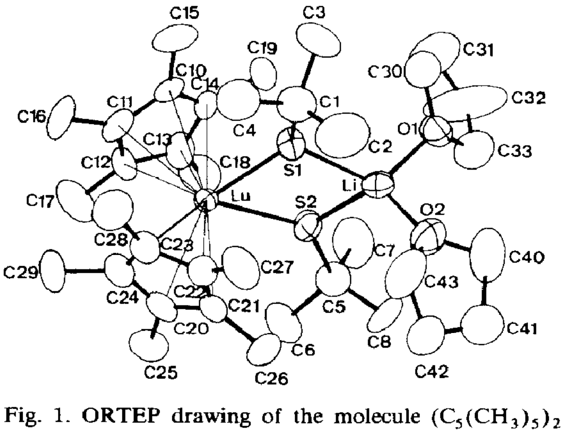


Fig. 1. ORTEP drawing of the molecule $(C_5(CH_3)_5)_2Lu(\mu\text{-}S^tC_4H_9)_2Li(THF)_2$ (7), hydrogen atoms omited and atom numbering.

Table 1

Bond lengths (Å) for $(C_5Me_5)_2Lu(\mu\text{-}S^tC_4H_9)_2Li(THF)_2$ (7)

Lu...Li [a]	3.89(2)	S(1)...S(2) [a]	3.252(4)	C(10)-C(11)	1.41(2)
Lu-S(1)	2.809(3)	Lu-S(2)	2.723(3)	C(11)-C(12)	1.43(2)
S(1)-C(1)	1.853(12)	S(2)-C(5)	1.863(12)	C(12)-C(13)	1.44(2)
C(1)-C(2)	1.54(2)	C(5)-C(6)	1.56(2)	C(13)-C(14)	1.39(2)
C(1)-C(3)	1.54(2)	C(5)-C(7)	1.57(2)	C(14)-C(10)	1.40(4)
C(1)-C(4)	1.53(2)	C(5)-C(8)	1.52(2)	C(10)-C(15)	1.52(2)
Li-S(1)	2.41(2)	Li-S(2)	2.48(2)	C(11)-C(16)	1.53(2)
Li-O(2)	1.95(2)	Li-O(2)	1.95(2)	C(12)-C(17)	1.52(2)
Lu-C(10)	2.662(11)	Lu-C(20)	2.640(10)	C(13)-C(18)	1.51(2)
Lu-C(11)	2.680(12)	Lu-C(21)	2.653(11)	C(14)-C(19)	1.52(2)
Lu-C(12)	2.650(11)	Lu-C(22)	2.674(11)	C(20)-C(21)	1.43(2)
Lu-C(13)	2.617(10)	Lu-C(23)	2.650(10)	C(21)-C(22)	1.41(2)
Lu-C(14)	2.651(10)	Lu-C(24)	2.674(11)	C(22)-C(23)	1.41(2)
Lu-Cp1 [b]	2.364(10)	Lu-Cp2 [b]	2.370(10)	C(23)-C(24)	1.42(2)
average Lu-C(η^5)	2.66(2)			C(20)-C(24)	1.40(2)
O(1)-C(30)	1.42(2)	O(2)-C(40)	1.41(2)	C(20)-C(25)	1.530(15)
C(30)-C(31)	1.54(2)	C(40)-C(41)	1.58(3)	C(21)-C(26)	1.51(2)
C(31)-C(32)	1.42(2)	C(41)-C(42)	1.51(2)	C(22)-C(27)	1.53(2)
C(32)-C(33)	1.52(3)	C(42)-C(43)	1.49(3)	C(23)-C(28)	1.56(2)
C(33)-O(1)	1.44(2)	C(43)-O(2)	1.44(2)	C(24)-C(29)	1.53(2)

[a] Non-bonding distance. [b] Cp is the centroid of the cyclopentadienyl groups (C(10)-C(14) = Cp1, C(20)-C(24) = Cp2).

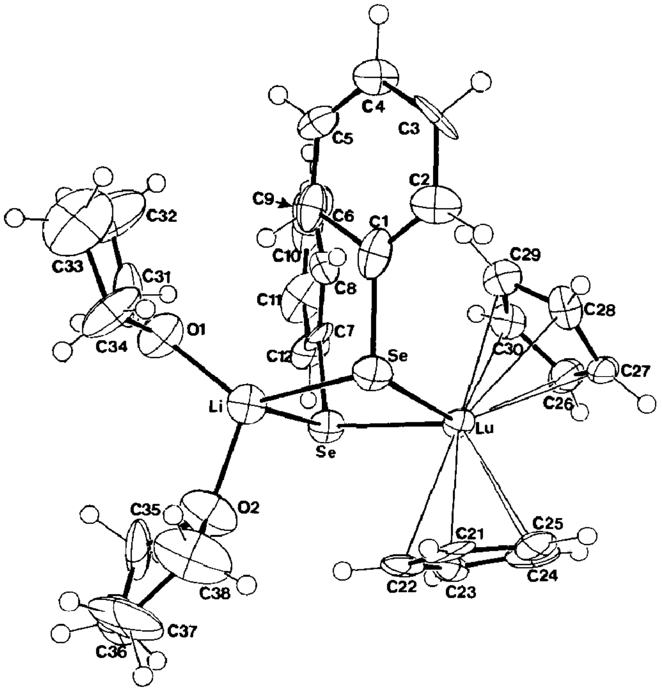


Fig. 2. ORTEP plot of a molecule of $(C_5H_5)_2Lu(\mu\text{-}SeC_6H_5)_2Li(THF)_2$ (8), and atom numbering.

Table 2

Bond angles (°) for $(C_5Me_5)_2Lu(\mu\text{-}S^tC_4H_9)_2Li(THF)_2$ (**7**)

S(1)-Lu-S(2)	73.6(1)	C(12)-C(11)-C(16)	125.7(11)	S(1)-C(1)-C(4)	111.5(9)
S(1)-Lu-Cp1 [a]	106.7(3)	C(13)-C(14)-C(19)	129.9(9)	C(2)-C(1)-C(3)	108.0(1)
S(1)-Lu-Cp(2)	111.7(3)	C(13)-C(12)-C(17)	125.0(10)	C(2)-C(1)-C(4)	111.6(11)
S(2)-Lu-Cp(1)	106.1(3)	C(14)-C(10)-C(15)	128.1(10)	C(3)-C(1)-C(4)	108.5(11)
S(2)-Lu-Cp(2)	112.3(3)	C(14)-C(13)-C(18)	126.6(10)	Li-O(1)-C(30)	120.4(9)
Cp(1)-Lu-Cp(2)	131.5(3)	Lu-S(2)-Li	99.7(4)	Li-O(1)-C(33)	121.7(9)
S(1)-Li-S(2)	83.5(6)	Lu-S(2)-C(5)	136.9(4)	O(1)-C(30)-C(31)	105.2(11)
S(1)-Li-O(1)	118.9(9)	Li-S(2)-C(5)	120.0(6)	C(30)-C(31)-C(32)	107(2)
S(1)-Li-O(2)	119.1(8)	C(20)-C(21)-C(22)	107.5(10)	C(31)-C(32)-C(33)	108(2)
S(2)-Li-O(1)	113.1(8)	C(21)-C(22)-C(23)	107.9(10)	C(32)-C(33)-O(1)	106.0(14)
S(2)-Oi-O(2)	120.0(9)	C(22)-C(23)-C(24)	108.6(10)	C(33)-O(1)-C(30)	109.5(9)
O(1)-Li-O(2)	102.6(10)	C(23)-C(24)-C(20)	107.4(10)	S(2)-C(5)-C(6)	109.8(8)
Lu-S(1)-Li	101.8(4)	C(24)-C(20)-C(21)	108.6(9)	S(2)-C(5)-C(7)	107.2(9)
Lu-S(1)-C(1)	136.2(4)	C(20)-C(21)-C(26)	125.6(10)	S(2)-C(5)-C(8)	109.0(9)
Li-S(1)-C(1)	119.5(6)	C(20)-C(24)-C(29)	125.4(10)	C(6)-C(5)-C(7)	111.2(12)
C(10)-C(11)-C(12)	107.6(9)	C(21)-C(22)-C(27)	125.6(11)	C(6)-C(5)-C(8)	109.4(11)
C(11)-C(12)-C(13)	106.5(10)	C(21)-C(20)-C(25)	127.3(11)	C(7)-C(5)-C(8)	110.2(10)
C(12)-C(13)-C(14)	108.7(9)	C(22)-C(23)-C(28)	124.7(11)	Li-O(2)-C(40)	131.1(10)
C(13)-C(14)-C(10)	108.4(9)	C(22)-C(21)-C(26)	125.9(11)	Li-O(2)-C(43)	123.0(11)
C(14)-C(10)-C(11)	108.8(9)	C(23)-C(24)-C(29)	124.7(10)	O(2)-C(40)-C(41)	101.5(15)
C(10)-C(11)-C(16)	126.0(11)	C(23)-C(22)-C(27)	125.9(10)	C(40)-C(41)-C(42)	107.3(15)
C(10)-C(14)-C(19)	125.6(10)	C(24)-C(20)-C(25)	123.4(11)	C(41)-C(42)-C(43)	100.8(4)
C(11)-C(12)-C(17)	127.0(11)	C(24)-C(23)-C(28)	126.1(11)	C(42)-C(43)-O(2)	108.0(13)
C(11)-C(10)-C(15)	122.5(10)	S(1)-C(1)-C(2)	108.9(9)	C(43)-O(2)-C(40)	105.2(12)
C(12)-C(13)-C(18)	123.6(10)	S(1)-C(1)-C(3)	108.2(8)		

[a] Cp is the centroid of the cyclopentadienyl groups (C(10)-C(14) = Cp1, C(20)-C(24) = Cp2).

Table 3

Bond lengths (Å) for $(C_5H_5)_2Lu(\mu\text{-}SeC_6H_5)_2Li(THF)_2$ (**8**)

Lu-Se(1)	2.798(7)	Lu-C(21)	2.60(1)
Lu-Se(2)	2.800(6)	Lu-C(22)	2.60(2)
Li-Se(1)	2.7(1)	Lu-C(23)	2.63(2)
Li-Se(2)	2.6(1)	Lu-C(24)	2.59(2)
Se(1)-C(1)	1.90(2)	Lu-C(25)	2.60(2)
Se(2)-C(7)	1.96(2)	Lu-C(26)	2.57(2)
		Lu-C(27)	2.58(2)
		Lu-C(28)	2.63(2)
		Lu-C(29)	2.63(2)
		Lu-C(30)	2.61(2)

Table 4

Bond angles (°) for $(C_5H_5)_2Lu(\mu\text{-}SeC_6H_5)_2Li(THF)_2$ (**8**)

Se(1)-Lu-Se(2)	94.6(2)	Se(1)-Lu-Li	47(2)
Se(2)-Lu-Li	47(2)	Se(1)-Lu-Cp(1) [a]	101.8
Se(1)-Lu-Cp(2) [a]	112.7	Se(2)-Lu-Cp(1)	99.0
Se(2)-Lu-Cp(2)	111.9	Cp(1)-Lu-Cp(2)	130.6
Lu-Se(1)-Li	81.7(3)		

[a] Cp is the centroid of the cyclopentadienyl groups (C(21)-C(25) = Cp1, C(26)-C(30) = Cp2).

As-bridged complexes $(C_5H_5)_2Lu(\mu\text{-}PPh_2)_2Li(tmed)$, dihedral angle 148.7° [6e], and $(C_5H_5)_2Lu(\mu\text{-}AsPh_2)_2Li(tmed)$, dihedral angle 150.8° [1]. The Cp(1)-Lu-Cp(2) angle and the mean value of the ten LuC(η^5) distances (2.66(2) Å) lie in the expected range. The cyclopentadienyl rings are planar (maximum deviation from the median plane 0.015 Å). The Lu-S distance (2.709(3) and 2.723(3) Å) is comparable with the Yb-S distance in $(C_5Me_5)_2YbS_2CNEt_2$ (2.70(1) Å [4]) (ionic radii for Yb and Lu with coordination number 8: 0.985 and 0.977 Å, respectively [13]). The S(1)-Lu-S(2) angle is, of course, larger than the S-Yb-S angle in the dithiocarbamate [4].

An ORTEP plot of the crystal structure of $(C_5H_5)_2Lu(\mu\text{-}SeC_6H_5)_2Li(THF)_2$ (**8**) is shown in Fig. 2, and selected bond lengths and angles are listed in Tables 3 and 4. In contrast to the outcome for compound **7**, some of the thermal parameters (atoms C(3), C(21)) did not refine acceptably, which we assume is a consequence of the lack of an absorption correction. Although we believe that the overall molecular geometry is right, we judge the refinement not good enough to warrant a detailed discussion of bond length and angles in **8**. Our results show the coordination around lutetium also distorted tetrahedrally with Lu-Se distances of 2.80 Å and Li-Se distances of 2.6 and 2.7 Å. The dihedral angle between the planes Se-Lu-Se and Se-Li-Se is 166.5°. Both phenyl groups are on one side of the puckered $Lu(\mu\text{-}Se)_2Li$ ring, which is in contrast to the situation in **7** where the t-butyl groups are above and below the $Lu(\mu\text{-}S)_2Li$ ring.

Experimental

Because of the air and moisture sensitivity of these compounds, all syntheses were carried out with the rigorous exclusion of oxygen and water by Schlenk, high vacuum line, and glove-box (Braun, Garching, West-Germany) techniques. Argon was used exclusively and was purified by passage through a copper catalyst (BASF) to remove oxygen and P_4O_{10} supported on alumina (Merck) to remove water.

Toluene, benzene, tetrahydrofuran and their deuterated analogs were distilled from either sodium or potassium benzophenone ketyl. Diethyl ether and pentane were distilled from Na/K alloy benzophenone ketyl. C_6H_5SeH (71% yield) was prepared from LiC_6H_5 and Se in diethyl ether followed by acidification with HCl dissolved in ether [14]. $t\text{-}C_4H_9SH$ (Merck) was distilled and stored over molecular sieves, while $t\text{-}C_4H_9OH$ (Merck) was distilled from the sodium alkoxide. Anhydrous $LuCl_3$ was prepared from the oxide [15*], NH_4Cl, and concentrated HCl. NaC_5H_5 was prepared in THF from freshly distilled cyclopentadiene and cleaned sodium.

C_5Me_5H was prepared as described by Burger, Delay, and Mazenod [16]. $(C_5H_5)_2Lu(t\text{-}C_4H_9)(THF)$ (1) [3c], $(C_5H_5)_2Lu(\mu\text{-}CH_3)_2Li(THF)_2$ (2) [11], and $(C_5Me_5)_2Lu(\mu\text{-}CH_3)_2Li(THF)_2$ (4) [17], were prepared as previously described.

^1H and ^{13}C NMR spectra were recorded for samples in sealed 5 mm tubes on a Bruker WP 80 or WH 270 MHz spectrometer. Elemental analyses were performed by a Perkin–Elmer CHN-Analyzer 240. Satisfactory analyses could be obtained by using a special Schlenk tube and small aluminium cans for weighing these extremely sensitive compounds. Melting points were determined in capillaries sealed under vacuum.

tert-Butoxydicyclopentadienyllutetium-tetrahydrofuran (3). (a) A 0.40 ml (4.35 mmol) sample of $t\text{-}C_4H_9OH$ in 50 ml ether was added dropwise to a stirred solution of 1.90 g (4.38 mmol) **1** in 150 ml of ether at −78 °C. After completion of the addition, the mixture was allowed to warm to room temperature and stirred for 1 h. The solution was allowed to settle and then decanted. The solvent was removed under reduced pressure and the resultant solid was extracted with 20 ml of toluene. The pale yellow solution was decanted and cooled to −20 °C to give 1.06 g (54%) $(C_5H_5)_2Lu(O\text{-}t\text{-}C_4H_9)(THF)$ (3) as a colorless crystalline solid: m.p. 187 °C (dec); ^1H NMR (C_6D_6, 25 °C) δ 1.28 (s, 9H, $t\text{-}C_4H_9$), 1.43 (t, 4H, THF), 3.42 (t, 4H, THF), 6.39 (s, 10H, C_5H_5). Anal. Found: C, 47.92; H, 5.70. $C_{18}H_{27}LuO_2$ calcd.: C, 48.00; H, 6.04%.

(b) A 0.52 ml (5.6 mmol) sample of $t\text{-}C_4H_9OH$ in 20 ml of ether was added dropwise to a solution of 1.35 g (2.78 mmol) of **2** in 50 ml of ether at −78 °C. The addition was stopped when no further gas evolution was observed. The mixture was allowed to warm to room temperature and stirred for 1 h before being allowed to stand overnight. The solution was decanted, concentrated, and cooled to −20 °C to give 0.90 g (72%) **3** as a colorless crystalline solid: m.p. 187 °C (dec); ^1H NMR (C_6D_6, 25 °C) δ 1.29 (s, 9H, $t\text{-}C_4H_9$), 1.43 (m, 4H, THF), 3.43 (m, 4H, THF), 6.40 (s, 10H, C_5H_5). ^{13}C NMR (C_6D_6, 25 °C) δ 25.48 (THF), 34.19 (CH_3), 68.57 (THF), 69.87 (C–O), 109.51 (C_5H_5). Anal. Found: C, 48.40; H, 6.36. $C_{18}H_{27}LuO_2$ calcd.: C, 48.00; H, 6.04%.

t-Butoxybis(pentamethylcyclopentadienyl)lutetium-tetrahydrofuran (5). In an analogous manner to that described for **3** (method b), 0.262 g (3.54 mmol) of $t\text{-}C_4H_9OH$ in 15 ml of ether, and 1.118 g (1.77 mmol) of **4** in 50 ml of ether yielded 0.89 g (85%) of colorless crystals of $(C_5Me_5)_2Lu(O\text{-}t\text{-}C_4H_9)(THF)$ (5): m.p. 139 °C (dec); ^1H NMR (C_6D_6, 25 °C) δ 1.22 (s, 9H, $t\text{-}C_4H_9$), 1.73 (m, 4H, THF), 1.92 (s, 30H, C_5Me_5), 3.59 (m, 4H, THF); ^{13}C NMR (C_6D_6, 25 °C) δ 12.34 ($C_5(CH_3)_5$), 25.31 (THF), 35.36 ($C(CH_3)_3$), 72.16 ($C(CH_3)_3$), 72.69 (THF), 115.81 ($C_5(CH_3)_5$). Anal. Found: C, 56.41; H, 8.55. $C_{28}H_{47}LuO_2$ calcd.: C, 56.93; H, 8.02%.

Attempted reaction of 1 with $t\text{-}C_4H_9SH$. To a stirred solution of 1.62 g (3.73 mmol) of **1** in 125 ml of ether at −78 °C was added dropwise a solution of 0.42 ml (3.72 mmol) of $t\text{-}C_4H_9SH$ in 50 ml of ether. The mixture was allowed to warm to room temperature after completion of the addition, then was stirred for 1 h, and an aliquot then transferred by syringe to a round bottom flask equipped with a gas inlet and side arm with an attached NMR tube. The solvent was removed and C_6D_6 was added. The solution was decanted to the NMR tube which was sealed under vacuum. The NMR spectrum of the colorless solution showed only starting materials, and so the reaction mixture was refluxed for 4 h, after which the NMR spectrum showed only starting material and decomposition products.

Bis(tetrahydrofuran)lithium-di(t-butyl)dicyclopentadienyllutetate(III) (**6**). 0.53 ml (4.70 mmol) of t-C_4H_9SH in 10 ml of ether were added dropwise to a stirred solution of 1.14 g (2.34 mmol) of **2** in 30 ml of ether at −78°C. The addition was stopped when no further gas evolution was observed. The mixture was allowed to warm to room temperature and stirred for 2 h. After standing overnight, the supernatant liquid was decanted into another flask. The volume was reduced and the solution was cooled to −20°C to give 0.94 g (63%) of $(C_5H_5)_2Lu(SC_4H_9\text{-t})_2Li(THF)_2$ (**6**) as a white crystalline solid: m.p. 124°C (dec); ^1H NMR (C_6D_6, 25°C) δ 1.49 (m, 4H, THF), 1.77 (s, 9H, t-C_4H_9), 3.73 (m, 4H, THF), 6.46 (s, 5H, C_5H_5); ^{13}C NMR (C_6D_6, 25°C) δ 25.49 (THF), 38.03 ($(CH_3)_3CS$), 43.21 ($(CH_3)_3CS$), 68.57 (THF), 111.48 (C_5H_5). Anal. Found: C, 48.78; H, 7.27. $C_{26}H_{44}LiLuO_2S_2$ calcd.: C, 49.20; H, 6.99%.

Bis(tetrahydrofuran)lithium-di(t-butylthio)bis(pentamethylcyclopentadienyl)lutetate-(III) (*7*). In an analogous manner to that described for **3** (method b), 0.83 ml (7.4 mmol) of t-C_4H_9SH in 15 ml of ether, and 2.35 g (3.7 mmol) of **4** in 50 ml of ether yielded 2.94 g (92%) of colorless crystals of $(C_5Me_5)_2Lu(SC_4H_9\text{-t})_2Li(THF)_2$ (**7**): m.p. 113°C (dec); ^1H NMR (C_4D_8O, 25°C) δ 1.40 (s, 9H, t-C_4H_9), 1.72 (m, 4H, THF), 2.03 (s, 15H, C_5Me_5), 3.58 (m, 4H, THF); ^{13}C NMR (C_4D_8O, 25°C) δ 13.42 ($C_5(CH_3)_5$), 26.25 (THF), 38.86 ($C(CH_3)_3$), 44.21 ($C(CH_3)_3$), 68.13 (THF), 117.50 ($C_5(CH_3)_5$). Anal. Found: C, 56.12; H, 8.63; Li, 0.88; Lu, 22.86. $C_{36}H_{64}LiLuO_2S_2$ calcd.: C, 55.80; H, 8.32; Li, 0.90; Lu, 22.58%.

Bis(tetrahydrofuran)lithium-di(phenylseleno)dicyclopentadienyllutetate(III) (*8*). C_6H_5SeH (0.34 g, 2.16 mmol) in 10 ml of ether was added dropwise to a stirred solution of 0.52 g (1.07 mmol) of **2** in 40 ml of ether. The addition was stopped when no further gas evolution was observed. The mixture was stirred for 4 h at room temperature and then allowed to stand overnight. The colorless to pale yellow solution was decanted and the solvent was removed under reduced pressure. The residual white solid was extracted with toluene (10 ml), and the extract was cooled

Table 5

Crystal and data collection details for 7 and 8 [a]

	7	8
Formula	$C_{36}H_{64}LiLuO_2S_2$	$C_{30}H_{36}LiLuO_2Se_2$
Space group	$P2_1/n$	$P2_1/a$
a, Å	19.016(7)	21.60(3)
b, Å	17.206(6)	13.98(1)
c, Å	11.899(4)	11.43(1)
β, °	101.82(3)	120.68(7)
V, Å^3	3810.7	2967.3
ρ_{calcd}, g/cm^3	1.351	2.096
μ, cm^{-1}	25.9	
2θ limits, deg.	$3 \leq 2\theta \leq 48$	$3 \leq 2\theta \leq 45$
No of unique data	5979	3766
No of observed data	4228 ($I \geq 2\sigma(I)$)	2615 ($I \geq 3\sigma(I)$)
R	0.052	0.066
R_w	0.064	0.107
No of parameters	403	319

[a] Estimated standard deviations of the last significant digit are given in parentheses.

to −20 °C to yield 0.47 g (57%) of $(C_5H_5)_2Lu(SeC_6H_5)_2Li(THF)_2$ (**8**) as a colorless, light-sensitive, crystalline solid: m.p. 128 °C (dec); ^1H NMR (C_6D_6, 25 °C) δ 1.31 (m, 4H, THF), 3.55 (m, 4H, THF), 6.22 (s, 5H, C_5H_5), 7.11 to 7.28 (m, 3H, C_6H_5), 7.90 to 8.02 (m, 2H, C_6H_5); ^{13}C NMR (C_6D_6, 25 °C) δ 25.30 (THF), 68.81 (THF), 110.13 (C_5H_5), 124.68 (C_6H_5), 128.39 (C_6H_5), 137.02 (C_6H_5). Anal. Found: C, 44.90; H, 4.57. $C_{30}H_{36}LiLuO_2Se_2$ calcd.: C, 46.89; H, 4.72%.

Table 6

Final positional parameters for 7 (estimated standard deviations of the last significant digit are given in parantheses)

Atom	*x*	*y*	*z*
Lu	0.38082(2)	0.19393(2)	0.27505(3)
Li	0.4382(12)	0.3112(12)	0.020(2)
S(1)	0.4400(2)	0.3288(2)	0.2213(2)
C(1)	0.4956(6)	0.4069(7)	0.3014(11)
C(2)	0.5659(7)	0.4133(9)	0.2569(15)
C(3)	0.4547(8)	0.4845(7)	0.2760(12)
C(4)	0.5101(7)	0.3925(8)	0.4308(10)
S(2)	0.3638(2)	0.1961(2)	0.0422(2)
C(5)	0.3393(8)	0.1252(7)	−0.0778(10)
C(6)	0.3312(10)	0.0426(7)	−0.0288(12)
C(7)	0.2670(8)	0.1536(9)	−0.1548(11)
C(8)	0.3985(8)	0.1241(8)	−0.1469(11)
C(10)	0.2892(6)	0.2874(6)	0.3511(9)
C(11)	0.2903(6)	0.2188(7)	0.4168(10)
C(12)	0.2598(6)	0.1580(6)	0.3405(9)
C(13)	0.2402(6)	0.1923(7)	0.2282(9)
C(14)	0.2574(5)	0.2708(6)	0.2365(9)
C(15)	0.3096(7)	0.3662(7)	0.4055(12)
C(16)	0.3089(7)	0.2135(9)	0.5475(10)
C(17)	0.2360(7)	0.0785(8)	0.3731(13)
C(18)	0.1951(6)	0.1515(7)	0.1261(11)
C(19)	0.2403(6)	0.3300(7)	0.1397(11)
C(20)	0.4331(6)	0.0522(6)	0.3156(10)
C(21)	0.4864(6)	0.0939(7)	0.2706(10)
C(22)	0.5168(6)	0.1496(7)	0.3533(10)
C(23)	0.4819(6)	0.1434(7)	0.4469(9)
C(24)	0.4316(6)	0.0815(7)	0.4250(9)
C(25)	0.3927(7)	−0.0210(7)	0.2658(11)
C(26)	0.5147(8)	0.0716(8)	0.1654(11)
C(27)	0.5837(6)	0.1985(8)	0.3503(12)
C(28)	0.5040(8)	0.1890(8)	0.5620(10)
C(29)	0.4004(7)	0.0396(8)	0.5165(11)
O(1)	0.3876(4)	0.3868(4)	−0.0892(6)
C(30)	0.3450(8)	0.4459(7)	−0.0526(11)
C(31)	0.2709(10)	0.4397(11)	−0.1344(15)
C(32)	0.2798(12)	0.3928(15)	−0.2290(20)
C(33)	0.3577(8)	0.3663(9)	−0.2062(12)
O(2)	0.5288(5)	0.2981(5)	−0.0299(8)
C(40)	0.5460(10)	0.3056(14)	−0.1390(20)
C(41)	0.5908(10)	0.2290(10)	−0.1460(15)
C(42)	0.6176(9)	0.2009(10)	−0.0244(15)
C(43)	0.5915(10)	0.2645(13)	0.0416(15)

Crystal structures of 7 and 8. Single crystals of both **7** [18*] and **8** are very sensitive to moisture and air. They were mounted in the nitrogen beam of a Syntex $P2_1$ automatic diffractometer without placing them in capillaries by use of a procedure similar to that reported by Veith and Bärninghausen [19,20]. Standard search (Mo-K_α radiation, T −105(3)° C) and indexing procedures lead to primitive monoclinic unit cells (Table 5) for both compounds. All intensities ($0 \rightarrow h$, $0 \rightarrow k$, $-l \rightarrow l$) in the 2θ range (see Table 5) were collected. The raw data were corrected for Lorentz and polarization effects. None of the two data sets required a decay correction (2 intensity standards were monitored after each 200 intensity measurements). An empirical absorption correction (6ψ scans) was applied to the data set of **7**. Attempts to collect ψ-scans for **8** failed due to loss of the crystal.

Table 7

Fractional coordinates and isotropic thermal parameters for **8** (estimated standard deviations of the last significant digit are in parantheses)

atom	x	y	z	B_{iso} (Å^2)
Lu	0.51218(5)	0.38903(7)	0.25734(9)	1.63
Se(1)	0.5404(8)	0.2514(9)	0.1128(9)	2.57
Se(2)	0.4856(8)	0.2551(9)	0.4088(9)	2.60
Li	0.4931(17)	0.1346(25)	0.2350(36)	3.81
C(1)	0.6412(11)	0.2279(13)	0.2119(18)	2.44
C(2)	0.6881(11)	0.2750(15)	0.1824(17)	2.71
C(3)	0.7603(10)	0.2561(16)	0.2506(19)	2.91
C(4)	0.7904(10)	0.1910(16)	0.2596(17)	2.86
C(5)	0.7464(11)	0.1441(15)	0.3887(19)	2.97
C(6)	0.6725(11)	0.0156(15)	0.3183(20)	3.07
C(7)	0.0570(10)	0.0234(12)	0.5901(18)	2.18
C(8)	0.6351(11)	0.2195(15)	0.6121(21)	3.28
C(9)	0.6954(13)	0.1990(17)	0.7487(22)	4.61
C(10)	0.6803(16)	0.2103(19)	0.8539(22)	5.34
C(11)	0.6100(14)	0.2256(17)	0.8280(18)	4.37
C(12)	0.5566(12)	0.2396(15)	0.7001(17)	3.45
C(21)	0.3986(10)	0.3859(15)	0.0142(18)	2.87
C(22)	0.3755(10)	0.3524(15)	0.1035(20)	3.05
C(23)	0.3783(10)	0.4239(15)	0.1885(18)	2.89
C(24)	0.4058(11)	0.5085(15)	0.1546(18)	3.15
C(25)	0.4184(11)	0.4863(16)	0.0469(21)	3.95
C(26)	0.5747(11)	0.5281(16)	0.4235(18)	3.02
C(27)	0.5843(11)	0.5462(14)	0.3078(20)	2.77
C(28)	0.6321(11)	0.4780(15)	0.3172(16)	2.63
C(29)	0.6512(10)	0.4127(15)	0.4255(18)	2.96
C(30)	0.6164(10)	0.4482(13)	0.4934(17)	2.55
O(1)	0.4613(8)	−0.0210(11)	−0.3122(13)	3.72
C(31)	0.4291(15)	0.0207(17)	−0.4492(21)	4.46
C(32)	0.3639(15)	0.0631(22)	−0.4755(24)	6.29
C(33)	0.3781(17)	0.1003(23)	−0.3393(26)	7.08
C(34)	0.4495(14)	0.0452(17)	−0.2321(24)	4.94
O(2)	0.8922(7)	0.3969(12)	0.1085(13)	3.81
C(35)	0.8547(11)	0.4531(15)	0.1581(20)	4.17
C(36)	0.7823(12)	0.4628(18)	0.0466(24)	4.68
C(37)	0.7931(14)	0.4639(20)	−0.0770(25)	5.39
C(38)	0.8567(13)	0.4053(26)	−0.0369(21)	7.15

The structure solution for both compounds was straightforward. Space group assignments were uniquely defined by systematic absences. The lutetium position in both structures was determined from a three dimensional Patterson map and refined by least-squares methods. Subsequent Fourier maps revealed the positions of all non-hydrogen atoms. Those atoms were refined in steps by using first isotropic and then anisotropic thermal parameters. Hydrogen atoms were introduced at calculated positions (d(C–H) 0.95 Å [21]) and are unrefined.

Scattering factors were taken from the tabulations of Cromer and Mann [22]. All structure factors were corrected for the real and imaginary components of anomalous dispersion [23]. All calculations were carried out with the SHELX [24] system of programs. For additional crystal and data collection details see Table 5.

The structure of **7** (Tables 1, 2, 6, Fig. 1) refined nicely to a conventional *R*-value of 0.052. The *R* value for the refinement of **8** (Table 7) is 0.066. However, some of the thermal parameters (atoms C(3), C(21), Fig. 2) did not refine acceptably, and we assume this is due to the lack of absorption correction.

Acknowledgement

We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for generous support as well as the Technische Universität Berlin for a scholarship in connection with the TU Berlin/M.I.T. partnership program (M.G.).

References

1 H. Schumann, E. Palamidis, J. Loebel and J. Pickardt, Organometallics, 7 (1988) 1008.

2 For recent reviews see: (a) H. Schumann, Angew. Chem. 96 (1984) 475; Angew. Chem., Int. Ed. Engl. 23 (1984) 484; (b) H. Schumann and W. Genthe, in K.A. Gschneidner and L. Eyring, (Eds.), Handbook on the Physics and Chemistry of the Rare Earths, Elsevier, Amsterdam, 1984; Vol. 7, Chapter 53; (c) H. Schumann in T.J. Marks and I.L. Fragala (Eds.), Fundamental and Technological Aspects of Organo-*f*-Element Chemistry, D. Reidel, Dordrecht, 1985; p. 1–48.

3 (a) R.E. Magin, S.M. Manastyrskyj and M. Dubeck, J. Am. Chem. Soc., 85 (1963) 672; (b) P.L. Watson, ibid., 104 (1982) 337; (c) H. Schumann, W. Genthe, N. Bruncks and J. Pickardt, Organometallics, 1 (1982) 1194; (d) W.J. Evans, T.P. Hanusa and K.R. Levan, Inorg. Chim. Acta, 110 (1985) 191; (e) W.J. Evans and M.S. Sollberger, J. Am. Chem. Soc., 108 (1986) 6095.

4 T.D. Tilley, R.A. Andersen, A. Zalkin and D.H. Templeton, Inorg. Chem., 21 (1982) 2644.

5 Dicyclopentadienylytterbium(II) compounds react with selenium with formation of ytterbium-selenium bonds. R.A. Andersen, personal communication.

6 (a) H. Schumann and H. Jarosch, Z. Anorg. Allg. Chem., 426 (1976) 127; (b) G. Bielang and R.D. Fischer, J. Organomet. Chem., 161 (1978) 335; (c) H. Schumann and G.M. Frisch, Z. Naturforsch. B, 36 (1981) 1244; (d) W.J. Evans, I. Bloom, W.E. Hunter and J.L. Atwood, Organometallics, 2 (1983) 709; (e) H. Schumann, E. Palamidis, G. Schmid and R. Boese, Angew. Chem., 98 (1986) 726; Angew. Chem., Int. Ed. Engl., 25 (1986) 718.

7 H. Schumann, S. Nickel, E. Hahn and M.J. Heeg, Organometallics, 4 (1985) 800.

8 H. Schumann and M. Cygon, J. Organomet. Chem., 144 (1978) C43.

9 H. Schumann, I. Albrecht and E. Hahn, Angew. Chem., 97 (1985) 991; Angew. Chem., Int. Ed. Engl., 24 (1985) 985.

10 P.L. Watson. J.F. Whitney and R.L. Harlow. Inorg. Chem., 20 (1981) 3271.

11 H. Schumann, H. Lauke, E. Hahn, M.J. Heeg and D. van der Helm, Organometallics, 4 (1985) 321.

12 H. Schumann, F.W. Reier and E. Hahn, Z. Naturforsch. B, 40 (1985) 1289.

13 R.D. Shannon, Acta Crystallogr. A, 32 (1976) 75.

14 D.L. Klayman, Selenols and their Derivatives. In D.L. Klayman and W.H.H. Günther (Eds.), Organic Selenium Compounds: their Chemistry and Biology, J. Wiley, Sons, New York, 1973, p. 77–78.

15 We thank Prof. Dr. H.G. von Schnering, Max-Planck Institut für Festkörperchemie, Stuttgart, for a valuable gift of Lu_2O_3.

16 U. Burger, A. Delay and F. Mazenod, Helv. Chim. Acta, 57 (1974) 2106.

17 H. Schumann, I. Albrecht, J. Loebel, E. Hahn, M.B. Hossain and D. van der Helm, Organometallics, 5 (1986) 1296.

18 The structure of 7 has been briefly described previously [9]. Details of both crystal structure determinations have been deposited with the Fachinformationszentrum Energie, Physik, Mathematik, D 5714 Eggenstein-Leopoldshafen 2 and can be obtained by quoting the Journal, Authors and file number CSD 51477.

19 M. Veith and H. Bärninghausen, Acta Cryst. B, 30 (1974) 1806.

20 H. Schumann, W. Genthe, E. Hahn, M.B. Hossain and D. van der Helm, J. Organomet. Chem., 299 (1986) 67.

21 M.R. Churchill, Inorg. Chem., 12 (1973) 1213.

22 D.T. Cromer and J.B. Mann, Acta Cryst. A, 24 (1968) 321.

23 D.T. Cromer and D.J. Liberman, Chem. Phys., 53 (1970) 1891.

24 G.M. Sheldrick, SHELX-76 System of Programs, 1976.