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Synthesis and structure of organotin complexes of ytterbium

Leonid N. Bochkarev, Oleg V. Grachev, Sergey F. Ziltsov
Nizhny Novgorod State Pedagogical Institute, Nizhny Novgorod (Russia)

Lev N. Zakharov
Institute of Organometallic Chemistry, Russia Academy of Sciences, Nizhny Novgorod (Russia)

Yury T. Struchkov
A.N. Nesmeyanov Institute of Organoelement Compounds, Russia Academy of Sciences, Moscow (Russia)

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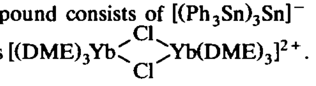
Abstract

Reactions of Ph_3SnCl, $PhSnCl_3$ and $Ph_3SnSnPh_3$ with ytterbium in THF lead to the formation of the complex $(Ph_3Sn)_2Yb(THF)_4$ (1) * in high yields. According to X-ray data, tin atoms in complex 1 are covalently bonded with the ytterbium atom. Ionic organotin complex of ytterbium $[(Ph_3Sn)_3Sn]_2^-[Yb_2Cl_2(DME)_6]^{2+}$ (2) was synthesised in 75% yield by the reaction of Ph_2SnCl_2 with ytterbium. According to X-ray analysis, the compound consists of $[(Ph_3Sn)_3Sn]^-$ anions and dimeric ytterbium cations with μ_2-bridged chlorine atoms



$[(DME)_3Yb{<}\overset{Cl}{\underset{Cl}{\quad}}{>}Yb(DME)_3]^{2+}$.

Introduction

It is known that alkyl- and aryliodides react readily with samarium, europium and ytterbium to give Grignard-type derivatives RLnI [2,3,4]. Reactivity of such compounds is investigated [2,5–8].

Reactions of metallic lanthanoids with organosilicon, -germanium and -tin halides, *i.e.* halides of elements/analogs of carbon are investigated to a lesser extent.

Previously we have found [9] that metallic europium and ytterbium react without any activation with organotin iodides R_3SnI (R = Bu, Ph) to form Grignard-like compounds R_3SnLnI (Ln = Eu, Yb). Yields of such complexes, depending on the lanthanoide and the organotin iodide, are 5–20%. Other products of the reactions are distannane R_3SnSnR_3 and LnI_2. It is assumed that the complex

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Correspondence to: Dr. L.N. Bochkarev.

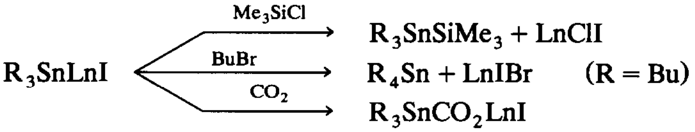
* Complex 1 has recently been obtained by a different method and structurally characterized [1].

R_3SnLnI, which forms in the initial stages of the reaction, reacts immediately owing to its high reactivity with starting R_3SnI to give R_3SnSnR_3 and LnI_2:

$$R_3SnI + Ln \xrightarrow[-40 \text{ to } +20^{\circ}C]{THF} R_3SnLnI$$

$$R_3SnLnI + R_3SnI \longrightarrow R_3SnSnR_3 + LnI_2$$

The complexes R_3SnLnI were not isolated from the reaction solution; their formation and yields were established by the following reactions with Me_3SiCl, BuBr and CO_2:



$$R_3SnLnI \begin{cases} \xrightarrow{Me_3SiCl} R_3SnSiMe_3 + LnClI \\ \xrightarrow{BuBr} R_4Sn + LnIBr \qquad (R = Bu) \\ \xrightarrow{CO_2} R_3SnCO_2LnI \end{cases}$$

It was found that organotin chlorides, Bu_3SnCl and Ph_3SnCl, do not react in similar conditions with ytterbium, while the reaction of Bu_3SnI with praseodymium yields $Bu_3SnSnBu_3$ and PrI_3 only [9].

Results and discussion

Continuing our investigation of the reactions of organotin halides with lanthanoids, we have found that triphenyltin chloride reacts in THF solution at room temperature with ytterbium activated by $HgBr_2$ or CH_2I_2 (1–2% mass). The interaction proceeds for 40 h and completes the formation of complex **1**.

$$2Ph_3SnCl + 2Yb \xrightarrow[20^{\circ}C]{THF} (Ph_3Sn)_2Yb(THF)_4 + YbCl_2(THF)_2$$

In the initial stages of the reaction during the first 12 h of intensive stirring of the reagents as has been established by special experiments, hexaphenyldistannane and $YbCl_2(THF)_2$ are formed in nearly quantitative yields. In the following stages (*ca.* 30 h), $Ph_3SnSnPh_3$ reacts with an excess of ytterbium and finally gives complex **1**, which has been isolated in 80% yield. The course of the reaction as well as the other reactions with metallic ytterbium was controlled by the amount of metal entering into the interaction. The ytterbium dichloride formed during the initial stages of the reaction probably acts as a catalyst in the following interaction of $Ph_3SnSnPh_3$ with ytterbium. To confirm this we carried out the reaction of $Ph_3SnSnPh_3$ with Yb in the absence of $YbCl_2(THF)_2$. In this case $Ph_3SnSnPh_3$ reacts with Yb more slowly and after 40 h only 35% of the ytterbium enter into the reaction; to complete the process, it is necessary to stir the reagents for 200 h after which *ca.* 100% of the ytterbium enters into the reaction. Complex **1** can then be isolated in 75% yield.

Thus, the general scheme of the reaction of Ph_3SnCl with Yb can be described as follows:

$$Ph_3SnCl + Yb \xrightarrow[20^{\circ}C]{THF} Ph_3SnYbCl$$

$$Ph_3SnYbCl + Ph_3SnCl \xrightarrow[20^{\circ}C]{THF} Ph_3SnSnPh_3 + YbCl_2(THF)_2$$

$$Ph_3SnSnPh_3 + Yb \xrightarrow[20^{\circ}C]{THF,\ YbCl_2(THF)_2} (Ph_3Sn)_2Yb(THF)_4$$

The first step of the interaction of Ph_3SnCl with ytterbium, as in the reactions of organotin iodides with Yb [9], is probably the formation of the Grignard-like complex $Ph_3SnYbCl$, which reacts immediately owing to its high reactivity with starting Ph_3SnCl to give hexaphenyldistannane and ytterbium dichloride.

Complex **1** has been isolated as a light-yellow crystalline diamagnetic substance, unstable in air and melting with decomposition on heating to 135–138°C. The compound is readily soluble in THF, benzene, poorly soluble in ether and insoluble in hexane. The IR spectrum of **1** shows the absorption bands (1420 (doublet), 1065 (doublet), 725, 695, 450 (doublet) cm^{-1}) of Ph_3Sn groups and absorption bands of coordinated THF (1025, 865 cm^{-1}).

Reaction of phenyltin trichloride with ytterbium unexpectedly also led to the formation of complex **1**. Interaction in this case probably proceeds through several consecutive stages also. On the basis of the final products, the general equation can be presented as follows:

$$6PhSnCl_3 + 10Yb \xrightarrow[20^\circ C]{THF} (Ph_3Sn)_2Yb(THF)_4 + 9YbCl_2(THF)_2 + 4Sn$$

The interaction between $PhSnCl_3$ and Yb starts at −40°C, but to complete the reaction it is necessary to stir the reagents for *ca.* 30 h at room temperature. Complex **1** has been isolated from this reaction in 65% yield.

X-Ray investigation confirmed that the product of these reactions is complex **1**, the structure of which has been established recently [1]. The molecule of **1** is a distorted octahedral complex of ytterbium with four oxygen atoms of THF molecules in equatorial positions and two tin atoms of Ph_3Sn groups in the axial positions.

The study of the reaction of diphenyltin dichloride with ytterbium has shown that the interaction proceeds at room temperature and is complete after 12 h with the formation of the ionic organotin complex of ytterbium $[(Ph_3Sn)_3Sn]_2^-[Yb_2Cl_2(DME)_6]^{2+}$ (**2**) [10]:

$$9Ph_2SnCl_2 + 10Yb \xrightarrow[20^\circ C]{THF} [(Ph_3Sn)_3Sn]_2Yb_2Cl_2(THF)_x + 8YbCl_2(THF)_2 + Sn$$

The organotin complex of ytterbium, after its separation from the other products of the reaction and crystallization from 1,2-dimethoxyethane (DME), has been isolated in 75% yield as yellow–brown diamagnetic crystals, unstable in air. Compound **2** is poorly soluble in DME and insoluble in benzene and hexane, and melts with decomposition on heating to 125–130°C. The IR spectrum shows the absorption bands (1425 (doublet), 1065 (doublet), 725, 695, 450 (doublet) cm^{-1}) characteristic of Ph_3Sn groups and absorption bands of coordinated DME (1060, 860 cm^{-1}).

X-Ray investigation has shown that crystals of **2** have an ionic structure, consisting of $[Yb(DME)_3Cl]_2^{2+}$ cations and $[(Ph_3Sn)_3Sn]^-$ anions.

Cation $[Yb(DME)_3Cl]_2^{2+}$ is a centrisymmetrical dimer in which two Yb atoms are each bonded to three chelate DME molecules and related by two μ_2-bridged chlorine atoms (Fig. 1). The dihedral angle between the middle plane of the chelate cycle O(5), C(10), C(11), O(6) of one DME molecule and the plane of the four-membered Yb_2Cl_2 cycle is 25°, whereas the analogous angles for two other DME molecules are 85 and 85°, *i.e.* these are almost perpendicular to the plane of the Yb_2Cl_2 cycle. Thus, the coordination number of the Yb atoms is eight. The

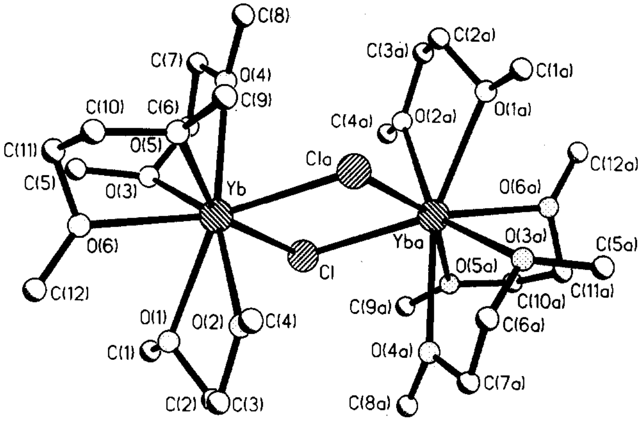


Fig. 1. The structure of the $[Yb(DME)_3Cl]_2^{2+}$ cation.

Yb–Cl (2.769(4) Å) and Yb–Cl(a) (2.772(4) Å) bond lengths are practically identical (Fig. 1) and significantly longer than the bridging Yb–Cl bond lengths in neutral complexes $[(C_5H_4Me)_2YbCl]_2$ 2.64 Å [11] and $[\{(C_5H_3(SiMe_3)\}_2YbCl]_2$ 2.65 Å [12]]. The ClYbCl(a) and YbClYb(a) bond angles in the four-membered Yb_2Cl_2 cycle are 79.0 and 101.0°, respectively. The Yb–O bond lengths are close to each other (Yb–O(3) 2.57(1) Å, Yb–O(4) 2.60 Å) for only one DME molecule, while for two other DME molecules these distances are significantly different (Yb–O(1) 2.57(2) Å, Yb–O(2) 2.48(1) Å and Yb–O(5) 2.70(1) Å, Yb–O(6) 2.53(1) Å). The Yb–O(DME) distances in the complexes **2** are longer than the Yb–O distances in $Cp_2Yb(DME)$ (2.50 and 2.45 Å) [13].

The unusual anion $[(Ph_3Sn)_3Sn]^-$ has a pyramidal structure: the central Sn atom is bonded to three Ph_3Sn groups by the Sn–Sn bonds (Fig. 2). The Sn–Sn–Sn bond angles are 93.8(1), 98.6(1) and 97.8(1)° (Table 2). The Sn(1)–Sn(2,3,4) bond lengths (2.827(2), 2.818(1), 2.823(1) Å, respectively) are somewhat longer than the sum of the covalent radii of the Sn atoms (2.80 Å by Pauling) [14]. The Sn–C bond lengths range from 2.15(2) to 2.19(1) Å (average 2.17(2) Å) and are close to the sum of the covalent radii of the Sn and $C(sp^2)$ atoms (2.14 Å) [14]. Coordination of the Sn(2,3,4) atoms is noticeably distorted from the ideal tetrahedral. For example, the Sn(1)–Sn(2,3,4)–C(Ph) bond angles are in the wide interval 100.7(7)–131.2(4)° (Table 2).

The disposition of ions in the crystal structure **2** is shown in Fig. 3. Two $[(Ph_3Sn)_3Sn]^-$ anions are situated in the crystal at both sides of the $[Yb(DME)_3Cl]_2^{2+}$ cation in such a way that the angle between the Yb---Sn(1) line and normal to the plane of the four-membered Yb_2Cl_2 cycle is 17.7°. The angle between the Sn(1)–Sn(3) line and normal to this plane is 16.8°.

The shortest intermolecular Sn...C distances in the structure are 4.089 Å (Sn(1)...C(3)) and 4.316 Å (Sn(1)...C(2)), while the Yb...Sn(1) distance is 7.423 Å.

Complex **2** is the first structurally characterized organotin derivative of a lanthanoide having an ionic composition.

Table 1

Bond lengths in structure **2** (Å)

Yb-Cl	2.769(4)	O(6)-C(12)	1.40(3)	C(37)-C(42)	1.38(3)
Yb-Cl'	2.772(4)	C(2)-C(3)	1.50(3)	C(38)-C(39)	1.38(3)
Yb-O(1)	2.57(2)	C(6)-C(7)	1.49(4)	C(39)-C(40)	1.36(3)
Yb-O(2)	2.48(1)	C(10)-C(11)	1.50(3)	C(40)-C(41)	1.35(4)
Yb-O(3)	2.57(1)	C(13)-C(14)	1.37(3)	C(41)-C(42)	1.36(3)
Yb-O(4)	2.60(2)	C(13)-C(18)	1.44(3)	C(43)-C(44)	1.35(2)
Yb-O(5)	2.70(1)	C(14)-C(15)	1.41(3)	C(43)-C(48)	1.39(3)
Yb-O(6)	2.53(1)	C(15)-C(16)	1.37(3)	C(44)-C(45)	1.42(3)
Sn(1)-Sn(2)	2.827(2)	C(16)-C(17)	1.35(3)	C(45)-C(46)	1.36(4)
Sn(1)-Sn(3)	2.818(1)	C(17)-C(18)	1.40(3)	C(46)-C(47)	1.36(3)
Sn(1)-Sn(4)	2.823(1)	C(19)-C(20)	1.46(3)	C(47)-C(48)	1.37(4)
Sn(2)-C(13)	2.16(2)	C(19)-C(24)	1.36(2)	C(49)-C(50)	1.35(3)
Sn(2)-C(19)	2.18(2)	C(20)-C(21)	1.41(3)	C(49)-C(54)	1.40(2)
Sn(2)-C(25)	2.17(2)	C(21)-C(22)	1.42(3)	C(50)-C(51)	1.39(3)
Sn(3)-C(31)	2.19(1)	C(22)-C(23)	1.33(3)	C(51)-C(52)	1.32(3)
Sn(3)-C(37)	2.15(2)	C(23)-C(24)	1.37(2)	C(52)-C(53)	1.38(4)
Sn(3)-C(43)	2.17(2)	C(25)-C(26)	1.38(2)	C(53)-C(54)	1.41(3)
Sn(4)-C(49)	2.17(2)	C(25)-C(30)	1.40(3)	C(55)-C(56)	1.38(2)
Sn(4)-C(55)	2.16(2)	C(26)-C(27)	1.38(3)	C(55)-C(60)	1.37(3)
Sn(4)-C(61)	2.16(2)	C(27)-C(28)	1.37(3)	C(56)-C(57)	1.36(3)
O(1)-C(1)	1.43(3)	C(28)-C(29)	1.37(2)	C(57)-C(58)	1.37(4)
O(1)-C(2)	1.42(2)	C(29)-C(30)	1.40(3)	C(58)-C(59)	1.34(3)
O(2)-C(3)	1.44(3)	C(31)-C(32)	1.42(3)	C(59)-C(60)	1.41(3)
O(2)-C(4)	1.43(2)	C(31)-C(36)	1.37(3)	C(61)-C(62)	1.37(2)
O(3)-C(5)	1.44(2)	C(32)-C(33)	1.42(3)	C(61)-C(66)	1.42(3)
O(3)-C(6)	1.44(3)	C(33)-C(34)	1.35(3)	C(62)-C(63)	1.40(2)
O(4)-C(7)	1.39(3)	C(34)-C(35)	1.39(3)	C(63)-C(64)	1.39(3)
O(4)-C(8)	1.45(3)	C(35)-C(36)	1.38(2)	C(64)-C(65)	1.39(3)
O(5)-C(9)	1.44(3)	C(37)-C(38)	1.39(3)	C(65)-C(66)	1.37(2)
O(5)-C(10)	1.42(2)				
O(6)-C(11)	1.42(3)				

Metallic samarium, europium, praseodymium, gadolinium, erbium and lutecium also react under similar conditions with organotin chlorides R_nSnCl_{4-n} (n = 1, 2, 3). These reactions are under investigation.

Experimental

All operations were performed under vacuum in sealed ampules. Solvents were thoroughly dried and distilled from sodium/benzophenone solution. The IR spectra were recorded on a Perkin-Elmer 577 spectrometer. Samples of the solids were prepared in the form of a suspension in Vaseline oil under dry argon.

X-Ray experiments were carried out with a Siemens R3/PC diffractometer at 193 K (λ Mo-K_α; θ–2θ scan in the range $2° \leq 2\theta \leq 54°$, 9293 reflections with $F > 4\sigma(F)$). The crystals of **2** are triclinic, $a = 11.427(2)$, $b = 15.861(3)$, $c = 19.126(4)$ Å, $\alpha = 75.40(2)$, $\beta = 75.30(2)$, $\gamma = 86.61(2)°$, $D_c = 1.686$ g cm^{-3}, $Z = 2$, space group $P\bar{1}$. The positions of the Yb and Sn atoms were located by direct methods; the positions of other non-hydrogen atoms were obtained on subsequent electron density synthesis. The structure was refined by the full-matrix least

Table 2

Bond angles (deg) in structure **2**

Yb–Cl–Yb′	79.0(1)	C(15)–C(14)–C(13)	120.7(20)
O(1)–Yb–Cl	75.7(3)	C(16)–C(15)–C(14)	120.8(21)
O(2)–Yb–Cl	98.4(3)	C(17)–C(16)–C(15)	120.6(18)
O(2)–Yb–O(1)	64.1(4)	C(18)–C(17)–C(16)	119.6(18)
O(3)–Yb–Cl	79.0(3)	C(17)–C(18)–C(13)	121.3(18)
O(3)–Yb–O(1)	82.1(5)	C(20)–C(19)–Sn(2)	117.8(12)
O(3)–Yb–O(2)	145.4(5)	C(24)–C(19)–Sn(2)	122.9(14)
O(4)–Yb–Cl	92.0(3)	C(24)–C(19)–C(20)	119.2(15)
O(4)–Yb–O(1)	144.1(4)	C(21)–C(20)–C(19)	117.7(17)
O(4)–Yb–O(2)	151.7(5)	C(22)–C(21)–C(20)	119.4(20)
O(4)–Yb–O(3)	62.4(5)	C(23)–C(22)–C(21)	119.9(17)
O(5)–Yb–Cl	153.8(3)	C(24)–C(23)–C(22)	122.4(20)
O(5)–Yb–O(1)	127.5(4)	C(23)–C(24)–C(19)	121.1(18)
O(5)–Yb–O(2)	84.4(4)	C(26)–C(25)–Sn(2)	120.4(14)
O(5)–Yb–O(3)	113.1(4)	C(30)–C(25)–Sn(2)	121.9(12)
O(5)–Yb–O(4)	75.1(4)	C(30)–C(25)–C(26)	117.6(18)
O(6)–Yb–Cl	142.9(4)	C(27)–C(26)–C(25)	120.9(18)
O(6)–Yb–O(1)	73.0(4)	C(28)–C(28)–C(26)	121.4(16)
O(6)–Yb–O(2)	85.3(4)	C(29)–C(28)–C(27)	118.7(21)
O(6)–Yb–O(3)	77.5(4)	C(30)–C(29)–C(28)	120.7(19)
O(6)–Yb–O(4)	102.0(5)	C(29)–C(30)–C(25)	120.6(15)
O(6)–Yb–O(5)	63.1(5)	C(32)–C(31)–Sn(3)	119.5(12)
Sn(3)–Sn(1)–Sn(2)	93.8(1)	C(36)–C(31)–Sn(3)	120.6(12)
Sn(4)–Sn(1)–Sn(2)	98.6(1)	C(36)–C(31)–C(32)	119.3(14)
Sn(4)–Sn(1)–Sn(3)	97.8(1)	C(33)–C(32)–C(31)	117.2(18)
C(13)–Sn(2)–Sn(1)	110.0(5)	C(34)–C(33)–C(32)	121.7(21)
C(19)–Sn(2)–Sn(1)	112.6(5)	C(35)–C(34)–C(33)	120.8(18)
C(19)–Sn(2)–C(13)	102.5(6)	C(36)–C(35)–C(34)	118.3(19)
C(25)–Sn(2)–Sn(1)	124.3(4)	C(35)–C(36)–C(31)	122.4(19)
C(25)–Sn(2)–C(13)	100.7(7)	C(38)–C(37)–Sn(3)	122.1(12)
C(25)–Sn(2)–C(19)	104.2(7)	C(42)–C(37)–Sn(3)	122.6(13)
C(31)–Sn(3)–Sn(1)	105.7(4)	C(42)–C(37)–C(38)	115.2(17)
C(37)–Sn(3)–Sn(1)	108.5(5)	C(39)–C(38)–C(37)	121.0(18)
C(37)–Sn(3)–C(31)	103.8(6)	C(40)–C(39)–C(38)	121.4(24)
C(43)–Sn(3)–Sn(1)	131.2(4)	C(41)–C(40)–C(39)	118.5(22)
C(43)–Sn(3)–C(31)	101.9(6)	C(42)–C(41)–C(40)	120.5(21)
C(43)–Sn(3)–C(37)	102.8(6)	C(41)–C(42)–C(37)	123.3(20)
C(49)–Sn(4)–Sn(1)	110.9(4)	C(44)–C(43)–Sn(3)	121.2(15)
C(55)–Sn(4)–Sn(1)	126.3(4)	C(48)–C(43)–Sn(3)	120.6(11)
C(55)–Sn(4)–C(49)	101.0(6)	C(48)–C(43)–C(44)	118.2(18)
C(61)–Sn(4)–Sn(1)	108.2(4)	C(45)–C(44)–C(43)	121.4(21)
C(61)–Sn(4)–C(49)	102.1(6)	C(46)–C(45)–C(44)	119.1(18)
C(61)–Sn(4)–C(55)	105.7(6)	C(47)–C(46)–C(45)	119.5(25)
C(1)–O(1)–Yb	122.9(14)	C(48)–C(47)–C(46)	121.4(27)
C(2)–O(1)–Yb	110.8(12)	C(47)–C(48)–C(43)	120.3(18)
C(2)–O(1)–C(1)	110.9(16)	C(50)–C(49)–Sn(4)	123.8(11)
C(3)–O(2)–Yb	122.2(11)	C(54)–C(49)–Sn(4)	119.9(14)
C(4)–O(2)–Yb	123.5(13)	C(54)–C(49)–C(50)	116.1(16)
C(4)–O(2)–C(3)	110.2(17)	C(51)–C(50)–C(49)	124.7(18)
C(5)–O(3)–Yb	130.0(11)	C(52)–C(51)–C(50)	118.8(25)
C(6)–O(3)–Yb	109.3(11)	C(53)–C(52)–C(51)	120.6(21)
C(6)–O(3)–C(5)	112.6(15)	C(54)–C(53)–C(52)	120.1(20)
C(7)–O(4)–Yb	120.5(15)	C(53)–C(54)–C(49)	119.7(21)
C(8)–O(4)–Yb	126.0(12)	C(56)–C(55)–Sn(4)	119.5(14)

Table 2 (continued)

C(8)–O(4)–C(7)	111.5(17)	C(60)–C(55)–Sn(4)	123.2(13)
C(9)–O(5)–Yb	132.8(10)	C(60)–C(55)–C(56)	117.2(18)
C(10)–O(5)–Yb	115.0(13)	C(57)–C(56)–C(55)	121.0(20)
C(10)–O(5)–C(9)	110.7(15)	C(58)–C(57)–C(56)	120.9(19)
C(11)–O(6)–Yb	108.7(12)	C(59)–C(58)–C(57)	119.8(22)
C(12)–O(6)–Yb	130.4(12)	C(60)–C(59)–C(58)	119.2(20)
C(12)–O(6)–C(11)	114.6(15)	C(59)–C(60)–C(55)	121.9(17)
C(3)–C(2)–O(1)	110.1(15)	C(62)–C(61)–Sn(4)	122.2(13)
C(2)–C(3)–O(2)	107.4(19)	C(66)–C(61)–Sn(4)	120.1(11)
C(7)–C(6)–O(3)	109.0(16)	C(66)–C(61)–C(62)	117.6(15)
C(6)–C(7)–O(4)	107.8(19)	C(63)–C(62)–C(61)	122.8(17)
C(11)–C(10)–O(5)	107.9(15)	C(64)–C(63)–C(62)	118.5(17)
C(10)–C(11)–O(6)	107.8(16)	C(65)–C(64)–C(63)	119.8(17)
C(14)–C(13)–Sn(2)	121.5(14)	C(66)–C(65)–C(64)	120.8(18)
C(18)–C(13)–Sn(2)	121.2(14)	C(65)–C(66)–C(61)	120.5(16)
C(18)–C(13)–C(14)	117.0(16)		

squares method with anisotropic thermal parameters for all non-hydrogen atoms. In refinement, the following weighting scheme $w = 1/\sigma^2(F)$ was used. Hydrogen atoms participated in the refinement of the structure with fixed isotropic thermal parameters (adopted B_{iso} 0.08 Å^2) in positions calculated from the geometrical conditions. The final discrepancy factors were $R = 0.050$, $R_w = 0.060$. Bond lengths and angles are given in Tables 1 and 2, respectively, atomic coordinates in Table 3 and the anisotropic thermal parameters in Table 4. All calculations were performed with the SHELX PLUS programs.

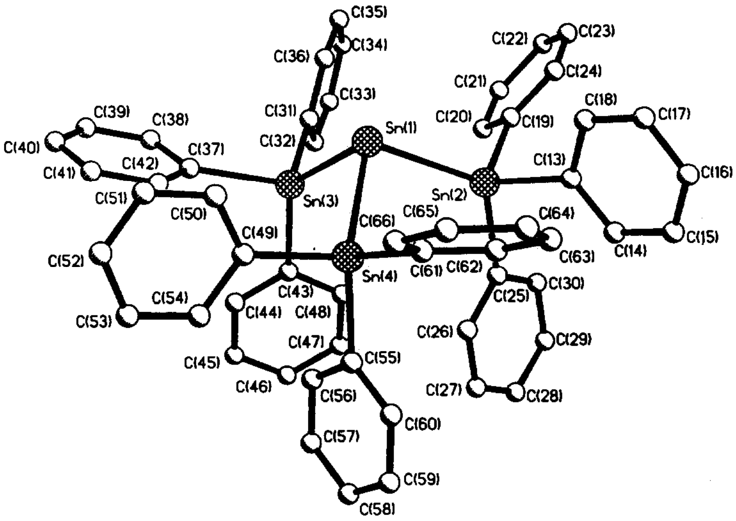


Fig. 2. The structure of the $[(Ph_3Sn)_3Sn]^-$ anion.

Table 3

Atom coordinates ($\times 10^4$) and temperature factors ($Å^2 \times 10^3$) in structure 2

Atom	x	y	z	U^a
Yb	4983(1)	4160(1)	6070(1)	36(1)
Sn(1)	3429(1)	2574(1)	2137(1)	28(1)
Sn(2)	3367(1)	2640(1)	657(1)	31(1)
Sn(3)	977(1)	3033(1)	2560(1)	32(1)
Sn(4)	3153(1)	757(1)	2731(1)	31(1)
Cl	6593(4)	5024(3)	4776(2)	42(2)
O(1)	6589(11)	4788(8)	6530(7)	47(5)
O(2)	4339(11)	5420(8)	6624(7)	51(5)
O(3)	6600(13)	2987(8)	5895(7)	59(6)
O(4)	4569(13)	2967(9)	5446(8)	61(6)
O(5)	2798(14)	3495(9)	6877(7)	63(6)
O(6)	4847(14)	3298(9)	7396(6)	61(6)
C(1)	7846(20)	4593(17)	6321(13)	76(11)
C(2)	6410(18)	5697(12)	6471(12)	54(8)
C(3)	5149(21)	5860(14)	6879(12)	68(10)
C(4)	3107(18)	5568(15)	6985(14)	70(10)
C(5)	6959(20)	2284(12)	6439(11)	65(9)
C(6)	6656(20)	2756(13)	5206(11)	61(9)
C(7)	5468(22)	2376(14)	5250(12)	69(10)
C(8)	3390(20)	2678(13)	5447(11)	63(9)
C(9)	1583(21)	3717(16)	6811(12)	77(11)
C(10)	2787(22)	2946(14)	7588(10)	69(10)
C(11)	4039(22)	2584(13)	7564(12)	70(10)
C(12)	4963(26)	3569(16)	8017(11)	89(12)
C(13)	4999(17)	2087(11)	98(9)	41(7)
C(14)	4962(17)	1459(12)	−275(10)	47(7)
C(15)	6031(22)	1060(13)	−588(11)	62(9)
C(16)	7134(18)	1285(14)	−522(11)	54(8)
C(17)	7215(15)	1898(12)	−158(10)	43(7)
C(18)	6166(18)	2300(11)	162(10)	46(7)
C(19)	3422(18)	3973(11)	−32(9)	46(7)
C(20)	2277(18)	4425(12)	−38(10)	49(7)
C(21)	2312(23)	5285(13)	−489(12)	65(10)
C(22)	3442(22)	5656(12)	−939(10)	55(9)
C(23)	4458(23)	5208(12)	−908(11)	60(9)
C(24)	4462(17)	4370(11)	−483(10)	44(7)
C(25)	2010(15)	1996(11)	358(9)	38(6)
C(26)	1464(18)	1234(11)	828(10)	50(7)
C(27)	614(19)	809(12)	638(12)	60(8)
C(28)	318(17)	1104(12)	−32(11)	53(8)
C(29)	869(18)	1848(12)	−515(11)	53(8)
C(30)	1708(17)	2298(11)	−325(9)	44(7)
C(31)	875(14)	4415(10)	2004(9)	36(6)
C(32)	−129(16)	4719(12)	1704(10)	48(7)
C(33)	−115(20)	5606(12)	1309(11)	61(9)
C(34)	844(19)	6131(13)	1185(12)	61(9)
C(35)	1838(18)	5825(12)	1468(12)	61(9)
C(36)	1843(17)	4961(10)	1851(10)	47(7)
C(37)	524(15)	3016(11)	3726(9)	38(6)
C(38)	−109(18)	3693(12)	3997(10)	51(8)
C(39)	−361(20)	3679(18)	4743(13)	79(12)
C(40)	23(20)	3016(19)	5240(11)	75(11)

Table 3 (continued)

Atom′	x	y	z	U^a
C(41)	626(20)	2348(18)	4991(11)	75(11)
C(42)	873(19)	2354(13)	4254(10)	57(8)
C(43)	−644(14)	2510(10)	2429(9)	33(6)
C(44)	−1591(17)	2227(12)	3021(11)	54(8)
C(45)	−2671(18)	1919(13)	2934(14)	65(9)
C(46)	−2738(19)	1875(14)	2243(16)	72(11)
C(47)	−1782(22)	2153(16)	1647(15)	74(12)
C(48)	−741(17)	2465(14)	1730(12)	56(9)
C(49)	2903(15)	425(10)	3932(9)	33(6)
C(50)	3638(19)	710(12)	4280(10)	52(8)
C(51)	3519(23)	481(15)	5045(11)	67(10)
C(52)	2646(24)	−69(16)	5475(12)	72(10)
C(53)	1863(25)	−405(15)	5166(12)	80(11)
C(54)	1992(18)	−167(13)	4390(10)	54(8)
C(55)	1789(15)	−58(10)	2623(8)	35(6)
C(56)	580(15)	156(13)	2831(11)	53(8)
C(57)	−306(18)	−367(16)	2806(14)	74(11)
C(58)	−23(18)	−1123(15)	2574(13)	63(10)
C(59)	1141(19)	−1346(12)	2360(11)	53(8)
C(60)	2052(16)	−806(11)	2386(10)	44(7)
C(61)	4867(14)	148(10)	2364(9)	34(6)
C(62)	5392(16)	203(11)	1628(10)	42(7)
C(63)	6548(16)	−122(11)	1379(10)	47(7)
C(64)	7186(17)	−517(11)	1904(12)	53(8)
C(65)	6661(15)	−595(12)	2659(10)	45(7)
C(66)	5526(14)	−281(10)	2891(10)	39(6)

[a] Equivalent isotropic U is defined as one-third of the trace of the orthogonalized $U_{i,j}$ tensor.

Reaction of Ph_3SnCl with Yb

$HgBr_2$ was added to ytterbium in the form of filings (3.05 g, 17.63 mmol) in 25 ml of THF 0.03 g (0.08 mmol). The reagents were stirred for 5 h using a magnetic

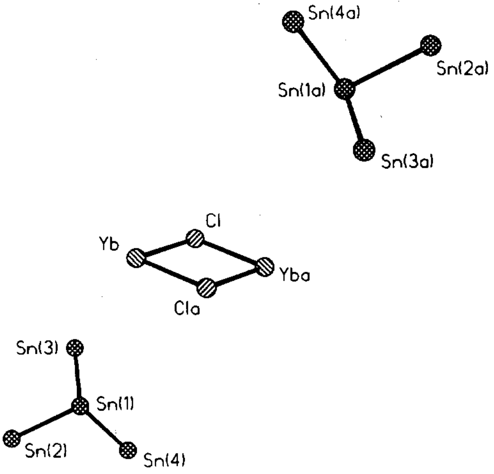


Fig. 3. The fragment of the crystal structure of **2**. The DME molecules and Ph groups are omitted.

Table 4

Anisotropic temperature factors [a] in structure **2** ($Å^2 \times 10^3$)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Yb	49(1)	33(1)	24(1)	3(1)	−12(1)	−8(1)
Sn(1)	29(1)	28(1)	26(1)	1(1)	−10(1)	−3(1)
Sn(2)	35(1)	31(1)	23(1)	2(1)	−8(1)	−3(1)
Sn(3)	30(1)	31(1)	31(1)	−1(1)	−9(1)	1(1)
Sn(4)	31(1)	27(1)	32(1)	5(1)	−13(1)	−1(1)
Cl	48(3)	45(2)	28(2)	5(2)	−12(2)	−7(2)
O(1)	46(8)	53(8)	41(7)	−9(6)	−8(6)	−13(6)
O(2)	52(8)	57(8)	45(7)	−3(6)	−17(6)	−20(6)
O(3)	77(10)	51(8)	44(8)	5(6)	−22(7)	5(7)
O(4)	63(9)	53(8)	66(9)	−11(7)	−17(8)	3(7)
O(5)	77(10)	62(9)	33(7)	15(6)	−7(7)	−18(8)
O(6)	90(11)	63(9)	20(6)	6(6)	−8(7)	−5(8)
C(1)	77(17)	97(18)	61(15)	−29(13)	−23(13)	−3(14)
C(2)	59(13)	51(12)	57(13)	−13(10)	-20(11)	−8(10)
C(3)	89(18)	56(13)	65(14)	−17(11)	−31(13)	7(12)
C(4)	46(13)	68(15)	94(18)	−19(13)	−16(12)	15(11)
C(5)	81(16)	43(11)	58(13)	19(10)	−30(12)	10(11)
C(6)	79(16)	43(12)	55(13)	−3(10)	−15(11)	−4(11)
C(7)	100(19)	46(12)	59(14)	−7(10)	−17(13)	−11(13)
C(8)	84(16)	50(12)	55(13)	1(10)	−28(12)	−17(11)
C(9)	76(17)	90(18)	54(14)	10(12)	−20(12)	−12(14)
C(10)	98(19)	73(15)	22(10)	24(10)	−17(11)	−31(14)
C(11)	104(19)	40(11)	61(14)	28(10)	−40(13)	−42(12)
C(12)	143(25)	80(17)	39(13)	8(12)	−24(14)	−55(17)
C(13)	55(12)	33(9)	32(9)	−2(8)	−10(8)	−2(8)
C(14)	43(11)	56(12)	40(10)	−10(9)	−11(9)	6(9)
C(15)	98(18)	43(11)	47(12)	−23(10)	−16(12)	18(12)
C(16)	40(11)	69(14)	47(12)	−4(10)	−11(9)	−1(10)
C(17)	26(9)	52(11)	42(10)	−4(9)	1(8)	1(8)
C(18)	72(13)	30(9)	34(10)	7(8)	−21(9)	−12(9)
C(19)	69(13)	37(10)	34(10)	−2(8)	−18(9)	−16(9)
C(20)	52(12)	41(11)	45(11)	−3(9)	−7(9)	9(9)
C(21)	95(18)	45(12)	64(14)	−9(11)	−47(14)	27(12)
C(22)	100(17)	29(10)	35(11)	8(8)	−29(11)	−15(11)
C(23)	104(18)	34(10)	42(11)	7(9)	−33(12)	−11(11)
C(24)	46(11)	37(10)	46(11)	−2(8)	−12(9)	−5(8)
C(25)	36(9)	42(10)	34(9)	3(8)	−13(8)	−9(8)
C(26)	61(13)	33(10)	47(11)	9(8)	−19(10)	−2(9)
C(27)	67(14)	42(11)	63(14)	18(10)	−25(11)	−26(10)
C(28)	51(12)	42(11)	70(14)	−13(10)	−26(10)	5(9)
C(29)	62(13)	49(11)	61(13)	−13(10)	−40(11)	9(10)
C(30)	60(12)	39(10)	27(9)	5(7)	−14(8)	5(9)
C(31)	38(9)	26(8)	52(10)	−9(7)	−27(8)	−8(7)
C(32)	38(10)	47(11)	53(11)	−3(9)	−9(9)	10(9)
C(33)	75(15)	42(11)	55(13)	6(9)	−20(11)	25(11)
C(34)	61(14)	39(11)	71(14)	4(10)	−12(11)	4(10)
C(35)	53(12)	35(10)	83(16)	16(10)	−21(11)	−14(9)
C(36)	52(12)	25(9)	60(12)	1(8)	−17(10)	−3(8)
C(37)	34(9)	38(9)	42(10)	−5(8)	−19(8)	2(8)
C(38)	65(13)	52(12)	35(10)	−15(9)	−9(9)	14(10)
C(39)	60(15)	111(21)	73(16)	−48(16)	−7(12)	19(14)
C(40)	63(14)	143(24)	25(10)	−24(13)	−21(10)	14(15)

Table 4 (continued)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(41)	60(14)	120(21)	33(12)	3(13)	−15(10)	10(14)
C(42)	72(14)	62(13)	37(11)	−19(9)	−13(10)	25(11)
C(43)	31(9)	28(8)	38(9)	−4(7)	−12(7)	7(7)
C(44)	46(11)	54(12)	57(12)	5(10)	−20(10)	−5(9)
C(45)	39(12)	54(13)	84(17)	14(11)	−11(11)	−15(10)
C(46)	44(13)	57(14)	123(23)	−8(14)	−48(15)	−1(10)
C(47)	75(17)	81(17)	88(19)	−37(15)	−45(15)	10(14)
C(48)	37(11)	76(14)	65(13)	−30(11)	−15(10)	2(10)
C(49)	45(10)	25(8)	31(9)	−13(7)	−10(8)	22(7)
C(50)	66(13)	51(11)	35(10)	−8(9)	−13(10)	15(10)
C(51)	94(18)	68(14)	37(11)	−11(11)	−19(12)	23(13)
C(52)	98(19)	79(16)	33(11)	−8(11)	−16(12)	15(15)
C(53)	110(21)	64(15)	41(13)	14(11)	2(13)	−7(14)
C(54)	50(12)	61(13)	38(11)	6(9)	−8(9)	3(10)
C(55)	44(10)	31(9)	23(8)	14(7)	−18(7)	0(7)
C(56)	30(10)	63(13)	74(14)	−30(11)	−15(9)	−2(9)
C(57)	27(11)	96(18)	100(19)	−31(15)	−8(11)	−11(11)
C(58)	42(12)	67(14)	80(16)	−6(12)	−23(11)	−20(11)
C(59)	73(15)	38(10)	57(12)	−9(9)	−32(11)	−1(10)
C(60)	42(10)	47(11)	48(11)	−14(9)	−21(9)	3(9)
C(61)	30(9)	29(8)	38(10)	−1(7)	−5(7)	−6(7)
C(62)	46(11)	42(10)	40(10)	−8(8)	−13(9)	−3(8)
C(63)	46(11)	39(10)	37(10)	10(8)	7(8)	−3(8)
C(64)	45(11)	29(9)	81(15)	−2(10)	−18(11)	4(8)
C(65)	35(10)	51(11)	47(11)	−4(9)	−19(9)	13(8)
C(66)	32(9)	39(9)	45(10)	5(8)	−23(8)	−8(7)

[a] The anisotropic temperature factor exponent takes the form $-2\pi(H^2a^{*}U_{11}+K^2b^{*}U_{22}+\cdots+2HKa^{*}b^{*}U_{12})$.

stirrer. The precipitate formed was separated from the metal. The metal was washed with hot THF (20 ml × 4) and dried *in vacuo*.

(a) Yb (3.00 g, 17.34 mmol), activated as described above, was added to a solution of Ph_3SnCl (1.62 g, 4.20 mmol) in 20 ml of THF. The mixture was stirred using a magnetic stirrer for 40 h at room temperature. The reaction solution became yellow–brown and a fine grey–green deposit formed. The solution and the deposit were separated from excess metal. It was found that 0.70 g (97.63%) of ytterbium entered into the reaction. The deposit was separated by centrifugation, then washed with THF (20 ml × 3) and dried *in vacuo* at room temperature to give 0.74 g (90.46%) of $YbCl_2(THF)_2$. Anal. Found: C, 25.22; H, 4.89; Cl, 18.23; Yb, 45.40. $C_8H_{16}Cl_2O_2Yb$ calc.: C, 24.76; H, 4.15; Cl, 18.28; Yb, 44.58%. The IR spectrum shows absorption bands of coordinated THF (1040, 875 cm^{-1}).

The reaction solution was concentrated to approx. 10 ml and cooled at 0°C for 10 h to yield yellow crystals of **1**. The mother liquor, after separation from the crystals, was concentrated to approx. 5 ml and cooled at −10°C during 10 h. The second portion of crystals of **1** was separated off. The mother liquor was concentrated once more to approx. 3 ml and cooled at −10°C during 24 h. The third portion of crystals was combined with the two previous ones and then this was recrystallized from THF (8 ml, 24 h, −10°C) to yield light-yellow crystals of **1** (1.96

g, 80.15%, m.p. 135–140°C (dec)). Anal. Found: C, 53.97; H, 5.97; Yb, 15.20. $C_{52}H_{62}O_4Sn_2Yb$ calc.: C, 53.77; H, 5.38; Yb, 14.90%. IR: 3040, 1420 (doublet), 1065 (doublet), 1025, 990, 865, 725, 695, 450 (doublet) cm^{-1}.

X-Ray analysis confirmed that the isolated organotin derivative of ytterbium was complex **1**.

(b) Ph_3SnCl (1.47 g, 3.81 mmol) in 20 ml of THF was added to Yb (3.12 g, 18.03 mmol) activated by $HgBr_2$. The mixture was stirred for 12 h at room temperature. The reaction solution and deposit were separated from excess ytterbium. It was found that 0.35 g (53.04%) of Yb entered into the reaction. After centrifugation, the deposit was washed with THF (20 ml × 3) and dried *in vacuo* to yield 0.68 g (91.60%) of $YbCl_2(THF)_2$ identified by elemental analysis and IR spectra.

The reaction solution was evaporated to dryness under vacuum, and the residue was washed with hexane and dried *in vacuo* to yield 1.30 g (97.39%) of $Ph_3SnSnPh_3$ (identified by ISC).

The isolated $Ph_4SnSnPh_3$ (1.20 g. 1.71 mmol) and $YbCl_2(THF)_2$ (0.45 g, 1.16 mmol) in 20 ml of THF were added to isolated excess Yb (2.74 g, 15.83 mmol). The mixture was stirred for 30 h at room temperature. The solution became yellow-brown. After separation of excess Yb, it was found that the total amount of metal entering into the reaction (on initial Ph_3SnCl) was 0.65 g (98.50%).

Complex **1** (1.66 g, 74.81%, m.p. = 134–138°C (dec)) was isolated using the above procedure and identified by elemental analysis and IR spectra.

Reaction of $Ph_3SnSnPh_3$ with Yb

$Ph_3SnSnPh_3$ (1.50 g, 1.95 mmol) in THF (20 ml) was added to Yb (3.29 g, 19.01 mmol) activated by $HgBr_2$. The mixture was stirred for 40 h at room temperature. The light-yellow reaction solution was separated from excess Yb. It was found that 0.12 g (35.64%) of the metal entered into the reaction.

The reaction solution was added to the isolated excess of Yb and the mixture was stirred for 160 h at room temperature. The yellow–brown solution was separated from excess Yb. It was found that 0.35 g (103.95%) of the metal entered into the reaction.

The reaction solution was evaporated to dryness *in vacuo*, the residue was washed with hexane and recrystallized from THF to yield light-yellow crystals of **1** (1.71 g, 75.52%, m.p. = 135–138°C (dec.)). Anal. Found: C, 53.50; H, 5.42; Yb, 14.41. $C_{52}H_{62}O_4Sn_2Yb$ calc.: C, 53.77; H, 5.38; Yb, 14.90%. The IR spectrum of the product was identical to the IR spectrum of complex **1** obtained from the reaction of Ph_3SnCl with Yb.

Reaction of $PhSnCl_3$ with Yb

$PhSnCl_3$ (1.52 g, 5.03 mmol) in THF (20 ml) was added at −70°C to Yb (3.30 g, 19.07 mmol). The mixture was allowed to warm slowly and stirred at room temperature for 30 h. The dark yellow–brown solution and fine grey–green deposit were separated from excess Yb. It was found that 1.37 g (94.48%) of the metal entered into the reaction.

The deposit was separated by centrifugation and 2.63 g (89.53%) of $YbCl_2(THF)_2$ and 0.21 g (52.75%) of Sn were obtained.

Complex **1** in the form of light-yellow crystals (0.64 g, 65.59%, m.p. 135–140°C (dec.)) was isolated from the reaction solution using the above procedure. Anal.

Found: C, 53.92; H, 5.80; Yb 14.41. $C_{52}H_{62}O_4Sn_2Yb$ calc.: C, 53.77; H, 5.38; Yb, 14.90%. The IR spectrum of the product was identical to the IR spectrum of complex **1** obtained from the reaction of Ph_3SnCl with Yb.

X-Ray analysis confirmed that the product isolated from the reaction of $PhSnCl_3$ with Yb is complex **1**.

Reaction of Ph_2SnCl_2 with Yb

Ph_2SnCl_2 (3.50 g, 10.18 mmol) in 40 ml of THF was added to Yb (7.22 g, 41.72 mmol). The mixture was stirred for 12 h at room temperature. The solution became yellow–brown and a fine grey–green deposit was formed. The solution and the deposit were separated from excess metal. It was found that 2.04 g, (104.22%) of ytterbium entered into the reaction.

The deposit was separated by centrifugation and 3.26 g (92.54%) of $YbCl_2(THF)_2$ and 0.11 g (81.94%) of metallic Sn were obtained.

The solvent was evaporated under vacuum from the solution. The residue was dissolved in DME (30 ml), kept at room temperature for 10 h and cooled to −10°C during 24 h to yield the compound **2** (2.81 g, 75.39%, m.p. 125–130°C (dec)) as yellow–brown crystals, unstable in air. Anal. Found: C, 48.01 H, 5.02; Cl, 1.79; Yb 9.92. $C_{66}H_{75}ClO_6Yb$ calc.: C, 48.12; H, 4.59; Cl, 2.15; Yb, 10.50%. IR: 3040, 1425 (doublet), 1065 (doublet), 1020, 995, 860, 725, 695, 450 (doublet) cm^{-1}.

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