Journal of Organometallic Chemistry, *443* (1993) C26–C28

JOM 23211PC

Preliminary Communication

Novel polynuclear organotin complexes of samarium and ytterbium

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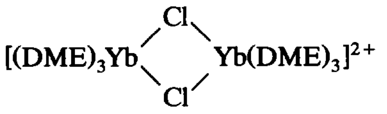
(Received September 2, 1992)

Abstract

Polynuclear complexes $[(Me_3Sn)_3Sn]_2Ln(THF)_4$ (Ln = Sm (**1**), Yb (**2**)) have been synthesized by reacting Me_3SnCl with samarium or ytterbium in THF. The crystals of **1** and **2** are orthorhombic (a = 21.511(2), b = 13.215(3), c = 20.640(4) Å, Z = 4, space group $Pca2_1$ for Ln = Sm and a = 21.534(3), b = 13.158(2), c = 20.616 Å, Z = 4, space group $Pca2_1$ for Ln = Yb). A similar organotin complex of ytterbium, $[(Me_3Sn)_3Sn]_2Yb(THF)_4$ (**3**) having the same composition but different structure than compound **2** has been isolated from the reaction of $MeSnCl_3$ with Yb.

The crystals of the compound **3** are tetragonal, a = 20.851(4), c = 26.311(5) Å, Z = 8, space group $I\bar{4}2d$. In all cases the molecules of $[(Me_3Sn)_3Sn]_2Ln(THF)_4$ have a distorted octahedral structure in which the central Ln (Ln = Sm, Yb) atom is bonded to four oxygen atoms of THF molecules in equatorial positions and two tin atoms of $(Me_3Sn)_3Sn$ groups in axial positions. The molecule of **3** has a C_2 symmetry and an approximately eclipsed arrangement of $(Me_3Sn)_3Sn$ groups. The Yb–Sn distance is 3.300(4) Å. The molecules of **1** and **2** have a staggered arrangement of the $(Me_3Sn)_3Sn$ groups with Ln–Sn distances of 3.402(4), and 3.386(4) Å for Ln = Sm, and 3.289(5) and 3.299(4) Å for Ln = Yb.

While studying the reactions of phenyltin chlorides with lanthanoids, we have recently found [1,2] that the reaction of Ph_2SnCl_2 with Yb leads to the formation of an ionic organotin complex of ytterbium, consisting of $(Ph_3Sn)_3Sn^-$ anions and dimeric ytterbium cations



(DME = 1,2-dimethoxyethane).

Upon continuation of our investigations on the reactions of organotin halides R_nSnX_{4-n} (n = 1–3) with lanthanoids [1–3] we found that the reactions of Me_3SnCl with samarium or ytterbium in THF at room temperature during 60–70 h lead to the formation of complexes **1** and **2**. The compounds have been isolated as airsensitive crystalline solids, light-yellow in the case of ytterbium and dark-green in the case of samarium, in 70–75% yields. The complexes **1** and **2** decompose without melting upon heating to 120–125°C, are readily soluble in THF, DME, benzene, and sparingly soluble in hexane. The IR spectra of **1** and **2** are almost identical and show the absorption bands (1175, 755, 520, 500 cm^{-1}) of Me_3Sn groups and absorption bands of coordinated THF (1025, 870 cm^{-1}). Compound **1**. Anal. Found: Sm, 9.00. $C_{34}H_{86}O_4Sn_8Sm$ calc.: Sm, 9.06%. Compound **2**. Anal. Found: Yb, 9.20. $C_{34}H_{86}O_4Sn_8Yb$ calc.: Yb, 10.29%.

The reaction of $MeSnCl_3$ with Yb in THF at room temperature for *ca.* 100 h also leads to the formation of an organotin complex of ytterbium, $[(Me_3Sn)_3Sn]_2Yb(THF)_4$ (**3**), having the same composition, but somewhat different structure, than compound **2**. Complex **3** has been isolated in 80% yield. The compounds **2** and **3** have identical IR spectra and similar properties. Compound **3**. Anal. Found: Yb, 10.21. $C_{34}H_{86}O_4Sn_8Yb$ calc.: Yb, 10.29%.

The other products of the reactions of Me_3SnCl with samarium and ytterbium, as well as in the reaction of $MeSnCl_3$ with Yb, are $LnCl_2(THF)_2$ and methyl derivatives of the lanthanoids, the composition and structure of which are currently under investigation.

Me_2SnCl_2 reacts with Yb in an analogous manner.

X-Ray diffraction studies have shown that the crystals of **3** are tetragonal [4], while the crystals of **1** and **2** are orthorhombic [5]. In all cases the molecules of $[(Me_3Sn)_3Sn]_2Ln(THF)_4$ (Ln = Sm, Yb) have a distorted octahedral structure in which the central Ln

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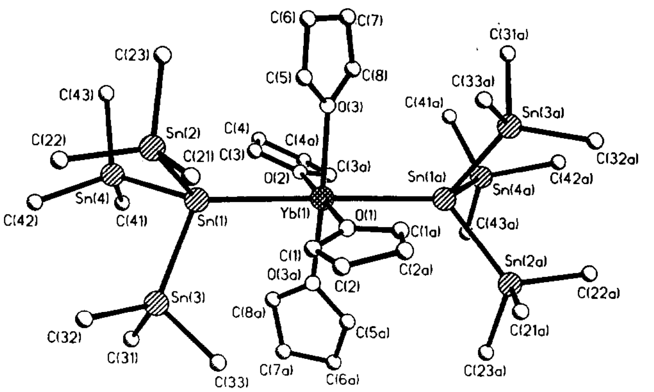

Fig. 1. The molecular structure of 3.

atom is bonded to four oxygen atoms of THF molecules in equatorial positions and two tin atoms of $(Me_3Sn)_3Sn$ groups in axial positions. The molecule of **3** has a C_2 symmetry (the Yb, O(1) and O(2) atoms are on a two-fold axis in the crystal structure) and an approximately eclipsed arrangement of the two $(Me_3Sn)_3Sn$ groups in relation to each other (Fig. 1). The molecules of **1** and **2** have an approximately staggered arrangement of the two $(Me_3Sn)_3Sn$ groups. Thus, the $(Me_3Sn)_3Sn$ groups in these molecules are bonded to the Ln (Sm, Yb) atom by the Sn-Ln bonds in contrast to compound $[(Ph_3Sn)_3Sn]_2^-[Yb_2Cl_2(DME)_6]^{2+}$, containing isolated $[(DME)_3Yb(\mu\text{-}Cl)_2Yb(DME)_3]^{2+}$ cations and $(Ph_3Sn)_3Sn^-$ anions [2]. The molecular structures of **1**, **2** and **3** are similar to the octahedral molecular structure of $(Ph_3Sn)_2Yb(THF)_4$ [6], in which organotin groups occupy axial positions and THF molecules are situated in equatorial positions too. The Ln–Sn distances in **1** (Ln = Sm), 3.402(4) and 3.386(4) Å are longer than those in **2** (Ln = Yb), 3.289(5), 3.299(4) Å and in **3** 3.300(4) Å by *ca.* 0.1 Å. The difference between Sm–Sn and Yb–Sn distances are close to the difference between ionic radii of six-coordinated Sm(2 +) and Yb(2 +), 1.11 and 1.02 Å, respectively [7]. The Yb–Sn distances found in **2** are shorter than those in $(Ph_3Sn)_2Yb(THF)_4$, 3.305(1) Å [6], and in $Ph_3SnYb(THF)_2(\mu\text{-}Ph)_3Yb(THF)_3$, 3.379(1) Å [8].

The Sn–Ln–Sn angles of 178.8(1)°, 178.5(1)°, and 176.2(1)° in **1**, **2** and **3**, respectively, are close to each other and significantly different from the value of the analogous angle in $(Ph_3Sn)_2Yb(THF)_4$, 164.5(1)° [6].

The Ln–O distances range from 2.49(4) to 2.54(4) Å (average 2.51 Å) in **1** and from 2.35(4) to 2.38(4) Å (average 2.36 Å) in **2**. In the molecule of **3** the Ln–O(THF) distances are in the narrow interval 2.40(1)–2.41(1) Å. These values are normal for Ln–O(THF) bond lengths.

All tin atoms in the molecules **1**, **2** and **3** have a distorted tetrahedral coordination. In all cases the Ln–Sn–Sn angles, 117.4(1)–123.7(1)° in **1**, 117.9(2)–124.2(2)° in **2** and 113.8(1)–128.9(1)° in **3** are increased when compared with the ideal tetrahedral angle, *i.e.* the Me_3Sn groups are bent away from the central part of the molecule. The range of Sn–Sn bond distances are 2.754(6)–2.800(6) Å (average 2.778 Å) in **1** and 2.775(6)–2.818(6) Å (average 2.786 Å) in **2**. The average Sn–C distances are 2.13 Å and 2.16 Å in **1** and **2**, respectively. In **3** for which X-ray data are more correct, the similar ranges of Sn–Sn and Sn–C bond distances are narrower, 2.798(4)–2.803(4) Å (average 2.800 Å) and 2.15(2)–2.19(2) Å (average 2.17 Å), respectively.

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4 The diffraction experiment was carried out at 173 K with Siemens P3/PC diffractometer (Mo Kα radiation, graphite monochromator, θ–2θ scan with $2\theta \leqslant 45°$, 5466 reflections collected in two independent ranges, 2698 independent reflections, 2477 observed reflections with $I > 2\sigma(I)$). Crystal data of **3**: $C_{34}H_{86}O_4Sn_8Yb_1$, tetragonal space group $I\bar{4}2d$, $a = 20.851(4)$, $c = 26.311(5)$ Å, $V = 11438$ Å^3, $Z = 8$, $D_{calc} = 1.95$ g cm^{-3}, μ(Mo Kα) = 5.07 mm^{-1}. The structure was refined with anisotropic thermal factors for all non-hydrogen atoms (including all hydrogen atoms as fixed isotropic contributions in calculated positions). The final R-factors are $R = 0.043$, $R_w = 0.053$, GOOF = 1.3. Absorption was taken into account by the DIFABS program. All calculations were performed using SHELXTL PLUS package.

5 The X-ray diffraction experiments for **1** and **2** were carried out at 173 K with Siemens P3/PC diffractometer (Mo Kα radiation, graphite monochromator, θ–2θ scan with $2\theta \leqslant 50°$, 2223 (for **1**) and 2399 (for **2**) independent reflections with $I > 2\sigma(I)$). Both crystals were destroyed during the experiment. Crystal data of **1**: $C_{34}H_{86}O_4Sn_8Sm_1$, orthorhombic, space group $Pca2_1$, $a = 21.511(2)$, $b = 13.215(3)$, $c = 20.640(4)$ Å, $V = 5867$ Å^3, $Z = 4$, $D_{calc} =$ 1.88 g cm^{-3}, μ(Mo Kα) = 4.37 mm^{-1}. Crystal data of **2**: $C_{34}H_{86}O_4Sn_8Yb_1$, orthorhombic, space group $Pca2_1$, $a = 21.534(3)$, $b = 13.158(2)$, $c = 20.616(4)$ Å, $V = 5841$ Å^3, $Z = 4$, $D_{calc} = 1.92$ g cm^{-3}, μ(Mo Kα) = 4.98 mm^{-1}. The structures were refined with anisotropic thermal factors for Sm, Sn, and Yb, Sn atoms and isotropic for other non-hydrogen atoms (including all hydrogen atoms as fixed isotropic contributions in calculated positions). The final R-factors are: R = 0.068, $R_w = 0.071$, GOOF = 2.5 for **1**, and $R = 0.083$, $R_w = 0.074$, GOOF = 2.3. for **2**. Absorption

was taken into account by the DIFABS program. All calculations were performed using SHELXTL PLUS package.

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