

## Preliminary Communication

### Synthesis and structure of organosilicon and organogermanium complexes of ytterbium $(\text{Ph}_3\text{E})_2\text{Yb}(\text{THF})_4$ with Yb–Si and Yb–Ge bonds

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#### Abstract

Complexes  $(\text{Ph}_3\text{Si})_2\text{Yb}(\text{THF})_4$  (**1**) and  $(\text{Ph}_3\text{Ge})_2\text{Yb}(\text{THF})_4$  (**2**) were synthesised by the reactions of  $\text{Ph}_3\text{SiCl}$  or  $\text{Ph}_3\text{GeCl}$  with ytterbium in THF and characterised by X-ray diffraction. Compounds **1** and **2** have similar centrosymmetrical octahedral structures with a central Yb atom bonded to four oxygen atoms of THF molecules in equatorial positions and two Si (or Ge) atoms of  $\text{SiPh}_3$  (or  $\text{GePh}_3$ ) fragments in axial positions. In the crystal of **2** there are two symmetrically independent molecules with the same structure. The Yb–Si and Yb–Ge distances in **1** and **2** are 3.158(2) and 3.170(2), 3.141(2) Å, respectively.

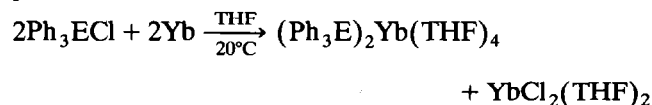
**Key words:** Silicon; Germanium; Ytterbium

During our systematic investigations of the reactions of organotin chlorides  $\text{R}_n\text{SnCl}_{4-n}$  ( $n = 1-3$ ) with metallic lanthanoids [1–3] we found that the reaction of  $\text{Ph}_2\text{SnCl}_2$  with Yb leads to the formation of an ionic organotin complex of ytterbium [1], consisting of  $(\text{Ph}_3\text{Sn})_3\text{Sn}^-$  anions and the dimeric ytterbium cation  $[(\text{DME})_3\text{Yb}(\mu\text{-Cl})_2\text{Yb}(\text{DME})_3]^{2+}$  (DME = 1,2-dimethoxyethane). In contrast reactions of  $\text{Ph}_3\text{SnCl}$  or  $\text{PhSnCl}_3$  with Yb lead to compound  $(\text{Ph}_3\text{Sn})_2\text{Yb}$

$(\text{THF})_4$ , containing direct Yb–Sn bonds [1]. The reactions of  $\text{Me}_3\text{SnCl}$  with samarium or ytterbium in THF at room temperature lead to the formation of polynuclear organotin complexes  $[(\text{Me}_3\text{Sn})_3\text{Sn}]_2\text{Ln}(\text{THF})_4$  (Ln = Sm, Yb) with Ln–Sn bonds [2].

Thus, the reaction of organotin chlorides  $\text{R}_n\text{SnCl}_{4-n}$  (R = Me, Ph;  $n = 1, 2, 3$ ) with lanthanoids is a convenient route to organotin derivatives of lanthanoids. We therefore decided to use this method for preparation of organosilicon and organogermanium compounds of lanthanoids.

We found that  $\text{Ph}_3\text{SiCl}$  or  $\text{Ph}_3\text{GeCl}$  react slowly with Yb in THF at room temperature and yield complexes **1** [4\*] and **2** [5\*].



E = Si, Ge.

Bis(triphenylsilyl)tetrakis(THF)ytterbium (**1**) has been isolated as a yellow crystalline solid decomposing without melting on heating to 110–115°C. The IR spectrum of **1** shows the absorption bands (1425, 1110, 735, 700, 430  $\text{cm}^{-1}$ ) of  $\text{Ph}_3\text{Si}$  groups and of coordinated THF (1035, 915, 865  $\text{cm}^{-1}$ ). Bis(triphenylgermyl)tetrakis(THF)ytterbium (**2**) has been isolated as a yellow-brown crystalline solid melting with decomposition upon heating to 120–125°C. The IR spectrum of **2** shows the absorption bands (1480, 1425, 1085, 1065, 1020, 995, 730, 695, 460  $\text{cm}^{-1}$ ) of  $\text{Ph}_3\text{Ge}$  groups and of coordinated THF (1040, 915, 865  $\text{cm}^{-1}$ ). Complexes **1** and **2** are unstable in air, soluble in THF and benzene, and insoluble in hexane.

X-ray diffraction studies [6\*] have shown that molecules of compounds **1** and **2** have the same centrosymmetrical octahedral structure in which the Yb atom is bonded to four oxygen atoms of THF molecules in equatorial positions and there are two Si (Ge) atoms of  $\text{Ph}_3\text{Si}$  ( $\text{Ph}_3\text{Ge}$ ) fragments in axial positions (Fig. 1). Thus, the molecular structures of **1** and **2** are similar to the structure of compounds  $(\text{Ph}_3\text{Sn})_2\text{Yb}(\text{THF})_4$  [7] and  $[(\text{Me}_3\text{Sn})_3\text{Sn}]_2\text{Ln}(\text{THF})_4$  (Ln = Sm, Yb) [2]. As we know the complex **1** is the first structurally characterised neutral organosilicon derivative of lanthanoids with a

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

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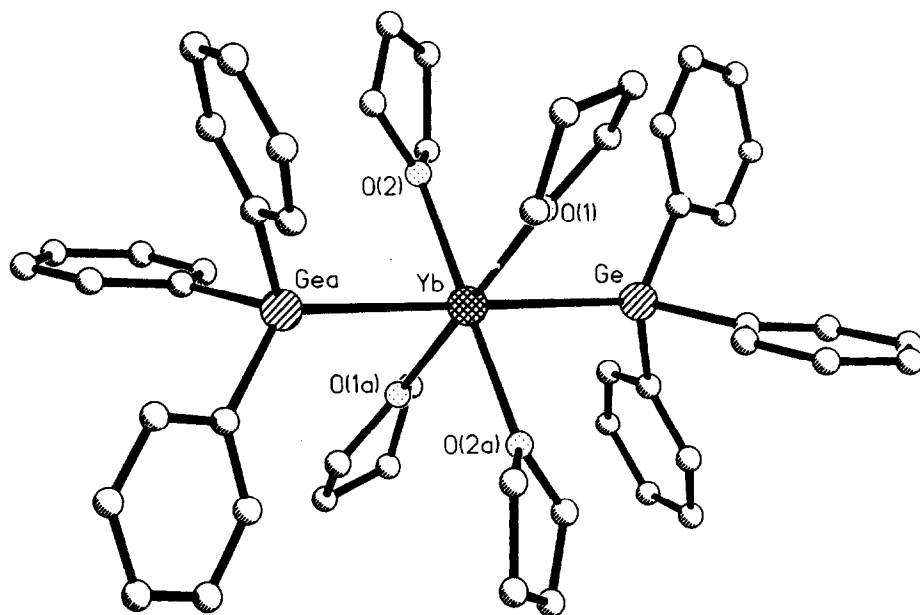


Fig. 1. The molecular structure of **2** (**1** has a similar structure).

direct Ln–Si bond and complex **2** is the first structurally characterised organogermanium derivative of lanthanoids containing the direct Ln–Ge bond. Only two X-ray structures of ionic compounds containing anions  $[\text{Cp}_2\text{Ln}(\text{SiMe}_3)_2]^-$  (Ln = Sm [8], Lu [9]) with Ln–Si bonds are known.

The Yb–Si distance in **1**, 3.158(2) Å, and the Yb–Ge distances in **2**, 3.170(2) and 3.141(2) Å for two independent molecules, are comparable. The first distance is significantly longer than that in the anions  $[\text{Cp}_2\text{Ln}(\text{SiMe}_3)_2]^-$ , 2.880 Å for Ln = Sm [8] and 2.888 Å for Ln = Lu [9]. It seems to be a result of more steric hindrance at the central Yb atom in **1**. It is interesting to note that the Yb–Ge distances in **2** are close to those found in  $(\text{Ph}_3\text{GeH})_2\text{Yb}(\text{THF})_4$ , namely 3.140 and 3.152 Å [10]. It should be noted that the differences between the Yb–Si and Yb–Ge distances in **1** and **2** and the Yb–Sn distances in  $(\text{Ph}_3\text{Sn})_2\text{Yb}(\text{THF})_4$ , 3.305 Å, [7] and in two different crystallographic forms of compound  $[(\text{Me}_3\text{Sn})_3\text{Sn}]_2\text{Yb}(\text{THF})_4$ , 3.289, 3.299, 3.300 Å, [2] are comparable with the differences between the covalent radii of the respective atoms (according to Pauling  $r(\text{Si}) = 1.17$ ,  $r(\text{Ge}) = 1.24$ ,  $r(\text{Sn}) = 1.40$  Å [11]). In the tetrahedral structure of  $[(^t\text{BuCH}_2)_3\text{Sn}]_2\text{Yb}(\text{THF})_2$  with less steric hindrance, the Yb–Sn distance 3.216 Å [12] is shorter than that in the octahedral molecules mentioned.

The Yb–O(THF) distances in **1** and **2** (2.444(3), 2.475(2) and 2.42(1), 2.43(1), 2.42(1), 2.42(1) Å, respectively) are slightly longer than those in  $(\text{Ph}_3\text{Sn})_2\text{Yb}(\text{THF})_4$ , 2.378–2.422 Å, [7] and  $[(\text{Me}_3\text{Sn})_3\text{Sn}]_2\text{Yb}(\text{THF})_4$ , 2.35–2.41 Å, [2].

The Si and Ge atoms in these molecules have a distorted tetrahedral coordination. Two of the YbSi (Ge)C angles are significantly increased from the ideal tetrahedral angle (115.3(1)°, 122.4(1)° for Si and 117.6(4)°, 126.0(4)° for Ge). The Si–C(Ph) distances in **1** (1.915(3), 1.917(3), 1.926(3) Å) and the Ge–C(Ph) distances in **2** (2.00(1), 2.01(1), 2.02(2) Å) like the Sn–C(Ph) distances in the molecule of  $(\text{Ph}_3\text{Sn})_2\text{Yb}(\text{THF})_4$  are somewhat longer than typical values of these bond lengths.

#### Acknowledgment

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#### References and notes

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- 3 L.N. Bochkarev, O.V. Grachev and S.F. Zhiltsov, *Metalloorg. Khim.*, **6** (1993) 249.
- 4 The synthesis and isolation of **1** and **2** were performed under vacuum in sealed ampoules using thoroughly dried solvents. Preparation of **1**: Yb (3.34 g, 19.30 mmol) in the form of filings was added to a solution of  $\text{Ph}_3\text{SiCl}$  (1.00 g, 3.39 mmol) in 20 ml of THF. The mixture was stirred using a magnetic stirrer for ca. 150 h at room temperature. The excess of Yb and ytterbium dichloride were separated from dark-brown solution by centrifugation. The reaction solution was evaporated to dryness under vacuum to yield 1.24 g (75.0%) of crude complex **1** as dark-brown solid.

- Anal. Found: Yb, 19.01.  $C_{52}H_{62}O_4Si_2Yb$  calcd. Yb, 17.65%. After recrystallisation from THF (10 ml, 24 h, 0°C) complex **1** was obtained in the form of yellow crystals (0.70 g, 42.2%). Anal. Found: Yb, 17.94%.
- 5 Preparation of **2**: Yb (2.50 g, 14.45 mmol) in the form of filings was added to a solution of  $Ph_3GeCl$  (1.50 g, 4.42 mmol) in 20 ml of THF. The mixture was stirred using a magnetic stirrer for ca. 250 h at room temperature. The excess of Yb and ytterbium dichloride were separated from dark-brown solution by centrifugation. The reaction solution was evaporated to dryness under vacuum to yield 1.95 g, (82.6%) of crude complex **2** as dark-brown solid. Anal. Found: Yb, 17.50.  $C_{52}H_{62}Ge_2O_4Yb$  calcd.: Yb, 16.18%. After recrystallisation from benzene (15 ml, 3–5°C, 20 h) complex **2** was obtained as yellow-brown crystals containing 0.5 mole of solvated benzene (1.49 g, 60.8%). Anal. Found: Yb, 16.28%.
- 6 The X-ray diffraction experiments for **1** and **2** were carried out at 158 K with a Siemens P3/PC diffractometer (Mo  $K\alpha$  radiation, graphite monochromator,  $\theta$ – $2\theta$  scan mode,  $2 \leq 2\theta \leq 56^\circ$  (**1**) and  $2 \leq 2\theta \leq 48^\circ$  (**2**), 5906 (**1**) and 3772 (**2**) measured reflections from which 4334 (**1**) and 3280 (**2**) independent observed reflections with  $F > 3\sigma(F)$ ). Crystal data for **1**:  $C_{52}H_{62}O_4Si_2Yb$ , monoclinic space group  $P2_1/n$ ,  $a = 10.208(2)$ ,  $b = 11.927(3)$ ,  $c = 19.976(4)$  Å,  $\beta = 103.88(2)^\circ$ ,  $V = 2361(2)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_{calc} = 1.379$  g cm<sup>-3</sup>,  $\mu(Mo K\alpha) = 2.07$  mm<sup>-1</sup>. Crystal data for **2**:  $C_{52}H_{62}Ge_2O_4Yb \cdot 0.5C_6H_6$ , monoclinic space group  $P2_1/c$ ,  $a = 20.576(8)$ ,  $b = 14.945(3)$ ,  $c = 19.210(8)$  Å,  $\beta = 115.27(2)^\circ$ ,  $V = 5342(4)$  Å<sup>3</sup>,  $Z = 4$  (two symmetrically independent molecules),  $D_{calc} = 1.329$  g cm<sup>-3</sup>,  $\mu(Mo K\alpha) = 2.89$  mm<sup>-1</sup>. The structures were determined by a combination of the heavy atom method for **1** and the direct method for **2** with calculations of difference Fourier maps. The positions of hydrogen atoms in **1** were obtained directly whereas those in **2** were calculated. The structures were refined with anisotropic thermal factors for Yb, Si, Ge, and C atoms and isotropic for H atoms in **1**. The final  $R$ -factors are:  $R = 0.026$ ,  $R_w = 0.027$ ,  $GOF = 1.25$  for **1** and  $R = 0.048$ ,  $R_w = 0.049$ ,  $GOF = 1.15$  for **2**. The weighting scheme  $w^{-1} = \sigma(F) + aF^2$  was used for refinement of structures ( $a = 0.001$  and 0.0005 respectively for **1** and **2**). Absorption was taken into account by the DIFABS program. All calculations were performed using the SHELXTL PLUS package.
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