Journal of Organometallic Chemistry, 378 (1989) 363–373
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20060

Synthesis and structure of bis(triphenylgermane)tetrakis-(tetrahydrofuran)ytterbium

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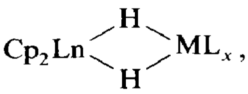
(Received May 17th, 1989)

Abstract

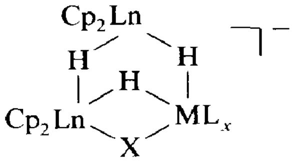
The reaction of the naphthalene complex of ytterbium $C_{10}H_8Yb(THF)_3$ with dihydrogen under ambient conditions gives the ytterbium dihydride $[H_2Yb(THF)]_n$. The reaction of the naphthaleneytterbium with Ph_3GeH in THF at room temperature gives the unusual germaneytterbium complex $(Ph_3GeH)_2Yb(THF)_4$. An X-ray diffraction study ($a = 9.980(2)$, $b = 17.305(4)$, $c = 13.883(3)$ Å, $\beta = 96.37(2)°$, $Z = 2$, space group $P2_1$, 4552 reflections, $R = 0.036$, $R_w = 0.031$) has shown that the Yb atom in the molecule of this complex has octahedral coordination; the four THF molecules are in the equatorial plane and the Ph_3GeH ligands are in the axial positions. The hydride H atoms of the Ph_3GeH groups form μ_2-bridges between Yb and Ge atoms.

Introduction

Organometallic hydrides are known for most of the rare earth elements. All of the hydrides, characterised by X-ray diffraction, have Ln^{III} and one of the following structures [1]:



$[Cp_3Ln—H—LnCp_3]^-$,



The general routes to these compounds are: (i) the hydrogenolysis or the thermolysis of Cp_2LnR or similar complexes, (ii) the reduction of Cp_2LnHal by sodium hydride,

$LiAlH_4$ or similar hydrides, and (iii) the cocondensation of Ln vapors with unsaturated hydrocarbons.

Here we report on the synthesis of two novel hydride complexes of ytterbium and an X-ray diffraction study of one of them. For preparation of these compounds naphthaleneytterbium complex $C_{10}H_8Yb(THF)_3$ (I) obtained recently [2] was used. Precise structure of the very reactive I has not been established as yet but it does not prevent its use in the synthesis of new organolanthanoids.

Results and discussion

We have found that when a suspension of I in THF is shaken under dihydrogen at room temperature and atmospheric pressure, I gradually dissolves and hydride II * forms. Under the same conditions, but in the absence of solvent, the dry powder of I gradually becomes a waxy dark-brown suspension. The yield of II is almost the same (70–80%) in both cases.

$$\underset{\text{(I)}}{C_{10}H_8Yb(THF)_3} + H_2 \longrightarrow \underset{\text{(II)}}{[H_2Yb(THF)]_n} + C_{10}H_8$$

The deuterium analogue of II is prepared when D_2 is used in place of H_2.

Freshly prepared II is an air-sensitive, dark-brown solid, that is soluble in THF and DME, sparingly soluble in toluene, and insoluble in hexane. Storage of II at room temperature in vacuo slowly releases H_2 and the solubility of II decreases. The structure of II is confirmed by elemental analysis, and by its reaction with diluted HCl which gives H_2 (93%), $YbCl_3$ (91%) and THF (90%). The IR spectrum of II is very poor. A few broad bands are present, one of which (1250 cm^{-1}) is attributable to stretching of the Yb–H–Yb bridges. This band is absent in the spectrum of the deuterium derivative which shows instead a weak absorption at 890 cm^{-1}. These frequencies are in the region which is characteristic for ν(Ln–H(D)) in the spectra of the hydrides $[Cp_2LnH(D)]_2$ [1].

The related ytterbium hydride is formed when I is heated with Ph_3GeH in THF at 80 °C, but in this case it is impossible to separate properly the ytterbium hydride formed from Ph_6Ge_2 what is the second product of the reaction. The formation of Yb–H groups is confirmed by HD evolution upon deuterolysis of the darkbrown solid isolated in this reaction.

An unusual and novel complex has been obtained by reaction of I with Ph_3GeH at room temperature **. Under these conditions the brownish-yellow diamagnetic crystals of bis(triphenylgermane)tetrakis(tetrahydrofuran)ytterbium (III) are isolated from the reaction mixture.

$$\underset{\text{(I)}}{C_{10}H_8Yb(THF)_3} + 2Ph_3GeH \xrightarrow[20\,^{\circ}C]{THF} \underset{\text{(III)}}{(Ph_3GeH)_2Yb(THF)_4} + C_{10}H_8$$

Complex III decomposes slowly in air (5–10 min), melts at 129–133 °C(dec.) in vacuo, and is soluble in THF, DME, and aromatic solvents. Oxidation of III with

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* Preliminary communication [3].

** Preliminary communication [4].

dry oxygen gives triphenylgermane, triphenylgermanol and Yb_2O_3. The exothermic reaction with carbon dioxide in THF gives the tetramer of ytterbium triphenylgermylformiate $[(Ph_3GeCO_2)_2Yb \cdot THF]_4$. Its detailed synthesis and X-ray diffraction study will be published elsewhere.

The IR spectrum of III shows absorptions assignable to Ph_3Ge groups and THF molecules. Also present in the spectrum are a small band at 2030 cm^{-1} characteristic of Ge–H stretches in Ph_3GeH [5] and one at 1300 cm^{-1} which can be attributed to the Yb–H groups. It should be noted that the intensity of the band at 2030 cm^{-1} remains constant after multiple recrystallisations of III. Unfortunately our attempts to use ^1H NMR spectroscopy to identify the hydride protons in III failed.

The structure of complex III was established by X-ray diffraction. Unit cell parameters and intensities of 5408 reflections were measured with a Synthex $P2_1$ diffractometer at $-120\,°C$ (λ Mo-K_α, $\theta/2\theta$-scan in the range $2 \leqslant 2\theta \leqslant 55°$). 4552 reflections with $F > 4\sigma(F)$ were used in the structure determination and refinement. The crystals of II are monoclinic, $a = 9.980(2)$, $b = 17.305(4)$, $c = 13.883(3)$ Å, $\beta = 96.37(3)°$, $Z = 2$, $d_{calc.} = 1.49$ g cm^{-3}, space group $P2_1$. Positions of Yb and Ge atoms were found by a direct method using the MULTAN program. The positions of the other nonhydrogen atoms were revealed by subsequent electron-density syntheses. The structure was refined by a block-diagonal least squares methods with anisotropic thermal parameters for non-hydrogen atoms. Positions of H atoms of Ph rings were calculated by geometrical conditions. These were not refined but were recalculated after each cycle of the refinement.

The refinement was performed without restriction on sin θ/λ in two variants: (a) with absorption corrections (μ(Mo-K_α) = 34.2 cm^{-1}) by DIFABS program [6] (final discrepancy factors: $R = 0.036$, $R_G = 0.031$) and (b) without absorption coorections ($R = 0.043$, $R_G = 0.041$). In order to locate the hydride H atoms the difference (zero) electron density syntheses were calculated subtracting all the non-hydrogen atoms and the Ph-ring H atoms. Calculation difference syntheses was performed in four variants: (i) with absorption correction and using reflections with sin $\theta/\lambda \leqslant 0.4$ Å^{-1} (the base variant); (ii) without absorption corrections using reflections with sin $\theta/\lambda \leqslant 0.4$ Å^{-1}; (iii) with absorption corrections using all reflections and (iv) without absorption corrections using all reflections. Both hydride H atoms were revealed in all four variants but variant (iv) gave illogical geometrical parameters. Therefore only the variants (i), (ii) and (iii) will be discussed further. It should be noted that in variants (i) and (ii) having a restriction in sin θ/λ (i.e. taking into account reflections which have maximum contribution from H atoms), the relative weights of maximums of electron density syntheses corresponding to hydride H atoms are significantly larger than in variant (iii). We believe that variant (i) is the best to use in the discussion of the structure (vide infra).

The positions of the hydride H atoms as determined by each of the variants differ slightly. To examine the structure the difference synthesis was calculated for a model of the structure from which one of H atoms of the Ph rings and the hydride H atoms had been omitted. In this synthesis the electron density maxima corresponding to the hydride H atoms were about ~ 1.5 higher than the maximum corresponding to the omitted H atom of Ph ring.

All calculations were performed using INEXTL programs [7]. Atomic coordinates obtained in refinement of structure with absorption corrections are given in Table 1, H atom coordinates for all variants are given in Table 2, bond lengths and

Table 1

Atomic coordinates of Yb, Ge ($\times 10^5$), O and C ($\times 10^4$), and their anisotropic thermal factors ($\times 10^2$ for Yb, Ge atoms and $\times 10$ for O and C atoms) $T = \exp -1/4(B_{11}h^2a^{\star 2} + B_{22}k^2b^{\star 2} + \ldots + 2B_{23}klb^{\star}c^{\star})$ in the structure of II.

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Yb	25146(2)	58681(12)	24950(10)	274(1)	177(1)	285(1)	24(1)	−50(1)	−2(1)
Ge1	13778(10)	72780(6)	12220(8)	294(4)	202(4)	326(5)	92(4)	−16(4)	74(4)
Ge2	36413(9)	44623(5)	37699(7)	197(3)	203(4)	197(4)	−2(3)	20(3)	−2(3)
O1	569(6)	5120(3)	1803(5)	34(3)	21(3)	57(4)	4(2)	−27(3)	−17(3)
O2	4062(8)	5585(4)	1338(5)	62(5)	22(3)	49(4)	−1(3)	21(4)	5(3)
O3	4232(7)	6600(4)	3460(6)	54(4)	33(4)	53(4)	−4(3)	−18(3)	−7(3)
O4	1006(7)	6222(4)	3725(5)	50(4)	34(3)	39(4)	9(3)	14(3)	0(3)
C1	2000(7)	7264(4)	−120(6)	16(3)	9(3)	30(4)	2(3)	−3(3)	4(3)
C2	2744(9)	7696(6)	−465(8)	33(4)	36(5)	38(6)	9(4)	−14(4)	−8(4)
C3	3282(11)	7652(7)	−1360(8)	58(6)	46(6)	30(5)	5(5)	10(5)	13(5)
C4	2839(9)	7172(6)	−1964(7)	34(5)	48(6)	27(4)	2(4)	4(4)	2(4)
C5	1928(11)	6630(6)	−1691(9)	43(5)	41(6)	45(6)	16(5)	3(5)	−8(5)
C6	1492(11)	6633(6)	−711(9)	43(6)	36(6)	56(8)	15(5)	8(5)	−10(5)
C7	−635(10)	7525(6)	875(8)	35(5)	17(4)	40(6)	−1(4)	1(5)	7(4)
C8	−1283(10)	7518(7)	−98(9)	33(5)	43(6)	46(7)	−7(5)	−12(5)	8(5)
C9	−2653(9)	7722(8)	−174(9)	24(4)	68(8)	64(7)	19(5)	−32(5)	2(6)
C10	−3372(9)	7872(7)	489(9)	16(4)	54(6)	61(8)	4(4)	−0(4)	1(6)
C11	−2669(9)	7797(7)	1501(8)	22(4)	70(7)	35(5)	8(4)	10(4)	−7(5)
C12	−1393(11)	7578(7)	1696(9)	33(5)	51(7)	46(6)	8(5)	9(5)	6(5)
C13	1995(9)	8342(5)	1648(6)	31(4)	27(4)	18(4)	6(3)	3(3)	3(3)
C14	3381(11)	8491(7)	1861(8)	47(5)	47(6)	29(5)	−6(5)	−6(4)	−7(4)
C15	3837(11)	9225(7)	2163(8)	44(5)	72(7)	38(6)	−33(5)	−7(5)	−6(5)
C16	2879(10)	9801(4)	2291(9)	60(6)	7(3)	69(8)	−10(3)	−2(6)	−18(4)
C17	1691(15)	9680(7)	2132(14)	88(10)	23(6)	140(15)	−8(6)	7(10)	−20(8)
C18	1245(10)	8998(6)	1782(9)	41(5)	33(5)	60(8)	−3(4)	−9(51)	−6(5)
C19	3019(9)	3421(5)	3327(7)	33(4)	27(4)	27(4)	−2(3)	2(3)	−2(3)
C20	1631(9)	3306(5)	3130(7)	28(4)	30(4)	31(5)	1(3)	4(3)	−2(4)

C21	1054(10)	2592(6)	2793(8)	39(5)	36(5)	38(5)	−2(4)	9(4)	−3(4)
C22	1843(11)	1982(7)	2676(9)	46(6)	62(8)	54(7)	−12(5)	−7(5)	−5(6)
C23	3352(10)	2080(6)	2897(8)	35(5)	35(5)	45(5)	3(4)	−1(4)	−9(4)
C24	3917(9)	2820(5)	3218(7)	30(4)	20(4)	44(5)	−2(3)	5(4)	−3(4)
C25	3105(8)	4557(5)	5082(7)	24(4)	33(4)	31(4)	−8(3)	5(3)	4(4)
C26	2077(8)	3947(5)	5452(6)	24(4)	26(4)	22(4)	−9(3)	1(3)	4(3)
C27	1742(9)	4025(6)	6416(8)	27(4)	54(5)	42(6)	−4(4)	6(4)	2(5)
C28	2303(11)	4731(6)	6992(8)	48(6)	43(5)	35(6)	7(5)	10(5)	−11(5)
C29	3120(10)	5229(6)	6622(8)	41(5)	30(5)	39(5)	3(4)	5(4)	−10(4)
C30	3472(8)	5117(5)	5731(6)	25(3)	24(4)	30(4)	1(3)	4(3)	−3(3)
C31	5589(7)	4276(4)	4113(6)	11(3)	17(3)	26(4)	5(2)	−1(3)	2(3)
C32	6430(9)	4106(5)	3398(6)	33(4)	38(4)	17(4)	0(3)	0(3)	−8(3)
C33	7863(9)	3937(6)	3580(8)	21(4)	50(6)	51(6)	4(4)	5(4)	−1(5)
C34	8373(10)	3910(6)	4447(8)	30(5)	43(5)	56(6)	3(4)	8(4)	−1(5)
C35	7594(10)	4035(5)	5266(7)	39(5)	37(4)	28(5)	−7(4)	11(4)	−1(4)
C36	6194(8)	4184(5)	5029(63)	26(4)	31(4)	23(4)	12(3)	2(3)	−2(3)
C37	874(12)	4478(7)	1065(10)	58(7)	58(7)	81(9)	0(6)	−8(6)	−29(7)
C38	−483(16)	4276(9)	711(13)	92(11)	110(10)	175(12)	13(8)	−75(9)	−95(9)
C39	−1266(12)	5026(9)	605(9)	79(7)	130(10)	90(8)	15(7)	−78(6)	−37(7)
C40	−646(11)	5399(5)	1266(9)	48(5)	21(4)	99(8)	−2(4)	−19(5)	−12(5)
C41	4853(13)	6055(5)	891(10)	94(9)	22(4)	95(10)	11(4)	44(8)	21(5)
C42	4909(10)	5708(7)	−164(8)	44(5)	66(7)	50(6)	3(5)	24(4)	9(5)
C43	4742(13)	4984(7)	−66(9)	72(7)	79(8)	68(6)	−6(6)	46(6)	−14(6)
C44	4328(15)	4940(5)	815(10)	145(11)	17(4)	67(9)	−1(5)	43(8)	13(4)
C45	4217(10)	7292(6)	3935(8)	54(5)	35(5)	61(7)	−7(4)	14(5)	−16(5)
C46	5410(11)	7647(7)	4101(9)	60(6)	52(7)	61(8)	−2(5)	8(6)	−16(6)
C47	6441(11)	6945(6)	4018(10)	36(5)	40(5)	103(8)	2(4)	−19(6)	8(5)
C48	5761(10)	6338(6)	3349(9)	39(5)	58(6)	68(7)	3(5)	−10(5)	3(5)
C49	118(10)	5587(6)	4118(8)	41(5)	45(6)	63(6)	3(4)	20(5)	14(5)
C50	−199(12)	5824(7)	5010(10)	75(7)	45(6)	106(8)	−6(6)	39(6)	20(7)
C51	624(15)	6728(9)	5121(11)	114(11)	99(11)	56(9)	−9(9)	−13(8)	−26(8)
C52	678(10)	6998(5)	4053(8)	56(5)	17(4)	53(5)	11(4)	16(4)	1(4)

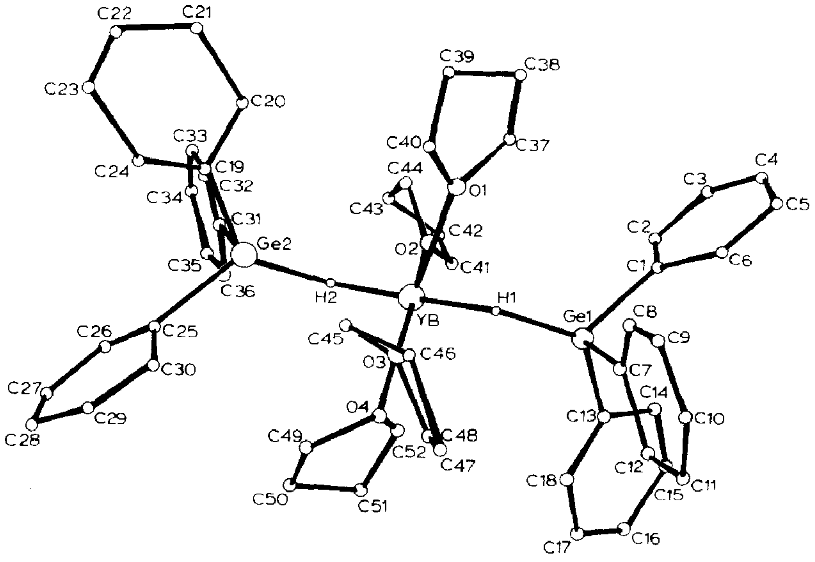


Fig. 1. The structure of III.

angles are listed in Table 3 and 4, respectively.

Complex III is an octahedral complex of Yb; the four THF occupy equatorial, and two Ph_3GeH ligands occupy axial positions (Fig. 1). The hydride atoms (H1 and H2) of the Ph_3GeH groups are μ_2-bridges connecting the Yb atom with the Ge1 and Ge2 atoms. The H1YbO(1,2) and H2YbO(3,4) angles (88, 89 and 78, 83° respectively) are less than, but the H1YbO(3,4) and H2YbO(1,2) angles (96, 91 and 97, 30 °) are greater than, the ideal value of 90 °; the OYbO angles in the equatorial plane are 83.4(2)–99.9(2) °.

The Yb–O distances in II (2.399(8)–2.479(7) Å) are slightly longer than in $Cp_2YbMe(THF)$ (2.311 Å [8]) and are almost as long as similar bonds in $(Me_5C_5)_2Yb(THF)$ (2.412 Å [9]), $(Me_3SiC_5H_4)_2Yb(THF)_2$ (2.42 and 2.39 Å [10]) and in octahedral complexes of $CpYbX(THF)_3$. In the latter the lengths of the *equatorial* and *axial* Yb–O(THF) bonds are 2.336, 2.365 and 2.417 Å for X = Cl [11], and, 2.335, 2.348 and 2.428 Å for X = Br [12].

Table 2

Coordinates of H atoms (derived by the different variants of refinement)

Atom	x	y	z	Variant
H2	0.309	0.524	0.332	(i)
H1	0.193	0.661	0.180	
H2	0.293	0.521	0.317	(ii)
H1	0.207	0.656	0.182	
H2	0.321	0.505	0.326	(iii)
H1	0.168	0.690	0.168	
H2	0.300	0.540	0.349	(iv)
H1	0.200	0.633	0.150	
0				

The coordination of Ge atoms in both Ph_3GeH groups is noticeably distorted from the ideal tetrahedral coordination. The CGeC angles at Ge1 (97.9(4)–100.2(4)°) and Ge2 (98.8(4)–104.8(4)°) atoms are smaller than the ideal tetrahedral angle, i.e. Ph groups appear to be bent away from the equatorial plane of the complex.

Table 3

The bond lengths *d* (Å) in the structure of II (the distances with H atoms calculated on their "base" coordinates, i.e. with absorption corrections and using reflections with sin θ/λ 0.4 $Å^{-1}$)

Bond	*d*	Bond	*d*
Yb–O1	2.440(6)	C6–C1	1.43(2)
Yb–O2	2.399(8)	C7–C8	1.43(2)
Yb–O3	2.413(8)	C8–C9	1.40(2)
Yb–O4	2.475(7)	C9–C10	1.26(2)
Yb–H1	1.67	C10–C11	1.51(2)
Yb–H2	1.64	C11–C12	1.33(2)
Ge1–H1	1.48	C12–C7	1.44(2)
Ge2–H2	1.56	C13–C14	1.41(2)
Ge1–C1	2.028(9)	C14–C15	1.40(2)
Ge1–C7	2.06(1)	C15–C16	1.41(2)
Ge1–C13	2.010(9)	C16–C17	1.20(2)
Ge2–C19	1.982(9)	C17–C18	1.33(2)
Ge2–C25	1.961(9)	C18–C13	1.38(2)
Ge2–C31	1.975(7)	C19–C20	1.40(2)
C1–C2	1.19(2)	C20–C21	1.42(2)
C2–C3	1.41(2)	C21–C22	1.34(2)
C3–C4	1.23(2)	C22–C23	1.51(2)
C4–C5	1.39(2)	C23–C24	1.45(2)
C5–C6	1.47(2)	C24–C19	1.39(2)
C25–C26	1.59(2)	C47–C48	1.51(2)
C26–C27	1.42(2)	C48–O3	1.62(1)
C27–C28	1.53(2)	O4–C49	1.55(1)
C28–C29	1.33(2)	C49–C50	1.38(2)
C29–C30	1.34(2)	C50–C51	1.76(20)
C30–C25	1.35(2)	C51–C52	1.56(20)
C31–C32	1.40(2)	C52–O4	1.47(1)
C32–C33	1.46(2)		
C33–C34	1.25(2)		
C34–C35	1.46(2)		
C35–C36	1.42(2)		
C36–C31	1.36(2)		
O1–C37	1.57(1)		
C37–C38	1.43(2)		
C38–C39	1.51(2)		
C39–C40	1.23(2)		
C40–O1	1.43(1)		
O2–C41	1.33(1)		
C41–C42	1.59(2)		
C42–C43	1.27(2)		
C43–C44	1.34(2)		
C44–O2	1.37(1)		
O3–C45	1.37(1)		
C45–C46	1.34(2)		
C46–C47	1.60(2)		

Table 4

The bond angles at CO (°) in the structure of II (the angles with H atoms calculated on their "base" coordinates)

Angles		Angles	
O1YbO2	99.9(2)	Ge2C19C20	117.4(6)
O1YbO3	169.1(2)	Ge2C19C24	122.0(7)
O1YbO4	83.4(2)	C20C19C24	120.6(8)
O2YbO3	90.5(2)	C19C20C21	123.0(8)
O2YbO4	176,7(2)	C20C21C22	120.3(9)
O3YbO4	86.4(2)	C21C22C23	118(1)
H1YbO1	88	C22C23C24	120.4(9)
H1YbO2	89	C23C24C19	117.4(8)
H1YbO3	96	Ge2C25C26	119.6(5)
H1YbO4	91	Ge2C25C30	126.9(7)
H2YbO1	97	C26C25C30	113.4(8)
H2YbO2	98	C25C26C27	117.9(8)
H2YbO3	78	C26C27C28	117.2(9)
H2YbO3	83	C27C28C29	121(1)
H1YbH2	171	C28C29C30	120(1)
H1Ge1C1	111	C29C30C25	130.1(9)
H1Ge1C7	126	Ge2C31C32	121.0(6)
H1Ge1C13	118	Ge2C31C36	124.7(6)
C1Ge1C7	100.2(4)	C32C31C36	113.6(7)
C1Ge1C13	99.6(4)	C31C32C33	125.1(8)
C7Ge1C13	97.9(4)	C32C33C34	117(1)
Ge1C1C2	129.1(7)	C33C34C35	123(1)
Ge1C1C6	114.3(7)	C34C35C36	116.1(8)
C2C1C6	116.6(9)	C35C36C31	124.2(8)
C1C2C3	130(1)	YbO1C37	115.5(6)
C2C3C4	120(1)	YbO1C40	128.0(6)
C3C4C5	117(1)	C37O1C40	96.5(7)
C4C5C6	121(1)	O1C37C38	99(1)
C5C6C1	114.3(9)	C37C38C39	106(1)
Ge1C7C8	123.1(8)	C38C39C40	100(1)
Ge1C7C12	114.4(7)	C39C40O1	122(1)
C8C7C12	122(1)	YbO2C41	130.2(7)
C7C8C9	114(1)	YbO2C44	134.2(7)
C8C9C10	129(1)	C41O2C44	95.2(9)
C9C10C11	115(1)	O2C41C42	106(9)
C10C11C12	123(1)	C41C42C43	105(1)
C11C12C7	116(7)	C42C43C44	102(1)
Ge1C13C14	119.5(7)	C43C44O2	122(1)
Ge1C13C18	129.7(7)	YbO3C45	132.9(6)
C14C13C18	110.8(9)	YbO3C48	114.9(6)
C13C14C15	120.6(9)	C45O3C48	110.6(8)
C14C15C16	119(1)	O3C45C46	115(1)
C15C16C17	122(1)	C45C46C47	102(1)
C16C17C18	120(1)	C46C47C48	109(1)
C17C18C13	127(1)	C47C48O3	96.4(8)
H2Ge2C19	125.3	YbO4C49	118.9(6)
H2Ge2C25	100.3	YbO4C52	127.9(6)
H2Ge2C31	122.1	C49O4C52	112.6(7)
C19Ge2C25	104.8(4)	O4C49C50	107.7(9)
C19Ge2C31	101.1(4)	C49C50C51	101(1)
C25Ge2C31	98.8(4)	C50C51C52	104(1)
		C51C52O4	93.0(8)

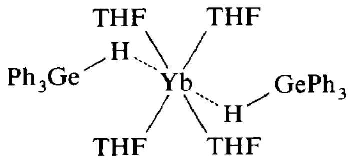
Corresponding distortions of H(1,2)Ge(1,2)C(Ph) angles are unequal: distortions of H1Ge1C(7,13) (126,118°), H2Ge2C(19,31) (125,122°) and H2Ge2C25 (100°) angles are significantly greater than the distortion of the H1Ge1C1 angle (111°). Considerable divergence in bond angles at the Ge atoms is apparently the result of repulsion of Ph rings and THF ligands and can be regarded as evidence for relatively the strong bonding of Yb atom with Ph_3GeH ligands in molecule of III.

As noted above, the hydride H atoms form μ_2-bridges between the Yb and the Ge atoms. The angles at H1 and H2 atoms are 176.8 and 156.1°, correspondingly, the H1YbH2 angle is 170.9°. The interatomic Yb–H(1,2) distances (1.6 and 1.6 Å) are longer than the Ge1–H1 (1.48 Å) and Ge2–H2 (1.56 Å) distances. The geometry of these YbHGe groups has been determined from difference synthesis, (i.e. variant (i) (vide supra)). The difference synthesis calculated by variant (ii) reveals a more symmetrical form of this fragment: the Yb–H and Ge–H distances in this case are 1.5, 1.5 and 1.6, 1.6 Å respectively; the YbH1Ge1 (169°) and YbH2Ge2 (169°) angles are equal, but the H1YbH2 angle (179°) is almost linear. The geometry of the YbHGe groups with the positions of H1 and H2 atoms from difference synthesis calculated in variant (iii) are somewhat different from the geometry determined from variant (i). The YbHGe angles in this case are equal but their values are significantly smaller (135°), H1YbH2 angle is 179°. The Yb–H1 and Yb–H2 distances are equal (1.6 Å) and shorter than the Ge1–H1 (1.7 Å) and Ge2–H2 (1.7 Å) separations.

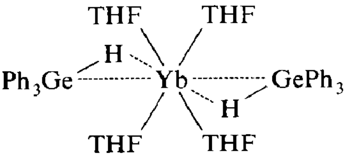
We have mentioned the ability of the H atoms to form μ_2- and μ_3-bridges in organolanthanoid derivatives. But only two structures are known in which μ_2-H-bridge is the only connecting-link between united parts of a molecule: viz. the linear Lu–H–Lu bridge in $[(Cp_3Lu)_2(\mu_2\text{-}H)]^-$ anion [13], the Lu–H distances in which are equal (2.09 Å), and the symmetrical Lu–H–Al bridge in the complex, $[Cp_2Lu(\mu_2\text{-}H)AlH_3(NEt_3)]_2$ [14]. The angle at the bridge H atom in this structure is 127°, the Lu–H and Al–H distances are equal, viz. 1.81 Å. The Yb–H distances in molecules of III are appreciably shorter than in the structures mentioned. The Ge–H distances in III are close to the Ge–H distances in GeH_4 1.527 Å [15] and Me_2GeH_2 1.532 Å [16,17] experimental established as well as calculated (1.482 and 1.486 Å respectively) [18].

The Yb $\cdots$ Ge distances in III (3.142(1), 3.149(1) Å) in variant (i) with absorption corrections and (3.140(2) and 3.152(2) Å) in variant (ii) without absorption corrections are actually equal. The separations are only ~ 0.25 Å longer than sum of metallic radii by Pauling (r(Yb) = 1.699 Å, r(Ge) = 1.22 Å [19]). Such rather short separations do not exclude the possible existence of a direct interaction between these atoms. It is interesting that the Er–Mo distance 3.143 Å in complex $[Cp(CO)Mo]_3Er\ (H_2O)_4\cdot(EtOH)$, that was classified as a direct Er–Mo bond [20], coincides with the Yb–Ge separations in III.

From the X-ray data quoted above two variants of bonding are possible in complex III, viz. **A** and **B**:



(A)



(B)

The first (**A**) implies the existence of μ_2-bridge H atoms, a formally zerovalent Yb atom, and the absence of direct Yb–Ge bonds (i.e. an "open" agostic $\mathrm{Ge}\overset{\mathrm{H}}{\diagup\quad\diagdown}\mathrm{Yb}$ bond). The second (**B**) implies the existence of a three-center two-electron bond (i.e. a "semi-closed" agostic $\mathrm{Ge}\overset{\mathrm{H}}{\underset{\cdots\cdots}{\diagup\ \diagdown}}\mathrm{Yb}$ bond). The Yb atom in this case is formally di-valent.

The three-center bonding, R_3EH ligands ($E = Si$, Ge) attacked to atoms of transition metals is confirmed by structural (such as a neutronographic study of $(MeC_5H_4)Mn(CO)_2HSiFPh_2$ [21]) and NMR [22] investigations, kinetic data on dissociation of the complexes [23], and their reactivity [24]. For the Yb complex III we think that variant **A** with the formally zerovalent ytterbium is possible. The confirmation for this supposition is found in the chemical properties of III and first of all the reaction with CO_2 which proceeds exothermically in contrast to the sluggishly proceeding carboxylation of Yb(II) compounds.

Experimental

All experiments were carried out in vacuo by Schlenk techniques. The solvents and reagents used had been thoroughly dried and deoxygenated. IR spectra were recorded on a Perkin-Elmer 577 spectrometer.

$[H_2Yb(THF)]_n$ (II). A suspension of I (0.7 g (1,35 mmol) in 10 ml of THF was placed in an evacuated 200 ml flask. The flask was filled with dihydrogen under atmospheric pressure and sealed. The mixture was shaken at room temperature for 12 h, during which the precipitate of I dissolved almost completely and the solution became a dark reddish-brown. After centrifugation, the solution was decanted from the unchanged I and 15 ml of hexane was added to the solution. The dark reddish-brown precipitate formed was separated from solution by decantation (after prior centrifugation of the mixture) washed with hexane and dried in vacuo. The yield of the dark-brown powder of II is 0.30 g (88%), m.p. > 200 ° C (dec.). (Found: C, 19,89; H, 3,45; Yb, 69,52. $C_4H_{10}OYb$ calc.: C, 19,44; H, 4,04; Yb, 70,02%). IR (Nujol): 1250, 1070, 1020, 790, 500, 450, 350 cm^{-1}.

The mother liquor was found to contain 0.17 g (96%) of naphthalene.

When the reaction of I with H_2 was carried out without solvent the powder of I was transformed into a waxy dark-brown liquor during 15 h. THF was added to the reaction mixture and the II that formed was isolated as described above.

Reaction of I with Ph_3GeH at 80 ° C. The mixture of I (1.41 g, 2.73 mmol), Ph_3GeH (1.5 g, 4.92 mmol) and 10 ml of THF was heated for 4h at 80 ° C with periodical shaking. The mixture was centrifuged, the solution was decanted from the unchanged I and the solvent was removed in vacuo. Sublimation of the solid residue (70 ° C, 0.1 torr) gave 0.31 g (91%) of naphthalene. The non-volatile part of the residue was extracted with toluene (20 ml × 2) to leave 0.2 g (13.4%) of Ph_6Ge_2 (m.p., mix. m.p. 315–318 ° C). Hexane (10 ml) was added to the toluene extracts to give a dark-brown precipitate (0.79 g) which was washed with hexane and dried in vacuo. Treatment of this product with D_2O in THF gave 71 ml (3.17 mmol) of HD, identified by mass-spectrometry, and ytterbium hydroxide. The ytterbium content (0.295 g, 1,70 mmol) of the precipitate was determined by titrometry. The ratio of HD/Yb is 1.86, i.e. the yield of HD is 84.5%, derived from the H_2Yb groups. In addition 0.37 g (24.8%) of Ph_6Ge_2 was found in organic layer.

$(Ph_3GeH)_2Yb(THF)_4$ (III). 1.07 g (2.06 mmol) of I was added to a solution of 2.77 g (9.08 mmol) of Ph_3GeH in 20 ml of THF. The mixture was shaken for 20 h at room temperature; the precipitate of I dissolved almost completely. The mixture was centrifuged, the red-brown solution was decanted from the precipitate and the solvent was removed in vacuo. The addition of 15 ml of toluene to the waxy, brown residue led to the formation of brownish-yellow crystals of III (1.37 g, 61%). Repeated crystallisations from toluene gave the product, m.p. 129–131° C (with dec.). (Found: C, 57.48; H, 5.7. $C_{52}H_{64}O_4Ge_2Yb$ calc.: C, 58.41; H, 5.80%). IR (Nujol): 3050, 2030, 1570, 1430, 1300, 1250, 1180, 1140, 1085, 1060, 1020, 990, 860, 740, 690, 670, 470, 320, 285, 270 cm^{-1}.

The naphthalene evolved was determined qualitively by GLC in toluene solution.

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