Synthesis and crystal structure of triphenyl[tris(tetrahydrofuran)]ytterbium, Ph₃Yb(THF)₃

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Triphenyl[tris(tetrahydrofuran)]ytterbium, $Ph_3Yb(THF)_3$ (1), was synthesized in high yields by the reaction of Yb with an excess of Ph_2Hg or Ph_3Bi in the presence of catalytic amounts of $Ybl_2(THF)_4$ as well as by the reaction of $Ph_2Yb(THF)_2$ (2) with Ph_2Hg or Ph_3Bi . The crystal structure of complex 1 was studied by X-ray structural analysis.

Key words: ytterbium, redox reactions; phenyl derivatives, X-ray structural analysis.

Organolanthanide compounds¹ involve the most poorly studied R_2Ln and R_3Ln homoleptic aryl derivatives.²⁻¹² Only the $(o-Me_2NCH_2C_6H_4)_3Lu$,⁴ $(THF)Ph_2Yb(\mu-Ph)_3Yb(THF)_3$,¹¹ and $Ph_3Ln(THF)_3$ $(Ln = Er \text{ or }Tm)^{12}$ complexes have been structurally characterized. Data on other related compounds are unavailable, which is, apparently, due to limitations of methods for synthesis and experimental difficulties associated with purification and isolation of these derivatives in the individual form. However, homoleptic aryl derivatives of lanthanides are, undoubtedly, of interest from the theoretical standpoint and also as potent highly reactive reagents and catalysts in organic synthesis.

The $Ph_3Yb(THF)_3$ complex (1) was first prepared by the reaction of the naphthalene derivative of ytterbium, $C_{10}H_8Yb(THF)_2$, with Ph_2Hg in low yield.¹¹ In this work, complex 1 was synthesized by the redox reactions of $Ph_2Yb(THF)_2$ (2) or metallic ytterbium with Ph_2Hg or Ph_3Bi .

It is known^{9,10} that the reaction of Ph₂Hg with an excess of ytterbium, which was activated with a small amount of CH₂I₂, or with amalgamated ytterbium gave diphenylytterbium in yields of up to 75%. The resulting compound was identified *in situ* from the products of subsequent reactions with H₂O, Ph₃SnCl, and 9-fluorenone. An analogous reaction of Ph₂Hg with an excess of Yb in the presence of catalytic amounts of YbI₂(THF)₄ also gave a phenyl derivative of divalent ytterbium,¹² which was isolated as complex 2 (yields were up to 97%).

When studying redox transmetallation with the participation of rare-earth elements as a method for preparing phenyl derivatives of lanthanides, we found that the reaction of Yb with a small excess of Ph_2Hg or Ph_3Bi in the presence of catalytic amounts of $YbI_2(THF)_4$ afforded compound 1 (yields were up to 66%).

$$3 \operatorname{Ph}_{2}\operatorname{Hg} + 2 \operatorname{Yb} \xrightarrow{\text{THF, Ybl}_{2}(\text{THF})_{4}} 2 \operatorname{Ph}_{3}\operatorname{Yb}(\text{THF})_{3} + 3 \operatorname{Hg}$$

$$1$$

$$\operatorname{Ph}_{3}\operatorname{Bi} + \operatorname{Yb} \xrightarrow{\text{THF, Ybl}_{2}(\text{THF})_{4}} \operatorname{Ph}_{3}\operatorname{Yb}(\text{THF})_{3} + \operatorname{Bi}$$

The reaction of Ph₂Hg with Yb was completed in 5 days. In the case of Ph₃Bi, the reaction was completed in 3 weeks. Compound 1 is an air-unstable crystalline yellow compound, which decomposed upon heating to 115-120 °C in an evacuated tube. Compound 1 is moderately soluble in THF and dimethoxyethane, poorly soluble in benzene, and insoluble in hexane. The IR spectrum of complex 1 has absorption bands typical of Ph groups (v/cm⁻¹: 3010 w, 1405 m, 1225 w, 1065 w, 1045 m, 1015 s, 985 w, 910 w, 715 m, 700 s, 670 s, 665 m, 425 m) and coordinated THF (v/cm⁻¹: 1035 w, 865 s). The value of the effective magnetic moment (4.30 μ_B) confirms the trivalent state of ytterbium in complex 1.

The reactions of Yb with diphenylmercury and triphenylbismuth proceed, apparently, through intermediate diphenylytterbium followed by its oxidation with an excess of Ph_2Hg or Ph_3Bi to a phenyl derivative of trivalent ytterbium 1. To verify this suggestion, we studied the reactions of $Ph_2Yb(THF)_2$ with Ph_2Hg and Ph_3Bi . It was found that compound 2 reduced diphenylmercury and triphenylbismuth to give complex 1 as a final product.

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$$n \operatorname{Ph}_{2} \operatorname{Yb}(\operatorname{THF})_{2} + \operatorname{Ph}_{n} \operatorname{M} \quad \frac{\operatorname{THF}}{20 \circ C} \circ n \operatorname{Ph}_{3} \operatorname{Yb}(\operatorname{THF})_{3} + \operatorname{M}$$

$$2 \qquad 1$$

$$I = \operatorname{Hg}, n = 2$$

$$I = \operatorname{Bi} n = 3$$

Ν

Ν

The reactions of compound 2 with Ph₂Hg and Ph₃Bi were completed in 170 and 300 h, respectively. Complex 1 was isolated as an air-unstable finely crystalline brown compound (the decomposition temperature is 115-120 °C) in yields of 75.0 and 78.7%, respectively. The effective magnetic moment (4.0 µ_B) corresponds to the trivalent state of the lanthanide. The IR spectrum of the reaction product is identical to the spectrum of complex 1 obtained by the reaction of Yb with an excess of Ph₂Hg or Ph₃Bi. It should be noted that triphenylytterbium, which was prepared by the reactions with the participation of complex 2, apparently contained traces of by-products from which we failed to purify the target product.

The crystals of 1, which are isostructural to the crystals of $Ph_3Ln(THF)_3$ (Ln = Er or Tm),¹² consist of monomeric molecules. The Ln atoms in these complexes are in a distorted octahedral environment (Fig. 1). The C-Ln-C angles (99.2(2)-103.5(2)°, 99.8(2)- $102.9(2)^{\circ}$, and $99.5(4)-103.2(4)^{\circ}$ for Ln = Er, Tm, and Yb, respectively) are substantially larger than 90°, and therefore, the O-Ln-O angles $(80.6(1)-77.7(1)^\circ)$, $81.0(2) - 78.0(2)^\circ$, and $80.9(2) - 77.6(2)^\circ$ for Ln = Er, Tm, and Yb, respectively) are smaller than 90°. In the Y(OSiPh₃)₃(THF)₃ and Ce(OSiPh₃)₃(THF)₃ octahedral complexes, the O(R)-Ln-O(R) and O(THF)-Ln-O(THF) angles vary within similar ranges (100.8-102.3° and 79.6-82.2°, respectively, in Y(OSiPh₃)₃(THF)₃,¹³ and 100.4-103.3° and 76.5-83.1°, respectively, in $Ce(OSiPh_3)_3(THF)_3^{14}).$

In the mononuclear $Ph_3Ln(THF)_3$ molecules (Ln = Er, Tm, or Yb) the Ln-C σ -bond lengths are as follows: 2.412(5), 2.442(5), and 2.440(6) Å for Ln = Er; 2.421(6), 2.425(6), and 2.416(7) Å for Ln = Tm; and 2.39(1),



Fig. 1. Overall view of molecule 1.

2.40(1), and 2.43(1) Å for Ln = Yb. The differences in the average values of the Er-C, Tm-C, and Yb-C distances in the Ph₃Ln(THF)₃ molecules (2.431, 2.421, and 2.410 Å for Ln = Er, Tm, and Yb, respectively) are close to the differences in the values of the radii of the six-coordinate Er³⁺, Tm³⁺, and Yb³⁺ ions (0.01 Å) according to Shannon (0.890, 0.880, and 0.868 Å, respectively).15 The Ln-C bond lengths in the abovementioned molecules agree with the Ln-C(Ar) distances observed in other organolanthanide complexes: Lu-C (aver.), 2.435 Å in $(o-Me_2NCH_2C_6H_4)_3Lu;^4$ Yb-C (aver.), 2.42 Å for the terminal Ph group in $(THF)Ph_2Yb(\mu-Ph)_3Yb(THF)_3;^{11}$ Gd-C (aver.), 2.412 Å in PhGdCl₂(THF)₄;¹⁶ Sm-C (aver.), 2.511 Å in (Me₅C₅)₂SmPh(THF);¹⁷ Lu-C (aver.), 2.345 Å in $Cp_2LuC_6H_4Me-p(THF)$;¹⁸ and Y-C (aver.), 2.41 Å in $Cp_2YC_6H_4CH_2NMe_2-o.$ ¹⁹

Experimental

All operations were carried out in evacuated sealed tubes with the use of thoroughly dried and degassed solvents. The IR spectra were recorded on a Perkin-Elmer-577 spectrometer; samples were prepared under an argon atmosphere as Nujol mulls. Magnetochemical measurements were carried out as described previously.²⁰

The $YbI_2(THF)_4$ complex was prepared by the reaction of Yb with I_2 in THF.

Reaction of Yb with an excess of Ph2Hg. A mixture of Yb chips (0.27 g, 1.56 mmol), Ph_2Hg (0.99 g, 2.78 mmol), and YbI₂(THF)₄ (0.03 g, 0.04 mmol) in THF (10 mL) was kept without stirring at -5 °C for 5 days. The solution developed a reddish-brown color, and a finely dispersed black precipitate of metallic mercury and large yellow crystals were formed. The solution was separated from the crystals and Hg by decantation. The crystals were dissolved in THF (8 mL) at 50-60 °C. The solution was separated from the precipitate of Hg (0.45 g, 96.2%) by centrifugation and decantation, slowly cooled to 5 °C, and kept at this temperature for 20 h. The yellow crystals that formed were separated from the solution, washed with cold THF (2×2 mL), and dried in vacuo at ~20 °C for 10-15 min. Complex 1 was obtained in a yield of 0.64 g (66.3%). Found (%): Yb, 28.08. $C_{30}H_{39}O_3$ Yb. Calculated (%): Yb, 28.00. Single crystals of compound 1 were studied by X-ray structural analysis.

Reaction of Yb with an excess of Ph₃Bi. A mixture of Yb chips (0.22 g, 1.27 mmol), Ph₃Bi (0.75 g, 1.70 mmol), and YbI₂(THF)₄ (0.03 g, 0.04 mmol) in THF (10 mL) was kept without stirring at -5 °C for 3 weeks. The solution developed a reddish-brown color, and a finely dispersed black precipitate of metallic bismuth and large yellow crystals were formed. Subsequent isolation and purification of the reaction products were carried out analogously to those described above. Metallic Bi (0.26 g, 97.8%) and yellow crystals of complex 1 (0.50 g, 63.3%; decomp.p. 115–120 °C) were obtained. Found (%): Yb, 27.88. The IR spectrum of product 1 is identical to the spectrum of triphenylytterbium obtained by the reaction of Yb with Ph₂Hg.

Synthesis of diphenyl[bis(tetrahydrofuran)]ytterbium (2). A mixture of Yb chips (1.53 g, 8.84 mmol), Ph_2Hg (0.50 g, 1.40 mmol), and $Ybl_2(THF)_4$ (0.03 g, 0.04 mmol) in THF (10 mL) was stirred using a magnetic stirrer for 6 h. The redbrown solution was separated from an excess of Yb and

 Table 1. Principal bond lengths (d) and bond angles (ω) in molecule 1

Bond	d/Å	Angle	ω/deg	Angle	ω/deg
Yb(1)-O(1)	2.409(7)	O(1)-Yb(1)-O(2)	80.9(2)	O(1) - Yb(1) - O(3)	79.7(2)
Yb(1) - O(2)	2.388(8)	O(2) - Yb(1) - O(3)	77.6(3)	O(1) - Yb(1) - C(1)	166.8(3)
Yb(1) - O(3)	2.388(7)	O(2) - Yb(1) - C(1)	91.9(3)	O(3) - Yb(1) - C(1)	88.0(3)
Yb(1)-C(1)	2.39(1)	O(1) - Yb(1) - C(7)	91.1(3)	O(2) - Yb(1) - C(7)	86.1(4)
Yb(1) - C(7)	2.43(1)	O(3) - Yb(1) - C(7)	162.3(4)	C(1) - Yb(1) - C(7)	99.5(4)
Yb(1) - C(13)	2.40(1)	O(1) - Yb(1) - C(13)	85.5(3)	O(2) - Yb(1) - C(13)	163.7(3)
		O(3) - Yb(1) - C(13)	91.2(3)	C(1) - Yb(1) - C(13)	99.6(4)
		C(7) - Yb(1) - C(13)	103.2(4)		

metallic mercury that formed (0.28 g, 100%) by centrifugation and decantation. Then THF was removed from the solution. The residue was washed with hexane and dried *in vacuo* at ~20 °C for 3-5 min. Complex 2 was obtained as a diamagnetic dark-brown powder in a yield of 0.64 g (96.9%), decomp.p. 90-95 °C. Found (%): Yb, 38.03. $C_{20}H_{26}O_2$ Yb. Calculated (%): Yb, 36.84. IR, v/cm⁻¹: 3020 w, 1405 m, 1290 m, 1250 m, 1220 w, 1020 s, 965 m, 910 w, 795 m, 720 s, 695 s, 660 w, 610 w, 440 w (Ph); 1065 w. 865 s (coordinated THF).

Reaction of complex 2 with Ph₂Hg. A mixture of compound 2 (0.66 g. 1.40 mmol) and Ph₂Hg (0.5 g, 1.40 mmol) in THF (15 mL) was kept at ~20 °C for 5 h. The finely dispersed precipitate that formed was separated by centrifugation. The precipitate contained 0.07 g (49.7%) of metallic Hg. Then the rate of formation of metallic Hg slowed down substantially. After 145 h, the yield of mercury was 96.0%, and after 170 h (when the reaction was completed), the total amount of Hg that formed was 0.14 g (100.0%). Then THF was removed from the reaction solution. The residue was washed with hexane (5×15 mL) and dried *in vacuo* at ~20 °C for 10–15 min. Complex I was obtained as a brown powder in a yield of 0.66 g (75.7%), decomp.p. 115–120 °C. Found (%): Yb, 27.50. $\mu_{eff} \approx$ 4.0 μ_{B} . The IR spectrum of the product is identical to that of complex I obtained by the reaction of Yb with Ph₂Hg.

Reaction of complex 2 with Ph₃Bi. A mixture of compound 2 (1.32 g, 2.80 mmol) and Ph₃Bi (0.8 g, 1.82 mmol) in THF (15 mL) was kept at -20 °C. The course of the reaction was monitored taking into account the amount of metallic bismuth formed. After 300 h, bismuth was obtained in a yield of 0.19 g (100.0%). Subsequent operations associated with isolation and purification of the target product were carried out analogously to those described above. Complex 1 was obtained as a brown powder in a yield of 1.37 g (78.7%), decomp.p. 115–120 °C. Found (%): Yb, 27.25. μ_{eff} = 3.88 μ_B . The IR spectrum of the product is identical to that of complex 1 prepared by the reaction of Yb with Ph₂Hg.

X-ray structural analysis of complex 1 was carried out on a Syntex P2₁ diffractometer (-80 °C, Mo-K α radiation, graphite monochromator, $\theta/2\theta$ scanning technique in the range of 2° < 2 θ < 46°). The crystals are monoclinic, at -80 °C, a = 35.999(16) Å, b = 11.218(4) Å, c = 14.039(8) Å, $\beta = 101.96(3)^\circ$, V = 5546(1) Å³, space group C2/c, Z = 4, $d_{calc} = 1.487$ g cm⁻³, μ (Mo-K α) = 3.39 mm⁻¹. A total of 4309 independent reflections were measured, of which 2163 reflections with $I > 2\alpha(I)$ were used in the refinement. The structure of 1 was solved by direct methods and refined by the full-matrix least-squares method with anisotropic thermal parameters for all nonhydrogen atoms. The positions of H atoms were refined using the riding model with fixed thermal parameters, U = 0.08 Å². At the final stage of the refinement, the following

Table 2. Atomic coordinates $(\times 10^4)$ and equivalent isotropic thermal parameters $(U_{iso} \times 10^3)$ in the structure of 1

Atom	x	у	z	$U_{\rm iso}/{\rm \AA}^2$
Yb(1)	-3698(1)	-1766(1)	-7057(1)	21(1)
O(1)	-3344(2)	-1100(7)	-5501(5)	29(3)
O(2)	-4202(2)	-1694(7)	-6189(5)	27(2)
O(3)	-3623(2)	-3607(6)	-6185(5)	31(3)
C(1)	-4086(3)	-2806(9)	-8389(8)	27(4)
C(2)	-4303(4)	-3886(10)	-8451(9)	35(5)
C(3)	-4506(4)	-4329(11)	-9319(11)	46(5)
C(4)	-4505(4)	-3743(14)	-10186(10)	50(6)
C(5)	-4308(4)	-2687(14)	-10170(10)	50(6)
C(6)	-4105(4)	-2254(11)	-9290(10)	37(5)
C(7)	-3871(4)	269(9)	-7540(8)	32(5)
C(8)	-4245(4)	682(11)	-7696(9)	39(5)
C(9)	-4342(4)	1855(14)	-7948(8)	48(5)
C(10)	-4068(5)	2692(12)	-8046(10)	47(6)
C(11)	-3696(5)	2305(11)	-7928(8)	43(5)
C(12)	-3603(4)	1137(11)	-7654(8)	37(5)
C(13)	-3090(3)	-2000(9)	-7483(8)	29(4)
C(14)	-2765(3)	-1286(10)	-7188(8)	31(4)
C(15)	-2417(3)	-1457(10)	-7443(9)	37(5)
C(16)	-2382(4)	-2420(12)	-8050(9)	40(5)
C(17)	-2688(4)	-3151(11)	-8375(8)	36(4)
C(18)	-3023(4)	-2913(9)	-8109(8)	33(5)
C(19)	-3319(4)	90(10)	-5089(9)	45(5)
C(20)	-2913(4)	345(13)	-4801(10)	56(6)
C(21)	-2728(4)	-853(13)	-4531(11)	56(6)
C(22)	-3027(4)	-1769(12)	-4933(8)	42(4)
C(23)	-4569(4)	-2270(12)	-6467(10)	47(5)
C(24)	-4788(4)	-1861(19)	-5742(12)	76(8)
C(25)	-4638(4)	-675(14)	-5452(11)	59(7)
C(26)	-4226(4)	-795(11)	-5453(9)	37(5)
C(27)	-3426(4)	-4653(10)	-6496(8)	35(4)
C(28)	-3448(5)	-5597(12)	-5752(11)	63(7)
C(29)	-3511(4)	-4915(10)	-4869(10)	51(5)
C(30)	-3762(3)	-3910(10)	-5326(8)	41(5)

Note. Values of U_{iso} were determined as 1/3 of the trace of the ortogonalized U(i,j) tensor.

weighting scheme was used: $w^{-1} = \sigma^2(F) + 0.001F^2$. An absorption correction was applied using the DIFABS program.²¹ The final values of the *R* factors were as follows: R = 0.042, $R_w = 0.045$, S = 1.03. All calculations were carried out on a PC computer using the SHELXTL PLUS program package.²² The principal bond lengths and bond angles in the structure of 1 are given in Table 1. The atomic coordinates and equivalent isotropic thermal parameters are listed in Table 2.

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