

Synthesis and crystal structure of triphenyl[tris(tetrahydrofuran)]ytterbium, $\text{Ph}_3\text{Yb}(\text{THF})_3$

L. N. Bochkarev,^{a*} T. A. Zheleznova,^a A. V. Safronova,^a M. S. Drozdov,^a S. F. Zhil'tsov,^a
L. N. Zakharov,^b G. K. Fukin,^b and S. Ya. Khorshev^b

^aNizhnii Novgorod State Pedagogical University,
1 ul. Ulyanova, 603600 Nizhnii Novgorod, Russian Federation.
Fax: +7 (831 2) 36 4446. E-mail: lnb@orgchem.nnov.ru

^bG. A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences,
49 ul. Tropinina, 603600 Nizhnii Novgorod, Russian Federation.
Fax: +7 (831 2) 66 1497. E-mail: imoc@infotel.ru

Triphenyl[tris(tetrahydrofuran)]ytterbium, $\text{Ph}_3\text{Yb}(\text{THF})_3$ (**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 $\text{YbI}_2(\text{THF})_4$ as well as by the reaction of $\text{Ph}_2\text{Yb}(\text{THF})_2$ (**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.

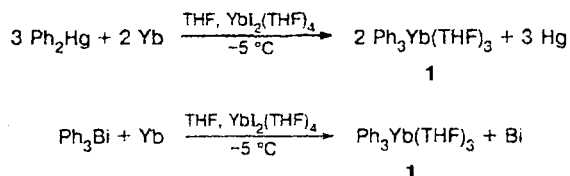
Organolanthanide compounds¹ involve the most poorly studied R_2Ln and R_3Ln homoleptic aryl derivatives.^{2–12} Only the (*o*- $\text{Me}_2\text{NCH}_2\text{C}_6\text{H}_4$)₃Lu,⁴ $(\text{THF})\text{Ph}_2\text{Yb}(\mu\text{-Ph})_3\text{Yb}(\text{THF})_3$,¹¹ and $\text{Ph}_3\text{Ln}(\text{THF})_3$ ($\text{Ln} = \text{Er}$ 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 $\text{Ph}_3\text{Yb}(\text{THF})_3$ complex (**1**) was first prepared by the reaction of the naphthalene derivative of ytterbium, $\text{C}_{10}\text{H}_8\text{Yb}(\text{THF})_2$, with Ph_2Hg in low yield.¹¹ In this work, complex **1** was synthesized by the redox reactions of $\text{Ph}_2\text{Yb}(\text{THF})_2$ (**2**) or metallic ytterbium with Ph_2Hg or Ph_3Bi .

It is known^{9,10} that the reaction of Ph_2Hg with an excess of ytterbium, which was activated with a small amount of CH_2I_2 , 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 H_2O , Ph_3SnCl , and 9-fluorenone. An analogous reaction of Ph_2Hg with an excess of Yb in the presence of catalytic amounts of $\text{YbI}_2(\text{THF})_4$ 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 $\text{YbI}_2(\text{THF})_4$ afforded compound **1** (yields were up to 66%).



The reaction of Ph_2Hg with Yb was completed in 5 days. In the case of Ph_3Bi , 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 (ν/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 (ν/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 $\text{Ph}_2\text{Yb}(\text{THF})_2$ with Ph_2Hg and Ph_3Bi . It was found that compound **2** reduced diphenylmercury and triphenylbismuth to give complex **1** as a final product.

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

Bond	$d/\text{\AA}$	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. $90-95^\circ\text{C}$. Found (%): Yb, 38.03. $\text{C}_{20}\text{H}_{26}\text{O}_2\text{Yb}$. Calculated (%): Yb, 36.84. IR, ν/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 Ph_2Hg . A mixture of compound **2** (0.66 g, 1.40 mmol) and Ph_2Hg (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 **1** was obtained as a brown powder in a yield of 0.66 g (75.7%), decomp.p. $115-120^\circ\text{C}$. Found (%): Yb, 27.50. $\mu_{\text{eff}} = 4.0 \mu_{\text{B}}$. The IR spectrum of the product is identical to that of complex **1** obtained by the reaction of Yb with Ph_2Hg .

Reaction of complex 2 with Ph_3Bi . A mixture of compound **2** (1.32 g, 2.80 mmol) and Ph_3Bi (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. $115-120^\circ\text{C}$. Found (%): Yb, 27.25. $\mu_{\text{eff}} = 3.88 \mu_{\text{B}}$. The IR spectrum of the product is identical to that of complex **1** prepared by the reaction of Yb with Ph_2Hg .

X-ray structural analysis of complex 1 was carried out on a Syntex P₂ diffractometer (-80°C , Mo- $K\alpha$ radiation, graphite monochromator, $\theta/2\theta$ scanning technique in the range of $2^\circ < 2\theta < 46^\circ$). The crystals are monoclinic, at -80°C , $a = 35.999(16) \text{\AA}$, $b = 11.218(4) \text{\AA}$, $c = 14.039(8) \text{\AA}$, $\beta = 101.96(3)^\circ$, $V = 5546(1) \text{\AA}^3$, space group $C2/c$, $Z = 4$, $d_{\text{calc}} = 1.487 \text{ g cm}^{-3}$, $\mu(\text{Mo-}K\alpha) = 3.39 \text{ mm}^{-1}$. A total of 4309 independent reflections were measured, of which 2163 reflections with $I > 2\sigma(I)$ 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 calculated from geometrical considerations. The H atoms were refined using the riding model with fixed thermal parameters, $U = 0.08 \text{\AA}^2$. At the final stage of the refinement, the following

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

Atom	x	y	z	$U_{\text{iso}}/\text{\AA}^2$
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 orthogonalized $U(i,j)$ 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.

This work was financially supported by the Russian Foundation for Basic Research (Project Nos. 96-03-32672 and 97-03-32928).

References

1. M. N. Bochkarev, L. N. Zakharov, and G. S. Kalinina, *Organoderivatives of Rare Earth Elements*, Kluwer Academic Publishers, Dordrecht—Boston—London, 1995.
2. F. A. Hart, A. G. Massey, and M. S. Saran, *J. Organomet. Chem.*, 1970, **21**, 147.
3. L. E. Manzer, *J. Am. Chem. Soc.*, 1978, **100**, 8068.
4. A. L. Wayda, J. L. Atwood, and W. E. Hunter, *Organometallics*, 1984, **3**, 939.
5. M. Booij, N. H. Kiers, H. J. Heeres, and J. H. Teuben, *J. Organomet. Chem.*, 1989, **364**, 79.
6. G. B. Deacon and D. G. Vince, *J. Organomet. Chem.*, 1976, **112**, C1.
7. G. B. Deacon, W. D. Raverty, and D. G. Vince, *J. Organomet. Chem.*, 1977, **135**, 103.
8. G. B. Deacon, A. J. Koplick, W. D. Raverty, and D. G. Vince, *J. Organomet. Chem.*, 1979, **182**, 121.
9. G. Z. Suleimanov, R. N. Khandozhko, R. Yu. Mekhdiiev, P. V. Petrovskii, T. A. Agdamskii, N. E. Kolobova, and I. P. Beletskaya, *Dokl. Akad. Nauk SSSR*, 1985, **284**, 1376 [*Dokl. Chem.*, 1985 (Engl. Transl.)].
10. T. A. Starostina, R. R. Shifrina, L. F. Rybakova, and E. S. Petrov, *Zh. Obshch. Khim.*, 1987, **57**, 2402 [*J. Gen. Chem. USSR*, 1987, **57** (Engl. Transl.)].
11. M. N. Bochkarev, V. V. Khramenkov, Yu. F. Rad'kov, L. N. Zakharov, and Yu. T. Struchkov, *J. Organomet. Chem.*, 1992, **429**, 27.
12. L. N. Bochkarev, T. A. Stepantseva, L. N. Zakharov, G. K. Fukin, A. I. Yanovsky, and Yu. T. Struchkov, *Organometallics*, 1995, **14**, 2127.
13. M. J. McGeary, P. S. Coan, K. Folting, W. E. Streib, and K. G. Caulton, *Inorg. Chem.*, 1989, **28**, 3283.
14. P. S. Gradeff, K. Yunlu, T. J. Deming, J. M. Olofson, R. J. Doedens, and W. J. Evans, *Inorg. Chem.*, 1990, **29**, 420.
15. R. D. Shannon, *Acta Crystallogr.*, 1976, **A32**, 751.
16. G. Lin, Z. Jin, Y. Zhang, and W. Chen, *J. Organomet. Chem.*, 1990, **396**, 307.
17. W. J. Evans, I. Bloom, W. E. Hunter, and J. L. Atwood, *Organometallics*, 1985, **4**, 112.
18. H. Schumann, W. Genthe, N. Bruncks, and J. Pickardt, *Organometallics*, 1982, **1**, 1194.
19. M. D. Rausch, D. F. Foust, R. D. Rogers, and J. P. Atwood, *J. Organomet. Chem.*, 1984, **265**, 241.
20. A. V. Protchenko and M. N. Bochkarev, *Pribory i tekhnika eksperimenta [Instruments and Experimental Techniques]*, 1990, 194 (in Russian).
21. N. Walker and D. Stuart, *Acta Crystallogr.*, 1983, **A39**, 158.
22. G. M. Sheldrick, *Structure Determination Software Program Package (PC Version)*, Siemens Analytical X-ray Instruments, Inc., Madison (WI), 1989.

Received July 14, 1997