ORGANOMETALLICS

Volume 14, Number 5, May 1995

Communications

Synthesis and Crystal Structure of $Ph_3Ln(THF)_3$ (Ln = Er, Tm)

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Received October 11, 1994[⊗]

Summary: Triphenyllanthanoids $Ph_3Ln(THF)_3$ *(Ln = Er (**1**), Tm (**2**)) were synthesized in THF by reaction of metallic lanthanoids with* Ph_2Hg *or* Ph_3Bi *in the presence of catalytic amounts of* LnI_3*. The X-ray diffraction studies of **1** and **2** have shown that these species represent monomeric complexes with a distorted fac-octahedral arrangement of ligands around the Ln atom.*

Known synthetic pathways to homoleptic lanthanoid aryls of R_2Ln and R_3Ln type are not of general utility for the entire lanthanoid series. Thus, the reaction of PhLi and $LnCl_3$ yields Ph_3Sc and Ph_3Y, whereas the anionic $[Ph_4Ln]Li$ complexes were isolated in the case of La and Pr.[1] Chelating (aminotolyl)lithium reagents allowed the synthesis of σ-aryls $[o\text{-}Me_2NCH_2C_6H_4]_3Ln$ of Sc, Y, Pr, Yb and Lu);[2-4] however, no characterizable products have been isolated in the case of Pr, Nd, Sm, and Tb.[3]

Transmetalation reactions of R_2Hg and metallic lanthanoids have been successfully used for preparation of polyfluorophenyl complexes R_2Ln (R = C_6F_5, $o\text{-}HC_6F_4$, $p\text{-}HC_6F_4$; Ln = Sm, Eu, Yb)[5-7] and (benzene)tricarbonylchromium derivatives $[(OC)_3CrPh]_2Ln(THF)_n$ (Ln = Sm, Eu, Yb; n = 1, 2).[8] Diphenylmercury was found to be unreactive toward free Yb,[6] while slow interaction was observed with the amalgamated metal,[8] and violent reaction has been reported[9] for ytterbium activated with CH_2I_2. Phenylytterbium species are formed in these processes in 35–75% yields and identified *in situ* by reactions with H_2O, Ph_3SnCl, and 9-fluorenone. They have been formulated as Ph_2Yb.[8,9]

[⊗] Abstract published in *Advance ACS Abstracts*, March 15, 1995.

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0276-7333/95/2314-2127$09.00/0

It has been recently reported that the (naphthalene)ytterbium compound $C_{10}H_8Yb(THF)_2$ reacts readily with Ph_2Hg to form the binuclear complex $(THF)Ph_2Yb(\mu\text{-}Ph)_3Yb(THF)_3$ as a major product, with only a small amount of $Ph_3Yb(THF)_3$.[10] Among $(aryl)_3Ln$ compounds, X-ray structural data are available only for $(o\text{-}Me_2NCH_2C_6H_4)_3Lu$[3] and the binuclear derivative $(THF)Ph_2Yb(\mu\text{-}Ph)_3Yb(THF)_3$[10]. The latter compound is thought to consist of associated $Ph_2Yb^{II}(THF)$ and $Ph_3Yb^{III}(THF)_3$ units.

We have recently observed the enhanced activity of lanthanoid metals in some reactions with organic and organometallic substrates in the presence of catalytic amounts of lanthanoid halides.[11-13] This catalytic activity of lanthanoid salt appears to be operative also in transmetalation of Ph_2Hg or Ph_3Bi and metallic lanthanoids. The reactions proceed in THF at room temperature in the presence of lanthanoid triiodides and lead to $Ph_2Ln(THF)_2$ (Ln = Eu, Yb) and $Ph_3Ln(THF)_3$ complexes (Ln = Ho, Er, Tm, Lu) in 75−95% yields. Herein we report the synthesis and the crystal structure of $Ph_3Ln(THF)_3$ (Ln = Er, Tm). The reactions of Eu, Yb, Ho, and other lanthanoids with Ph_2Hg and Ph_3Bi are currently under detailed investigation.

Er and Tm were found to react with Ph_2Hg in the presence of appropriate lanthanoid triiodides (3.0−5.0 mol %) over a period of 120−150 h. The yields of crude complexes **1** and **2** are usually 90−95%.[14]

$$3Ph_2Hg + 2Ln \xrightarrow[20\ ^\circ C]{THF,LnI_3} 2Ph_3Ln(THF)_3 + 3Hg$$

$$Ln = Er, Tm$$

The reaction of Er with Ph_3Bi in the presence of ErI_3 (4.0 mol %) is completed in ca. 200 h with the formation of complex **1** in 70% yield. The course of the reactions was monitored by the yield of metallic mercury or bismuth. After recrystallization from THF, complexes **1** and **2** were isolated in 40−45% yields as air-sensitive pale pink (**1**) and colorless (**2**) crystals. They are sparingly soluble in THF, poorly soluble in toluene, and insoluble in hexane. They decompose at 95−100 °C (**1**) and 120−125 °C (**2**). IR spectra of **1** and **2** are essentially identical and show the absorption bands of phenyl rings (3010 w, 1405 m, 1225 w, 1065 w, 1045 m, 1015 s, 985 w, 910 w, 715 m, 700 s, 670 s, 665 m, 625 m, 425 m cm^{-1}) and coordinated THF (1035 w, 865 br, s cm^{-1}).

The structures of **1** and **2** were determined by X-ray diffraction method.[15] Crystals of **1** and **2** are isostructural and consist of monomeric molecules. The Ln atoms in complexes **1** (Ln = Er) and **2** (Ln = Tm) have a distorted *fac*-octahedral environment (Figure 1). The C(1)−Ln−C(7), C(1)−Ln−C(13), and C(7)−Ln−C(13) angles (99.2(2), 99.8(2), and 103.5(2)° for Ln = Er; 99.8(2), 101.4(2), and 102.9(2)° for Ln = Tm) are significantly more than 90°, whereas the O(1)−Ln−O(2), O(1)−Ln−O(3), and O(2)−Ln−O(3) angles (80.6(1), 79.3(1), 77.7(1)° for Ln = Er; 81.0(2), 79.5(1), 78.0(2)° for Ln = Tm) are significantly less than 90°. Similar patterns in the O(R)−Ln−O(R) and O(THF)−Ln−O(THF) angles were found in the *fac*-octahedral complexes $Y(OSiPh_3)_3(THF)_3$ (100.8−102.3 and 79.6−82.2°)[16] and $Ce(OSiPh_3)_3(THF)_3$ (100.4−103.3° and 76.5−83.1°).[17]

The Ln−C(1), Ln−C(7), and Ln−C(13) distances are 2.412(5), 2.442(5), and 2.440(6) Å for Ln = Er in **1** and 2.421(6), 2.425(6), and 2.416(7) Å for Ln = Tm in **2**. The difference between the average Er−C (2.431(14) Å) and Tm−C (2.421(4) Å) distances in **1** and **2** is equal to the difference in the radii for six-coordinate Er^{3+} and Tm^{3+}, 0.01 Å, given by Shannon.[18] The Er−C and Tm−C distances in **1** and **2** may be compared with the Ln−C(aryl) distances found in other organolanthanoid complexes: the average Lu−C distance, 2.435 Å, in $(o\text{-}Me_2NCH_2C_6H_4)_3Lu$;[3] the average Yb−C distance, 2.42 Å, for terminal Ph groups in $(THF)Ph_2Yb(\mu\text{-}Ph)_3Yb(THF)_3$;[10] the Gd−C distance, 2.412 Å, in $PhGdCl_2(THF)_4$;[19] the Sm−C distance, 2.511 Å, in $(Me_5C_5)_2SmPh(THF)$;[20] the Lu−C distance, 2.345 Å, in $Cp_2LuC_6H_4Me\text{-}p(THF)$;[21] the average Y−C distance,

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(14) All operations in the synthesis and isolation of **1** and **2** were performed in vacuo in sealed ampules using thoroughly dried solvents. Preparation of **1**: A mixture of Ph_2Hg (0.5 g, 1.41 mmol), ErI_3 (0.03 g, 0.06 mmol), and erbium in the form of filings (1.35 g, 8.07 mmol) in 15 mL of THF was stirred using a magnetic stirrer for ca. 120 h at room temperature. The excess Er and the metallic mercury formed were separated from the brown solution by centrifugation and washed with warm THF (2 × 15 mL); 0.27 g (95.5%) of mercury was found in the excess erbium. The reaction solution and washings were combined and evaporated to dryness in vacuo at room temperature to yield 0.55 g (94.8%) of crude complex **1** as a brown solid. Anal. Calcd for $C_{30}H_{39}ErO_3$: C, 58.60; H, 6.39; Er, 27.20. Found: Er, 28.5. Crude complex **1** was dissolved in 5 mL of THF at 50 °C and slowly cooled to 0 °C to yield 0.26 g (45.0%) of **1** in the form of pale-pink hexagonal prisms. Dec pt: 95−100 °C. Anal. Found: C, 58.33; H, 6.34; Er, 26.95. Complex **2** was synthesized in a similar way from 0.5 g (1.41 mmol) of Ph_2Hg and 1.40 g (8.29 mmol) of Tm in the presence of 0.03 g (0.06 mmol) of TmI_3. The reaction time was 150 h. Yield of crude complex **2**: 0.53 g (91.4%). Anal. Calcd for $C_{30}H_{39}TmO_3$: C, 58.44; H, 6.38; Tm, 27.40. Found: Tm, 29.00. After recrystallization from THF complex **2** was obtained as colorless crystals (0.22 g, 40.0%). Dec pt 120−125 °C. Anal. Found: C, 58.31; H, 6.10; Tm, 27.17.

(15) X-ray data for **1** and **2** were collected at 153 K on a Siemens P3/PC diffractometer (Mo Kα radiation, graphite monochromator, $\Theta-2\Theta$ scan mode, $2 \le \Theta \le 25$ and $2 \le \Theta \le 24°$, 5001 and 4911 independent reflections measured, 3958 ($F > 4\sigma(F)$) and 3626 ($F > 6\sigma(F)$) reflections observed for **1** and **2**, respectively). Crystal data at 153 K for **1**: $C_{30}H_{39}O_3Er$, fw 614.9, space group $C2/c$, $a = 36.047(7)$ Å, $b = 11.244(2)$ Å, $c = 14.029(3)$ Å, $\beta = 102.12(3)°$, $V = 5559(3)$ Å^3, $Z = 8$, $D_{calc} = 1.469$ g/cm^3, $\mu = 3.085$ mm^{-1}. Crystal data at 153 K for **2**: $C_{30}H_{39}O_3Tm$, fw 616.5, space group $C2/c$, $a = 36.128(12)$ Å, $b = 11.257(5)$ Å, $c = 14.026(5)$ Å, $\beta = 102.07(3)°$, $V = 5578(4)$ Å^3, $Z = 8$, $D_{calc} = 1.468$ g/cm^3, $\mu = 3.239$ mm^{-1}. The structures of **1** and **2** were solved by direct methods. In both structures all non-H atoms were refined anisotropically. The phenyl H atoms were located in the difference Fourier maps (refined isotropically), and the tetrahydrofuran H atoms were calculated (refined in riding model with fixed isotropic parameters $U = 0.08$ Å^2). Absorption was taken into account by the DIFABS program (Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *39*, 158). The final refinements converged at $R = 0.044$, $R_w = 0.049$, and $S = 1.18$ for **1** and $R = 0.036$, $R_w = 0.046$, and $S = 1.33$ for **2**, for observed reflections. The $(\Delta/\sigma)_{av}$ values in the final cycles are 0.006 (**1**) and 0.002 (**2**). All calculations were performed using the SHELXTL-Plus package (Sheldrick, G. M. Structure Determination Software Program Package (PC version); Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1989).

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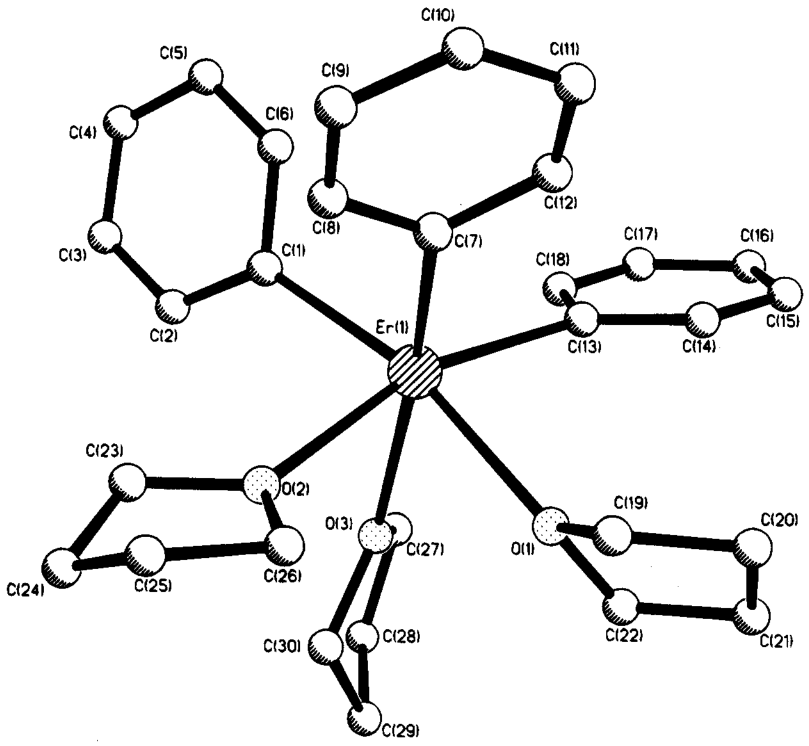

Figure 1. General view of **1** and atom labeling (**2** has a similar structure). Pertinent parameters (distances in Å and angles in deg): Ln−C(1), Ln−C(7), Ln−C(13) 2.412(5), 2.442(5), 2.440(6) (Ln = Er) and 2.421(6), 2.425(6), 2.416(7) (Ln = Tm); Ln−O(1), Ln−O(2), Ln−O(3) 2.423(3), 2.408(4), 2.419(3) (Ln = Er) and 2.429(4), 2.391(5), 2.401(4) (Ln = Tm); C(1) Ln−C(7), C(1)−Ln−C(13), C(7)−Ln−C(13) 99.2(2), 99.8(2), 103.5(2) (Ln = Er) and 99.8(2), 101.4(2), 102.9(2) (Ln = Tm); O(1)−Ln−O(2), O(1)−Ln−O(2), O(2)−Ln−O(3) 80.6(1), 79.3(1), 77.7(1) (Ln = Er) and 81.0(2), 79.5(1), 78.0(2) (Ln = Tm).

2.41 Å, in $Cp_2YC_6H_4CH_2NMe_2$-*o*.[22] The Yb−C distances for *μ*-bridging Ph groups in $(THF)Ph_2Yb(\mu\text{-}Ph)_3Yb(THF)_3$[10] (2.48−2.75 Å) and in $(THF)_2Ph_3SnYb(\mu\text{-}Ph)_3Yb(THF)_3$[23] (2.60−2.66 Å) are longer than the lengths of the above-mentioned terminal Ln−C bonds.

The Ln−O(1), Ln−O(2), and Ln−O(3) distances (2.423(3), 2.408(4), 2.419(3) Å for Ln = Er and 2.429(4), 2.391(5), 2.401(4) Å for Ln = Tm) in **1** and **2** are somewhat shorter than the average Ln−O(THF) distances for the $Ln(THF)_3$ *cis* fragment in the complexes $(THF)Ph_2Yb(\mu\text{-}Ph)_3Yb(THF)_3$[11] (2.44 Å) and $(THF)_2Ph_3SnYb(\mu\text{-}Ph)_3Yb(THF)_3$[24] (2.468 Å) with an octahedral environment around the Yb atom. The Er(Tm)-O(THF) distances in **1** and **2** are longer than those in cyclopentadienyllanthanoid complexes[24] if the differences in metal size and coordination number are considered. The steric crowding seems to be the predominant factor in such Ln−O(THF) bond lengthening. However, the trans influence of the *fac* phenyl groups can also be a reason. Unfortunately, the available X-ray data are not sufficient to evaluate such an influence in **1** and **2**.

Acknowledgment. We thank the Russian Foundation of Fundamental Research (Grant 93-03-5722) for financial support of this work.

Supplementary Material Available: Tables of crystallographic data, data collection, and solution and refinement details, positional and thermal parameters, and bond distances and bond angles for **1** and **2** (16 pages). Ordering information is given on any current masthead page.

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