Reactions of CpCuPPh₃ with Lanthanides and Their Compounds

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Abstract—CpCuPPh₃ reacts with Pr, Er, Yb, Cp₂Yb, and SmI₂(THF)₄ to form, in high yields, lanthanide cyclopentadienyl derivatives Cp₂Yb, Cp₃Ln (Ln = Pr, Er, Yb), and CpSmI₂(THF)₂. The initial agent CpCuPPh₃ can be prepared in 95–98% yield by the reaction of *t*-BuOCu with CpH in the presence of PPh₃.

Organolanthanide compounds, in particular, heterobimetallic derivatives show promise as catalysts of various organic reactions. One of the most general routes to organolanthanide derivatives of various types is redox metal interchange of rare-earth metals with organometallic compounds of main group and transition metals [1]. Our previous studies showed that reactions of lanthanides with the copper compounds CuC = CPh and $Ph_3GeCu(PPh_3)_3$ do not result in complete metal interchange and yield bimetallic complexes such as $\{[(PhC=C)_3Cu]Yb(THF)_2\}_2$ [2] or $\{ [Yb(THF)_6]^{2+} [(Ph_3Ge)_2Cu]_2^{-} \} \cdot 2THF [3].$ Here we report that $CpCuPPh_3$ (I), in contrast to CuC=CPh and $Ph_3GeCu(PPh_3)_3$, in reactions with Pr, Er, and Yb is completely reduced to the metal, and the lanthanides are converted to mononuclear cyclopentadienyl derivatives and not to bimetallic complexes.

$$\begin{aligned} 2CpCuPPh_{3} + Yb & \xrightarrow{THF, YbI_{2}}{20^{\circ}C, 15 \text{ h}} Cp_{2}Yb \\ & + 2Cu + 2PPh_{3}, \\ & 94\% & 94\% \\ & 3CpCuPPh_{3} + Ln \\ & \xrightarrow{THF, LnI_{3}}{20^{\circ}C, 30 \text{ h}} Cp_{3}Ln & + 3Cu & + 3PPh_{3} \\ & 76-99\% & 90-91\% & 97-98\% \\ & Ln &= Pr, Er. \end{aligned}$$

The reaction of **I** with Yb is complete in 15 h, and the reactions with Pr and Er, in 25-30 h. The high product yields allow these reactions to be suggested as preparative routes to cyclopentadienyl derivatives of bi- and trivalent lanthanides.

 Cp_2Yb , similar to metallic lanthanides, readily reduces I to form metallic copper and Cp_3Yb .

$$\begin{array}{c} CpCuPPh_3 + Cp_2Yb \\ \xrightarrow{\text{THF}} Cp_3Yb(\text{THF}) + Cu + PPh_3 \\ \xrightarrow{20^\circ\text{C}, 12 \text{ h}} 77\% & 84\% & 83\% \end{array}$$

It should be noted that CpNa and Cp₃La, in contrast to Cp₂Yb, do not react with **I**. The reaction of SmI₂(THF)₄ with **I** in a 1 : 1 ratio yields a mixed cyclopentadienyl derivative of trivalent samarium, CpSmI₂(THF)₂.

$$\begin{array}{c} \text{CpCuPPh}_3 + \text{SmI}_2(\text{THF})_4 \\ \xrightarrow{\text{THF}} & \text{CpSmI}_2(\text{THF})_2 + \text{Cu} + \text{PPh}_3. \\ & 89\% \qquad 91\% \quad 94\% \end{array}$$

Compound I was prepared for the first time in 61% yield by the reaction of BrCuPPh₃ with CpTl [4]. We found a better route to I: reaction of *t*-BuOCu with CpH in the presence of PPh₃. The target product can be isolated in 95–98% yield and used without additional purification.

EXPERIMENTAL

The IR spectra were recorded on a Perkin–Elmer-577 spectrophotometer. Samples were prepared under argon as mulls in mineral oil. Magnetochemical measurements were performed according to [5]. Volatile reaction products were analyzed with a Tsvet-129 gas chromatograph (300×0.3 -cm columns, stationary phase 5% SE-30 on Inerton-AW or 20% Apiezon on Chromosorb-W; katharometer; carrier gas helium). All manipulations were performed in sealed evacuated ampules using thoroughly dried and deoxygenated solvents.

Reaction of CpCuPPh₃ with Yb. A mixture of 1.07 g of CpCuPPh₃ and 1.20 g of Yb turnings in 20 ml of THF was stirred at room temperature for 15 h. Excess Yb and the fine black precipitate were separated from the red-violet solution by centrifugation. In the precipitate, 0.16 g (94%) of metallic copper was determined. From the supernatant, the solvent was removed by vacuum evaporation, and the residue was washed with hexane (4×20 ml) and dried in a

vacuum for 20 min at room temperature and for 4 h at 150°C. Cp₂Yb (0.40 g, 97%) was obtained as a brick red diamagnetic solid unstable in air. The IR spectrum of the product is identical to that of an authentic sample [6]. Found Yb, %: 57.00. $C_{10}H_{10}$ Yb. Calculated Yb, %: 57.06. The hexane extracts were combined, and the solvent was evaporated to leave 0.67 g (94%) of PPh₃.

The reactions of CpCuPPh₃ with Pr and Er were performed similarly. From 0.92 g of CpCuPPh₃ and 2.0 g of Pr, 0.25 g (95%) of Cp₃Pr was obtained. The IR spectrum of the product is identical to that of an authentic sample [7]. Found Pr, %: 41.89. $C_{15}H_{15}Pr$. Calculated Pr, %: 41.91. From 0.90 g of CpCuPPh₃ and 1 g of Er, 0.20 g (74%) of Cp₃Er was obtained. The IR spectrum of the product is identical to that of an authentic sample [7]. Found Er, %: 46.07. $C_{15}H_{15}Er$. Calculated Er, %: 46.13.

Reaction of Cp₂Yb with CpCuPPh₃. A colorless solution of 0.38 g of CpCuPPh₃ in 10 ml of THF was added to a dark red solution of 0.30 g of Cp₂Yb in 5 ml of THF. The reaction mixture became dark green, and a fine black precipitate formed. The mixture was kept for 12 h at room temperature for the reaction completion. The precipitate was separated by centrifugation. In the precipitate, 0.052 g (84%) of metallic copper was found. From the supernatant, the solvent was removed by vacuum evaporation, and the residue was washed with hexane $(4 \times 20 \text{ ml})$ and vacuum-dried. Cp₃Yb(THF) (0.33 g, 77%) was obtained as a dark green solid unstable in air. The effective magnetic moment (4.4 BM) corresponds to Yb^{3+} . IR spectrum, v, cm⁻¹: C_5H_5 , 3070 m, 1430 m, 1010 s, 770 s, 620 s; coordinated THF, 1070 m, 925 m, 890 m, 860 m. Found Yb, %: 39.0. C₁₉H₂₃OYb. Calculated Yb, %: 39.32. The hexane extracts were combined, and the solvent was vacuum-evaporated to leave 0.21 g (83%) of PPh₃.

Reaction of CpCuPPh₃ with SmI₂(THF)₄. A colorless solution of 0.51 g of CpCuPPh₃ in 10 ml of THF was added to a dark green solution of 0.91 g of SmI₂(THF)₄ in 5 ml of THF. The mixture was kept for 10 h at room temperature. The solution became yellow-green, and a fine black precipitate formed, which was separated by centrifugation. In the precipitate, 0.075 g (91%) of metallic copper was found. From the supernatant, the solvent was removed by vacuum evaporation, and the residue was washed with hexane (4 × 20 ml) and vacuum-dried for 20 min at

room temperature. $CpSmI_2(THF)_2$ (0.71 g, 89%) was obtained as a yellow solid unstable in air. The effective magnetic moment (1.8 BM) corresponds to Sm³⁺. IR spectrum, v, cm⁻¹: C₅H₅, 1430 m, 1010 s, 770 s, 620 s; coordinated THF, 1040 m, 925 m, 870 m. Found Sm, %: 24.31. C₁₃H₂₁I₂O₂Sm. Calculated Sm, %: 24.51. The hexane extracts were combined, and the solvent was vacuum-evaporated to leave 0.32 g (94%) of PPh₃.

CpCuPPh₃. A colorless solution of 1.92 g of PPh₃ in 10 ml of THF and 0.41 g of CpH were added to a light yellow solution of 1.00 g of *t*-BuOCu in 10 ml of THF. The mixture was kept for 5 h at room temperature. The solution gradually became colorless. The solvent was removed by vacuum evaporation, and the residue was washed with 20 ml of hexane and vacuum-dried. CpCuPPh₃ (2.80 g, 98%) was obtained as a colorless solid unstable in air. The IR spectrum of the product is identical to that of an authentic sample [4]. Found Cu, %: 16.15. $C_{23}H_{20}$ CuP. Calculated Cu, %: 16.25. In the volatile products, 0.51 g (96%) of *t*-BuOH was detected by GLC.

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