## **Reactivity of Triphenylmethyl** and Triphenylgermyl Derivatives of Lanthanides

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Abstract—Reactions of bis(triphenylmethyl)ytterbium and bis(triphenylgermyl)ytterbium with mercuric chloride, triphenylbismuth, iodine, tert-butyl alcohol, phenylacetylene, and cyclopentadiene were studied. The higher reactivity of the former compound in these reactions is explained by that the chemical bond in it is ionic, whereas in its germyl analog, covalent.

Triphenylmethyl [1] and triphenylgermyl [2] derivatives of lanthanides were synthesized earlier. X-ray diffraction was used to establish that the carbon analog  $[Ph_3C]_2^-[Yb(THF)_6]^{2+}$  has ionic bonds, whereas the cooresponding germyl compound  $(Ph_3Ge)_2Yb(THF)_4$  has covalent Ge-Yb bonds.

Here we turned to previously unexplored reactions of the above organolanthanides with mercuric chloride, triphenylbismuth, iodine, and reagents with active hydrogen atoms (tert-butyl alcohol, phenylacetylene, and cyclopentadiene CpH).

Bis(triphenylmethyl)ytterbium and bis(triphenylgermyl)ytterbium react with mercuric chloride in THF or benzene at room temperature just during reagent mixing. However, the directions of these prosesses differ from each other. The first compound acs as a reducer and is oxidized to bis(triphenylmethyl)ytterbium chloride by the stoichiometric reaction equation (1).

$$2(Ph_3C)_2Yb(THF)_6 + HgCl_2$$

$$\xrightarrow{THF} 2(Ph_3C)_2YbCl(THF)_3 + Hg.$$
90–95% 90% (1)

The covalent analog undergoes an exchange reaction by scheme (2).

$$(Ph_3Ge)_2Yb(THF)_4 + HgCl_2$$

$$\xrightarrow{C_6H_6} (Ph_3Ge)_2Hg + YbCl_2(THF)_4.$$
(2)
95%

Metallic mercury that might also be formed by decomposition of bis(triphenylgermyl)mercury was found only in trace amounts.

It is interesting to note that diphenylytterbium [3] whose C-Yb bond is more covalent in nature than in the triphenylmethyl derivative reacts with mercuric chloride (molar ratio 1:2) by two directions: redox (3a) and exchange (3b).

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$$2Ph_{2}Yb(THF)_{2} + HgCl_{2}$$

$$\xrightarrow{a} Ph_{2}YbCl(THF)_{2} + Hg,$$

$$\xrightarrow{b} Ph_{2}Hg + YbCl_{2}(THF)_{2}.$$

$$30\% \quad 40\%$$

$$(3)$$

Evidence for the high reductive activity of bis(triphenylmethy)ytterbium is provided by its reaction products with triphenylbismuth.

$$3(Ph_3C)_2Yb(THF)_6 + Ph_3Bi$$

$$\xrightarrow{THF} 3(Ph_3C)_2YbPh(THF)_3 + Bi.$$

$$70\% \qquad 90\% \qquad (4)$$

Unlike bis(triphenylmethy)ytterbium, bis(triphenylgermyl)ytterbium exhibits no reductive properties even toward iodine. At equimolar reagent ratio, hexaphenylgermanium and ytterbium(II) iodide are formed. Only when an excess of iodine is present, the resulting  $YbI_2$  is oxidized to form  $YbI_3$ .

The first stage invoves Ge-Yb bond fission in the starting compound.

$$(Ph_3Ge)_2Yb(THF)_4 + I_2 \xrightarrow{THF} Ph_3GeYbI + Ph_3GeI.$$
 (5)

Further mixed compounds undergo symmetrization.

 $Ph_3GeYbI + Ph_3GeI \longrightarrow Ph_3Ge-GePh_3 + YbI_2$ . (6)

The yields of the final products are close to quantitative (90-100%).

Iodine quantitatively oxidizes diphenylytterbium to an Yb(III) derivative [3].

$$2Ph_2Yb(THF)_2 + I_2 \xrightarrow{THF} 2Ph_2YbI(THF), \quad (7)$$

Bis(triphenylmethyl)ytterbium and bis(triphenylgermyl)ytterbium readily react with *tert*-butyl alcohol. The former compound begins to react during reagent mixing at  $-70^{\circ}$ C, and the latter, at  $20^{\circ}$ C.

$$(Ph_{3}C)_{2}Yb(THF)_{6} + 2t-BuOH$$

$$\xrightarrow{THF} t-(BuO)_{2}Yb + 2Ph_{3}CH, \qquad (8)$$

$$(Ph_{3}Ge)_{2}Yb(THF)_{4} + 2t-BuOH$$

$$\xrightarrow{THF} t-(BuO)_{2}Yb + 2Ph_{3}GeH. \qquad (9)$$

72%

The above reactions give rise to ytterbium(II) *tert*butoxide. The product is blue in color, it is insoluble in THF, benzene, and hexane, and melts at 300°C with decomposition.

88%

Since (triphenylmethyl)ytterbium proved to be very active in the reactions studied, we brought it into reaction with other reagents having active hydrogen: phenylacetylene and cyclopentadiene CpH. As the reagents were mixed in THF at  $-70^{\circ}$ C, the solution changed color. The reaction mixture was allowed to warm to room temperature and analyzed.

$$(Ph_{3}C)_{2}Yb(THF)_{6} + 2PhC \equiv CH$$

$$\xrightarrow{THF} (PhC \equiv C)_{2}Yb(THF)_{2} + 2Ph_{3}CH, \qquad (10)$$

$$(Ph_{3}C)_{2}Yb(THF)_{6} + 2CpH$$

$$\xrightarrow{THF} Cp_{2}Yb(THF) + 2Ph_{3}CH. \qquad (11)$$

$$57\% \qquad 80\%$$

These reactions can be used to synthesize phenylethynyl and cyclopentadienyl lanthanide derivatives in fairly high yields.

Thus, we showed that bis(triphenylgermyl)ytterbium and bis(triphenylmethyl)ytterbium are highly active in the reactions studied, which suggests wide use of such reactions in organic and organometallic synthesis. Moreover, we found that the direction of some of the reactions studied is much dependent on the nature of chemical bond in the organolathanide reagent.

## EXPERIMENTAL

All operations were performed in evacuated sealed ampules using thoroughly dried and degassed solvents.

The IR spectra were obtained on an IKS-25 spectrometer for samples suspended in mineral oil under argon. The electronic absorption spectra were obtained on an SF-16 spectrophotometer. The starting triphenylmethyl and triphenylgermyl derivatives of ytterbium were synthesized according to [1, 2].

**Reaction of (Ph<sub>3</sub>C)<sub>2</sub>Yb(THF)<sub>6</sub> with HgCl<sub>2</sub>.** A suspension of HgCl<sub>2</sub> (0.2219 g) in THF was added to a solution of  $(Ph_3C)_2Yb(THF)_6$  (1.78 g) in THF (25 ml), and the mixture was left to stand for 1 h at 20°C. The mixture changed color from bright red to yellowing brown. Mercury (0.15 g, 92%) was separated by centrifugation as a dark gray precipitate. The solvent was removed to isolate 1.41 g (95%) of  $(Ph_3C)_2YbCl(THF)_3$ , mp 195–200°C (decomp.). The electronic absorption spectrum contains a band at 930–1050 nm, characteristic of Yb<sup>3+</sup>. Found, %: Cl 3.03; Yb 18.71. C<sub>50</sub>H<sub>54</sub>ClO<sub>3</sub>Yb. Calculated, %: Cl 3.88; Yb 18.98.

**Reaction of (Ph<sub>3</sub>C)<sub>2</sub>Yb(THF)<sub>6</sub> with Ph<sub>3</sub>Bi.** A solution of Ph<sub>3</sub>Bi (0.15 g) in THF was added to a solution of (Ph<sub>3</sub>C)<sub>2</sub>Yb(THF)<sub>6</sub> (1.14 g) in 25 ml of THF. The mixture was heated at 40–50°C for 24 h. Therewith, it changed color from bright red to dark red, and a dark gray precipitate (bismuth) formed, which was separated by centrifugation (0.065 g, 90%). From the solution, 0.676 g (68%) of (Ph<sub>3</sub>C)<sub>2</sub>YbPh (THF)<sub>3</sub> was isolated. mp 75–80°C (decomp.). The electronic absorption spectrum contains bands at 430–465 and 950–1000 nm due to [Ph<sub>3</sub>C]<sup>-</sup> and Yb<sup>3+</sup>, respectively. Found Yb, %: 18.07.  $C_{56}H_{59}O_3$ Yb. Calculated Yb, %: 18.18.

**Reaction of (Ph\_3C)\_2Yb(THF)\_6 with t-BuOH.** tert-Butyl alcohol (0.048 g) was added to a solution of  $(Ph_3C)_2Yb(THF)_6$  (0.355 g) in THF, cooled to  $-70^{\circ}C$ . The reaction mixture was slowly heated to room temperature. A bluish precipitate formed in the light yellow solution and was washed with THF (7 × 10 ml) and dried in a vacuum to obtain 0.07 g (68%) of ytterbium bis(*tert*-butoxide) [4] as a blue material, mp 300°C. Found Yb, %: 54.14.  $C_8H_{18}O_2Yb$ . Calculated Yb, %: 54.20. From the THF solution, 0.16 g (100%) of Ph<sub>3</sub>CH was isolated, mp 93–95°C (mixed sample).

**Reaction of (Ph\_3C)\_2Yb(THF)\_6 with PhC=CH.** Crystalline  $(Ph_3C)_2Yb(THF)_6$  (1.4 g) was dissolved in THF. The solution was cooled with a mixture of acetone in liquid nitrogen to  $-70^{\circ}C$ , and PhC=CH (0.27 g) of THF was added to it. As the reagents were mixed, the mixture changed color from bright red to dark brown. It was slowly heated to room temperature. The solvent was removed in a vacuum, and the residue was washed with hexane ( $10 \times 10$  ml) and dried in a vacuum to obtain 0.51 g (77%) of (PhC=C)<sub>2</sub>. Yb(THF)<sub>2</sub> as a black material. mp > 250°C (decomp.). Found Yb, %: 33.42.  $C_{24}H_{26}O_2$ Yb. Calculated Yb, %: 33.31. From the hexane extracts, 0.55 g (88%) of Ph<sub>3</sub>CH was isolated, mp 93–95°C.

**Reaction of**  $(Ph_3C)_2Yb(THF)_6$  with CpH.  $(Ph_3C)_2Yb(THF)_6$  (0.39 g) was dissolved in THF. The solution was cooled with a mixture of acetone and liquid nitrogen to  $-70^{\circ}C$ , and a solution of CpH (0.05 g) in THF was added to it. As the reagents were mixed, the mixture changed color from red to reddish violet. It was slowly heated to room temperature, the solvent was removed in a vacuum. Therewith, the products changed color to bright yellow. The contents of the ampule was washed with hexane (7 × 10 ml). A product insoluble in hexane was dried in a vacuum to obtain 0.08 g (56%) of Cp<sub>2</sub>Yb(THF). mp 250°C (decomp.). Found Yb, %: 40.21. C<sub>14</sub>H<sub>18</sub>OYb. Calculated Yb, %: 40.33. From the hexane extracts, 0.14 g (80%) of Ph<sub>3</sub>CH was isolated, mp 91–93°C.

Reaction of  $(Ph_3Ge)_2Yb(THF)_4$  with HgCl<sub>2</sub>. A solution of (Ph<sub>3</sub>Ge)<sub>2</sub>Yb(THF)<sub>4</sub> (0.29 g) in 15 ml of C<sub>6</sub>H<sub>6</sub> was added to a suspension of 0.07 g of HgCl<sub>2</sub> in 10 ml of benzene. The reaction occurred as the regents were mixed. The solution changed color from yellow to light gray. After standing, a light gray precipitate formed. The benzene solution was decanted, and the precipitate was dried in a vacuum and analyzed in air. Treatment of the precipitate with concentrated ammonia gave no black coloration, implying lack of mercurous chloride. The precipitate that was found to be ytterbium chloride (0.06 g, 64%)was dissolved in 0.02 N HCl. The solution was decanted to leave on the bottom of the ampule traces of metallic mercury. The benzene solution was evaporated in a vacuum. The dry residue was bis(triphenylgermyl)mercury (0.19 g, 94%), decomp. point 213–215°C. Found Hg, %: 24.11. C<sub>36</sub>H<sub>30</sub>Ge<sub>2</sub>Hg. Calculated Hg, %: 24.83.

**Reaction of (Ph<sub>3</sub>Ge)<sub>2</sub>Yb(THF)<sub>4</sub> with I<sub>2</sub>.** A solution of iodine (0.029 g) in 5 ml of THF was added to a solution of  $(Ph_3Ge)_2Yb(THF)_4$  (0.26 g) in 15 ml of THF. The reaction began already at  $-30^{\circ}C$  and came to completion when the ampule had been heated to room temperature. A white precipitate formed. The yellow solution was decanted, and the precipiate was washed with cold THF (ca. 10 ml) and dried to obtain 0.06 g (46%, or 86% per taken iodine) of hexaphenyl-digermanium, mp 331–333°C (mixed sample). Tetra-

hydrofuran-soluble products were studied by electronic spectroscopy at 600–1100 nm. The lack of a band at 900–1000 nm provides evidence showing that the ytterbium atom has not been oxidized to the trivalent state.

A new portion of  $I_2$  (0.08 g) in 5 ml of THF was added to the soluble products [unreacted bis(triphenylgermyl)ytterbium]. The solution got almost colorless, and a red precipitate formed. From the precipitate, hexaphenyldigermanium and ytterbium(II) iodode were isolated in yields of 100 (0.07 g) and 88% (0.22 g) with respect to the starting organogermanium compound.

**Reaction of (Ph<sub>3</sub>Ge)<sub>2</sub>Yb(THF)<sub>4</sub> with** *t***-BuOH.** *tert***-Butyl alcohol (0.16 g) was added to a solution of (Ph<sub>3</sub>Ge)<sub>2</sub>Yb(THF)<sub>4</sub> (0.56 g) in 20 ml of THF. A dark blue precipitate immediately formed over the whole volume. The reaction mixture was left to stand at room temperature for 2 h, and the solution was decanted. The precipitate was washed with hexane (3 \times 10 ml). From the hexane solution, 0.23 g (72%) of triphenylgermane was isolated, mp 42°C (mixed sample). The hexane-insoluble amorphous blue material (0.15 g, 88%), decomp. point 300°C, was found to be (***t***-BuO)<sub>2</sub>Yb. Found Yb, %: 53.18. C<sub>8</sub>H<sub>18</sub>O<sub>2</sub>Yb. Calculated Yb, %: 54.20.** 

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