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A New Germylmercury Complex of Praseodymium With Ge–Pr Bond

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Despite the intensive search of preparation routes of organic derivatives of rare-earth elements [1–6] the number of synthesized organometallic compounds of lanthanides is not very great at present. No bimetallic organometallic compounds of lanthanides are known. However, the synthesis of such compounds and the study of their reactivity is of considerable interest. It is known [7] that as a rule the organometallic compounds containing pentafluorophenyl radicals are much more stable than non-fluorinated analogues. Recently the first pentafluorophenyl derivative of ytterbium has been synthesized as the highly air-sensitive complex $(C_6F_5)_2Yb(THF)_4$ (THF = tetrahydrofuran) [8]. But its phenyl analogue has not been prepared yet because of its extraordinary instability. There is only indirect evidence of formation of C_6H_5YbI [9] in the reaction of metallic ytterbium with C_6H_5I.

It has been also shown [10, 11] that pentafluorophenyl radicals stabilize metal–metal bonds in bimetallic organometallic compounds with Ge–Cd, Ge–Hg and Sn–Hg bonds. It could be expected that bimetallic organometallic compounds of lanthanides containing pentafluorophenyl radicals would be sufficiently stable. Therefore we have made an attempt to prepare the organometallic compound with Ge–Pr bond by a transmetallation reaction between bis[tris-pentafluorophenyl)germyl]mercury(I) and metallic praseodymium in dimethoxyethane (DME).

It has been established that the reaction of compound I with metallic praseodymium proceeds at room temperature to afford the complex of the composition $[(C_6F_5)_3Ge]_3Pr\cdot Hg[Ge(C_6F_5)_3]_2$ (II) in 86% yield:

$$5\underset{\text{I}}{[(C_6F_5)_3Ge]_2Hg} + 2Pr \xrightarrow[20\,^\circ C]{DME} 2\underset{\text{II}}{[(C_6F_5)_3Ge]_3Pr\cdot Hg[Ge(C_6F_5)_3]_2} + 3Hg \quad (1)$$

It is presumable that initially $[(C_6F_5)_3Ge]_3Pr$ is formed which readily gives complex II with the starting compound I. The formation of mercury complexes was observed earlier in the reaction of bis(trimethylsilyl)mercury with trimethylsilyllithium and alkali metals [12].

Complex II is a pale green crystalline solid, sensitive to the presence of water. It decomposes without melting at 270–280 °C. The compound is well soluble in THF and DME and almost insoluble in non-polar solvents.

The reaction of II with an excess of hydrogen chloride readily proceeds in THF and can be described by eq. 2:

$$\underset{\text{II}}{[(C_6F_5)_3Ge]_3Pr\cdot Hg[Ge(C_6H_5)_3]_2} + 4HCl \xrightarrow{THF} 4(C_6F_5)_3GeH + (C_6F_5)_3GeCl + PrCl_3 + Hg \quad (2)$$

The yields of the reaction products are almost quantitative.

It seems reasonable to suggest that the complex II has the ionic structure $\{[(C_6F_5)_3Ge]_2Pr\}^{+}\,{}^{-}\{Hg[Ge(C_6F_5)_3]_3\}$. It is confirmed by reactions with hydrogen chloride and tris(pentafluorophenyl)germanium bromide at a molar reagent ratio 1:1:

$$\text{II} + HCl \xrightarrow[20\,^\circ C]{THF} [(C_6F_5)_3Ge]_2Hg + (C_6F_5)_3GeH + [(C_6F_5)_3Ge]_2PrCl \quad (3)$$

$$\text{II} + (C_6F_5)_3GeBr \xrightarrow[20\,^\circ C]{THF} [(C_6F_5)_3Ge]_2Hg + (C_6F_5)_3GeGe(C_6F_5)_3 + [(C_6F_5)_3Ge]_2PrBr + (C_6F_5)_3GeH \quad (4)$$

Tris(pentafluorophenyl)germane (eq. 3) and hexakis(pentafluorophenyl)digermane (eq. 4) are formed due to the abstraction of $(C_6F_5)_3Ge$ group from mercury. We believe that reactions 3 and 4 are heterolytic. However in reaction 4 the homolytic processes probably take place together with the heterolytic ones. This is confirmed by the formation of $(C_6F_5)_3GeH$ (41.7%) and a small quantity of unidentified products. The formation of tris(pentafluorophenyl)germane in reaction 4 may be explained by the reaction of generated $(C_6F_5)_3Ge\cdot$radicals with the solvent. It should be noted that the formation of $(C_6F_5)_3Ge\cdot$radicals and their further transformation into $(C_6F_5)_3GeH$ was observed earlier in reactions of digermane $(C_6F_5)_3GeGeEt_3$ with $CuCl_2$, AgCl and $AuCl_3$ [13]. In order to ascertain the mechanism of reaction 4 it should be studied in more detail.

In the IR spectrum of the compound II there are absorption bands at 1650, 1520, 1480, 1380, 1290, 830 and 640 cm^{-1}, characteristic of C_6F_5 groups bonded to a germanium atom [14]. It is known [7, 15] that IR spectra of compounds of the type C_6F_5–X are characterized by absorption bands in the 760–900 cm^{-1} region. The frequencies of these bands depend on the nature of the substituent X. Analysis of IR spectra of compounds containing the C_6F_5–Ge–X grouping established that the frequencies of fragment C_6F_5–M is dependent on both the nature of M and the substituent X. For example, in the spectrum of $C_6F_5GeEt_3$ [16] the value of ν C_6F_5–Ge is equal to 808 cm^{-1}, for $(C_6F_5)_3GeOMe$ [14] 830 cm^{-1}, for $[(C_6F_5)_3Ge]_2Cd$ [10] 812 cm^{-1}, for $(C_6F_5)_4Ge$ [7] 819 cm^{-1}. The IR spectra of compounds I and II are shown in Figure 1. It is readily seen that in the spectrum of compound II two bands of weak intensity in the 800–900 cm^{-1} region are observed, which probably can be assigned to the vibrations of fragment C_6F_5–Ge in C_6F_5–Ge–Hg (860 cm^{-1}) and C_6F_5–Ge–Pr (810 cm^{-1}). This is confirmed by the fact that in the IR spectra of compounds $[(C_6F_5)_3Ge]_2PrX$ (X = Cl, Br) there is a band at 810 cm^{-1} but the band at 860 cm^{-1} is absent.

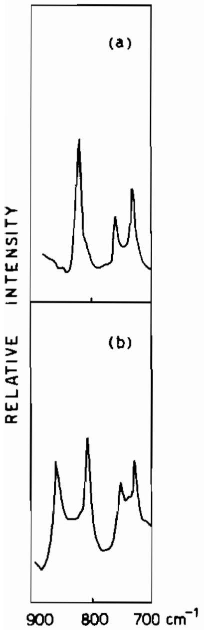

Figure 1. The infrared spectra of $[(C_6F_5)_3Ge]_2Hg$ (I) (a) and $[(C_6F_5)_3Ge]_3Pr{\cdot}Hg[Ge(C_6F_5)_3]_2$ (II) (b) in the 700–900 cm^{-1} region.

Experimental

All reactions were carried out in evacuated sealed ampoules. The melting points were determined in evacuated sealed capillaries. GLC analyses of products were carried out on a Tsvet –104 chromatograph with a catarometer detector using a 50 × 0.4 cm or 100 × 0.4 column packed with OV-17 (7%) on Chromaton N-AW-DMCS, with helium as the carrier gas. IR spectra were recorded on a double-beam Zeiss–Jena Model UR-20 spectrometer. Samples of the crystalline compounds were prepared *in vacuo* as Nujol mulls.

Synthesis of $[(C_6F_5)_3Ge]_3Pr{\cdot}Hg[Ge(C_6F_5)_3]_2$ *(II)*

A mixture of 3.50 g (1.09 mmol) of bis[tris(pentafluorophenyl)germyl]mercury(I) and 1.55 g (11.0 mg-atom) of finely divided praseodymium in 15 ml of DME was shaken at *ca.* 20 ℃ for 50 h. The resulting pale green solution was decanted from the precipitate in which 0.27 g (86.4%) of metallic mercury was determined. DME was removed by recondensation *in vacuo*. The residue was washed with toluene several times and dried *in vacuo* to give 2.86 g (85.8%) of II as the pale green solid, m.p. 270–280 ℃ (dec.). *Anal.* Calcd. for $C_{90}F_{75}Ge_2HgPr$: C, 33.67; Hg, 6.25; Pr, 4.39. Found: C, 32.87; Hg, 6.44; Pr, 4.17%.

Reaction of II with HCl

(a) A mixture of 1.10 g (0.34 mmol) of II and 0.20 g (5.49 mmol) of dry HCl in 20 ml of THF was left overnight at *ca.* 20 ℃. In order to complete the reaction, the mixture was heated at 70 ℃ for 2 h. The organic layer was decanted from the dark-grey precipitate, containing 0.06 g (87.3%) of mercury and 0.08 g (94.4%) of $PrCl_3$. GLC analysis of the organic layer revealed the presence of 0.62 g (78.7%) of tris(pentafluorophenyl)germane and 0.20 g (95.8%) of $(C_6F_5)_3GeCl$.

(b) A mixture of 1.04 g (0.32 mmol) of complex II and 0.012 g (0.33 mmol) of HCl in 20 ml of THF was left overnight at *ca.* 20 ℃. After removal of THF the residue was washed many times with toluene and dried *in vacuo* to afford 0.30 g (70.0%) of bis[tris(pentafluorophenyl)germyl] praseodymium chloride, m.p. 255–260 ℃ (dec.). *Anal.* Calcd. for $C_{36}ClF_{30}Ge_2Pr$: C, 32.66. Found: C, 32.01%. Toluene was removed from the toluene extract, the residue was washed with hexane and dried *in vacuo* to give 0.42 g (96.2%) of compound I, m.p. 229–231 ℃ (mixed m.p.). The IR spectrum of I is identical with that reported in ref. 10. GLC analysis of the hexane extract showed the presence of $(C_6F_5)_3GeH$ (0.19 g, 100%).

Reaction of II with Tris(pentafluorophenyl)germanium Bromide

To a solution of 1.34 g (0.42 mmol) of II in 10 ml of THF was added a solution of 0.28 g (0.43 mmol) of $(C_6F_5)_3GeBr$ in 5 ml of THF at room temperature. After 1 h the reaction was complete and hexakis(pentafluorophenyl)digermane precipitated. The liquid layer was decanted from the digermane, the latter was washed with THF and dried *in vacuo*. The yield was 0.40 g (83.5%); m.p. 313–318 ℃ (mixed m.p.). The IR spectrum of digermane is identical with that reported in ref. 17. After the THF had been distilled off the reaction solution, the pale green residue was washed many times with toluene and dried *in vacuo* to give 0.40 g (70.0%) of bis[tris(-pentafluorophenyl)germyl] praseodymium bromide; m.p. 240–245 ℃ (dec.). *Anal.* Calcd. for $C_{36}BrF_{30}Ge_2Pr$: C, 31.60; Pr, 10.30. Found: C, 32.32; Pr, 10.86%. Toluene was removed from the toluene extract, the crystalline residue was washed with hexane and dried *in vacuo* to afford 0.54 g (96.0%) of compound I; m.p. 229– 231 ℃ (mixed m.p.). GLC analysis of the hexane extract revealed the presence of $(C_6F_5)_3GeH$ (0.10 g, 41.7%) and four minor components which were not identified.

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