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Germylmercury Complex of Thallium(I)

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Compounds of thallium(III) are often used as donors of organic and organometallic radicals in transmetallation reactions [1–4]. This method is a synthetic pathway for organomercurials as well. A reverse reaction, *i.e.* transfer of radicals from mercury to thallium has not been reported before, though the reversibility of such processes has often been suggested [1, 5].

We have found that metallic thallium displaces mercury from $[(C_6F_5)_3Ge]_2Hg$. The reaction proceeds in dimethoxyethane to afford mercury (33% towards the total amount) and the thallium derivative. Elemental analysis of the compound is in accordance with the formula $[(C_6F_5)_3Ge]_2Hg\cdot TlGe(C_6F_5)_3\cdot 1.5$ DME.

$$3\ [(C_6F_5)_3Ge]_2Hg + Tl \xrightarrow[95^\circ,\ 5h.]{DME} 2[(C_6F_5)_3Ge]_2Hg\cdot TlGe(C_6F_5)_3\cdot 1.5DME + Hg$$

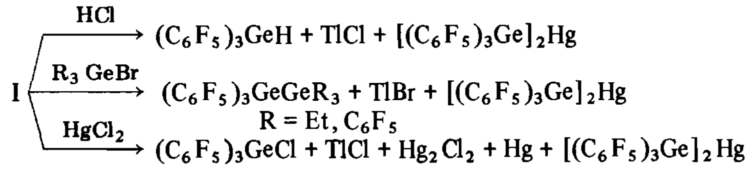
I

Product I is highly soluble in DME, THF and in aromatic solvents on heating. I crystallizes from toluene in the form of colourless crystals with m.p. 129–131 °C (dec.). In the solid state the complex I is stable in air for a few hours.

We have observed recently a similar fact of the displacement of mercury from $[(C_6F_5)_3Ge]_2Hg$ by lanthanide metals [6, 7]. The complexes of lanthanides obtained in these reactions obviously have a structure which differs from the reported one [6, 7], but the presence of $[(C_6F_5)_3Ge]_3Hg^-$ anions in those compounds is undoubted.

Resemblance of IR spectra and some other properties of lanthanide complexes and the product I suggests for the latter compound the ionic structure $\{[(C_6F_5)_3Ge]_3Hg\}^-Tl^+\cdot 1.5DME$. This is confirmed by the products of reactions I with HCl, R_3GeBr, $HgCl_2$ shown in scheme 1.

SCHEME 1



$$I \xrightarrow{HCl} (C_6F_5)_3GeH + TlCl + [(C_6F_5)_3Ge]_2Hg$$

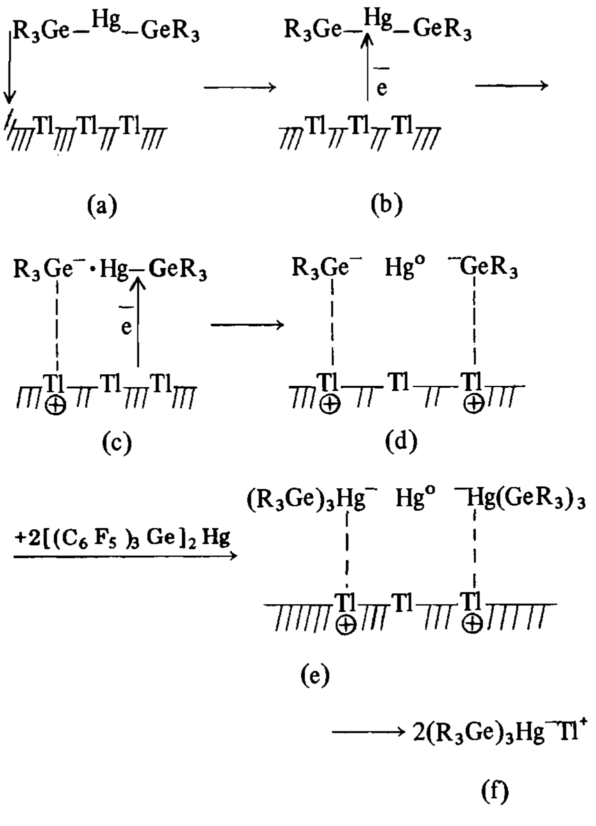
$$I \xrightarrow{R_3GeBr} (C_6F_5)_3GeGeR_3 + TlBr + [(C_6F_5)_3Ge]_2Hg \quad R = Et, C_6F_5$$

$$I \xrightarrow{HgCl_2} (C_6F_5)_3GeCl + TlCl + Hg_2Cl_2 + Hg + [(C_6F_5)_3Ge]_2Hg$$

Detailed investigation of the reaction of $[(C_6F_5)_3Ge]_2Hg$ with thallium has shown that yield of metallic mercury reaches 31–33% for the first 2 hours and does not increase during the next 3 hours of heating. However, when the reaction is carried out for 7–15 hours an additional amount of metallic mercury is isolated and the yield of it gradually reaches 100%. This process is accompanied by the decrease of thallium contents in the product and the onset of side reactions of nucleophilic substitution of F-atoms in C_6F_5-rings.

We suppose that transmetallation of $[(C_6F_5)_3Ge]_2Hg$ with metallic thallium can be described by scheme 2.

SCHEME 2



The process involves the following steps: (a) adsorption of $[(C_6F_5)_3Ge]_2Hg$ on the thallium surface, (b, c, d) transfer of the first and the second electrons to $(R_3Ge)_2Hg$ with the formation of Hg^0 and R_3Ge^- anions fixed on the charged thallium surface, (e) stabilization of R_3Ge^- anions by addition of $(R_3Ge)_2Hg$, (f) migration of Tl^+ cations into solution in the form of complex $(R_3Ge)_3Hg^-Tl^+$. Following processes proceeding at increasing reaction time leads to displacement of mercury from the complex and can be described by a similar scheme. Unstable thallium compound R_3GeTl or R_3Ge^- anions which are extremely active (in the absence of $(R_3Ge)_2Hg$) towards C–F bonds of C_6F_5-rings are forming in this case.

Synthesis of compound I and lanthanide complexes [6, 7], formation of ate-complexes in the reactions of alkali metals with organosilyl- [8] and organogermylmercurials [9] and the reported synthesis of complex $[Mg_4(OCH_2CH_2OMe)_6 \cdot 2DME][Hg(SiMe_2Ph)_3]_2$ by the reaction of metallic magnesium with $(PhMe_2Si)_2Hg$ [10] suggest that most of transmetallation reactions of $(R_3M)_2Hg$ (M = Si, Ge, Sn) involve the formation of $(R_3M)_3Hg^-$ or $(R_3M)_4Hg^{2-}$ complexes which are similar to the well known inorganic complexes X_3Hg^- and X_4Hg^{2-} [11].

Synthesis, isolation and reactions of complex I were carried out in evacuated sealed ampoules. Particular attention was paid to eradication of traces of moisture from solvents, reagents and apparati.

Experimental

Synthesis of Complex I

A solution of $[(C_6F_5)_3Ge]_2Hg$ (2.48 g, 1.48 mmol) in 7 ml of DME was added to 6.3 g (30.8 mg-atom) of finely divided thallium (washed with aqueous EtOH and DME). The mixture was shaken at 95 °C for 5 h. The resulting solution was decanted from the precipitate in which 0.123 g (33% towards total amount) of metallic mercury was determined. DME was removed by recondensation *in vacuo*. The residue was washed with hexane and dried *in vacuo* to give 2.4 g (84.8%) of complex I, m.p. 125–130 °C (dec). After recrystallization from toluene the product has m.p. 129–131 °C (with dec.). *Anal.* Calcd. for $C_{60}H_{15}F_{45}Ge_3HgO_3Tl$: C, 31.87; H, 0.67; F, 37.80; Hg, 8.87; Tl, 9.04. Found: C, 32.56; H, 0.85; F, 37.46; Hg, 9.04; Tl, 9.13%.

Reaction of I with Hydrogen Chloride

Hydrogen chloride (0.014 g, 0.4 mmol) was added to a solution of 0.9 g (0.4 mmol) of complex I in 5 ml of THF. TlCl (0.095 g, 100%) precipitated immediately. The liquid layer was decanted from TlCl. DME was removed from the solution, the residue was washed with hexane and dried *in vacuo* to afford 0.51 g (95%) of $[(C_6F_5)_3Ge]_2Hg$. GLC analysis of the hexane extract revealed the presence of $(C_6F_5)_3GeH$ (0.229 g, 100%).

Reaction of I with $(C_6F_5)_3GeBr$

To a solution of 0.946 g (0.42 mmol) of I in 5 ml of THF was added a solution of 0.275 g (0.41 mmol) of $(C_6F_5)_3GeBr$ in 3 ml of THF at room temperature. The liquid layer was decanted from precipitated TlCl (0.117 g, 98%) and was left overnight at *ca.* 20 °C. Hexakis(pentafluorophenyl)digermane is precipitated. The solution was decanted from the precipitate of digermane, the latter was washed with THF and sublimed *in vacuo*. The yield was 0.389 (81%). After removal of THF from the reaction solution the residue was washed with hexane and dried *in vacuo* to give 0.55 g (98%) of $[(C_6F_5)_3Ge]_2Hg$. GLC analysis of the hexane extract revealed presence of traces of $(C_6F_5)_3GeH$.

The yield of the digermane $(C_6F_5)_3GeGeEt_3$ identified by GLC analysis in the reaction of I with Et_3GeBr was 19%.

Reaction of I with $HgCl_2$

To a solution of 0.77 g (0.34 mmol) of I in 5 ml of THF was added 0.092 (0.34 mmol) of $HgCl_2$. A deposit of metallic mercury, Hg_2Cl_2 and TlCl precipitated. After 10 min at *ca.* 20 °C the reaction was complete. The organic layer was decanted from the precipitate. Metallic mercury (0.052 g, 76%) and Hg_2Cl_2 (0.008 g, 10%) were isolated by gradual sublimation of the precipitate. The unsublimed residue was identified as TlCl (0.081 g, 99%). Change of THF in the mother liquid with hexane leads to precipitate of $[(C_6F_5)_3Ge]_2Hg$ (0.441 g, 96%). GLC analysis of the hexane extract revealed the presence of 0.187 g, (90%) of $(C_6F_5)_3GeCl$ and 0.02 g of $(C_6F_5)_3GeH$.

Formation of tris(pentafluorophenyl)germane in this case and also in the reaction of I with $(C_6F_5)_3GeBr$ obviously is due to the presence of traces of moisture in the reaction mixture.

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