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REACTIVITY OF THALLIUM TRIS[TRIS(PENTAFLUOROPHENYL)GERMYL] MERCURATE

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Summary

Metallic lithium and dibenzenechromium displace thallium from $(R^f_3Ge)_3HgTl \cdot 1.5DME$ ($R^f = C_6F_5$, DME = 1,2-dimethoxyethane) to give $(R^f_3Ge)_3HgLi \cdot 3DME$ and $[(R^f_3Ge)_4Hg][Cr(C_6H_6)_2]_2$, respectively. Reactions of thallium germylmercurate with halides of metals and organometallics in DME/EtOH solution produce ionic compounds of $[(R^f_3Ge)_3Hg]^- \ M^+$ type, which (depending on "M") (a) may be isolated as pure compounds, (b) disproportionate, (c) form covalent derivatives R^f_3Ge–m or (d) undergo alcoholysis. A general scheme for the reactions has been proposed.

Introduction

Preliminary investigations of the properties of the germylmercury complex of univalent thallium, $(R^f_3Ge)_3HgTl \cdot 1.5DME$ (I), formed in the reaction between metallic thallium and $(R^f_3Ge)_2Hg$, have revealed a high activity of this compound in many reactions [1]. The products of the reactions had, in some cases, an ionic nature like that of the starting complex I, while in other cases they had only covalent metal–metal bonds. We have now investigated the reactions of I with some metals, metal halogenides and organometallics. The reactions were carried out to determine possibilities of I in synthesis of organometals and the factors influencing the pathways of these processes.

Results and discussion

Neutral dibenzenechromium displaces thallium from complex I in DME solution at room temperature. It seemed reasonable to expect the formation of the complex $[(R^f_3Ge)_3Hg][Cr(C_6H_6)_2]$ (II). But, along with metallic mercury, a more complex product III was isolated in 82% yield from the reaction mixture. III contained two cations of dibenzenechromium and a 5-nuclear doubly charged mercury anion. The same complex III was obtained in the reaction of dibenzenechromium iodide with I

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TABLE 1

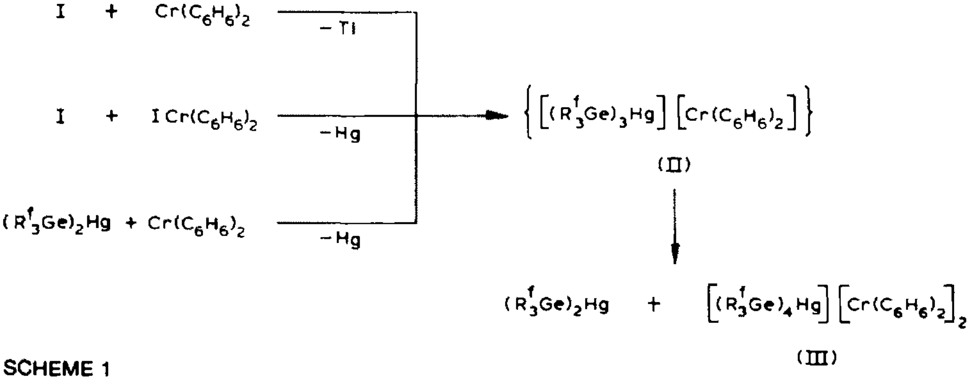
REACTION PRODUCTS OF $(R^f_3Ge)_3HgTl \cdot 1.5DME$ WITH HALIDES

Halide	Products, yield (%)
$(C_6H_6)_2CrI$	TlI (100), $[(R^f_3Ge)_4Hg][Cr(C_6H_6)_2]_2$ (99), $[(R^f_3Ge)_2HgI][Cr(C_6H_6)_2]$ (99)
$HgCl_2$	TlCl (100), $(R^f_3Ge)_2Hg$ (92)
ZnI_2	TlI (100), R^f_3GeH, $(R^f_3Ge)_2Hg$, $(EtO)_2Zn$ ^{a}
Ph_3SbBr_2	TlBr (100), R^f_3GeH (96), $(R^f_3Ge)_2Hg$ (100), $Ph_3Sb(OEt)_2$
Cp_2NbCl_2	TlCl (97), R^f_3GeH (68), $(R^f_3Ge)_2Hg$ (95), $[Cp_2NbOEt?]$
$CuCl_2$	TlCl (85), Cu_2Cl_2 (86), R^f_3GeH (58), $R^f_6Ge_2$ (10), $(R^f_3Ge)_2Hg$ (95)
Cp_2TiCl_2	TlCl (100), $[(R^f_3Ge)_3Hg]_2TiCp_2$ (73)
$MnCl_2$	TlCl (100), $[(R^f_3Ge)_3Hg]_2Mn \cdot 1.5DME$ (85)
$CoCl_2$	TlCl (95), $[(R^f_3Ge)_3Hg]_2Co$, R^f_3GeH, $(R^f_3Ge)_2Hg$ ^{a}
$NiCl_2$	TlCl (90), $[(R^f_3Ge)_3Hg]_2Ni$, R^f_3GeH, $(R^f_3Ge)_2Hg$ ^{a}

[a] The formation of these products is determined from IR spectra, GLC and liquid chromatography.

in DME/ethanol solution. The other products of this reaction are TlI and a polynuclear complex, $[(R^f_3Ge)_2HgI][Cr(C_6H_6)_2]$ (IV) (Table 1). The latter decomposes slowly on heating in DME solution in daylight. Therefore, carrying out the reaction under these conditions was accompanied by precipitation of metallic mercury, as it has been noted in the preliminary communication [2]. Product III is formed also in the reaction of dibenzenechromium with bis[tris(pentafluorophenyl)germyl]mercury.

The data obtained suggest that an extremely unstable complex $[(R^f_3Ge)_3Hg][Cr(C_6H_6)_2]$ (II) is formed initially in all three reactions (Scheme 1). Rapid disproportionation of this complex leads to product III and bis[tris(pentafluorophenyl)germyl]mercury, which reacts then with dibenzenechromium (in the first and third reactions) or with dibenzenechromium iodide (in the second reaction) to give IV.



SCHEME 1

In separate experiments we found that the interaction of $(R^f_3Ge)_2Hg$ with dibenzenechromium iodide proceeds readily under very mild conditions and results in high yield of complex IV.

$$(R^f_3Ge)_2Hg + ICr(C_6H_6)_2 \xrightarrow[20°C]{} \underset{(IV)}{[(R^f_3Ge)_2HgI][Cr(C_6H_6)_2]}$$

The reasons for the disproportionation of the intermediate complex II remain unclear. One of these is probably the higher stability of the 5-nuclear anion with an sp^3-hybridized mercury atom compared to the 4-nuclear anion containing sp^2-hybridized mercury [3]. At the same time it should be noted that such a disproportionation of polynuclear ionic complexes with other cations is not typical, as follows from the literature data [4–7] and from the results given below.

Complex III precipitates from toluene solution as yellow crystals. It is stable in air and decomposes at 210°C. Unlike most dibenzenechromium salts, III is very soluble in DME, THF, acetone and aromatic hydrocarbons (on heating). The ESR spectrum of III (g_i 1.986, α_H 3.5 G, α_{Cr} 35.18 G) corresponds to the spectrum of $(C_6H_6)_2Cr^+$. Complex IV has a similar ESR spectrum and other properties. The distinctive feature of IV is its very good solubility in aromatic solvents. This makes separation possible of both complexes III and IV in the reaction mixture. It is interesting to note that thermal stability of the iodine-containing germylmercury anion $[(R^f_3Ge)_2HgI]^-$ (decomposition of IV is at 165°C) is significantly higher than that of germylmercury halides R_3GeHgX [8,9], which decompose below 20°C.

The route of the reaction between complex III and hydrogen chloride in DME solution at 50°C is not typical for this type of compound. The main reaction products are the hydride R^f_3GeH (68%), $ClCr(C_6H_6)_2$ (50%) and a mercurychromium complex, $[Cl_3Hg][Cr(C_6H_6)_2]$ (74%), similar to those reported by Hein [10]. Here, HCl attacks the covalent Ge–Hg bond but not the ionic group as was observed for thallium [1] and lanthanide [7] complexes.

$$[(R^f_3Ge)_4Hg][Cr(C_6H_6)_2]_2 + 4HCl \rightarrow 4R^f_3GeH + ClCr(C_6H_6)_2 + [Cl_3Hg][Cr(C_6H_6)_2]$$

Besides the products mentioned in the equation, the reaction gives small quantities of R^f_3GeCl and metallic mercury.

It is known that oxidative-reductive transmetallation reactions are reversible both for common mononuclear compounds and for polynuclear ones. But we failed to realize the reverse reaction i.e. the interaction of Hg with I. The initial components were isolated after shaking in DME at 100°C for 20 h. On the contrary, metallic lithium displaces thallium from I as dibenzenechromium does. The reaction is not accompanied by subsequent displacement of mercury despite the high activity of the alkali metal.

$$I + Li \xrightarrow[20°C]{DME} \underset{(V)}{(R^f_3Ge)_3HgLi \cdot 3DME} + Tl$$

Under similar conditions, lithium reduces the dibenzenechromium cation in III to neutral $Cr(C_6H_6)_2$. The lithium derivative was not isolated in this case.

Complex V is a colourless compound, stable in moist air for a few days. It is very soluble in DME, THF and insoluble in alkanes. Its structure is confirmed by the reaction with HCl, which results in high yield of R^f_3GeH, $(R^f_3Ge)_2Hg$ and LiCl. On rapid heating the complex decomposes without melting at 186°C. On slow heating in an evacuated ampoule, the decomposition initiates at 150–160°C and is accompanied by sublimation of R^f_3GeH, , $R^f_6Ge_2$ and $(R^f_3Ge)_2Hg$. Decomposition of the thallium complex under similar conditions results in similar products.

Thallium-containing compounds are known to react with various halides. This property is also characteristic of complex I. In Table 1 are given the products of the reaction between I and halides of metals and organometallic halides. These reactions are complete at room temperature in a few minutes. Most of them proceed in DME/ethanol. With dibenzenechromium iodide the reaction may also take place in DME (or THF), but it proceeds at 70°C for 7 h and results in decomposition of IV (as noted above). Other halides do not react with I in the absence of alcohol or water even under drastic conditions. In our opinion, this testifies to the ionic nature of the process. Protic solvents promote the dissociation of the metal–halogen bonds and the rapid completion of the reaction. The thallium complex I was found to undergo alcoholysis under the given conditions. However, the rate of this reaction is far lower than that of the reaction between I and halogenides, so it has virtually no effect upon the yield of the products.

Earlier we reported that the reaction of I with an equimolar amount of mercuric chloride yields TlCl, mercury, germanium chloride R^f_3GeCl, $(R^f_3Ge)_2Hg$ and a small amount of calomel [1]. Reinvestigation of the process has shown that the course of the reaction changes dramatically when the I : $HgCl_2$ ratio is 2 : 1. The reaction gives germylmercury, $(R^f_3Ge)_2Hg$, in more than 90% yield, i.e. the formation of the covalent Ge–Hg bond takes place.

$$\mathrm{I} + HgCl_2 \begin{cases} \xrightarrow{1:1} TlCl + Hg + R^f_3GeCl + Hg_2Cl_2 + (R^f_3Ge)_2Hg \\ \xrightarrow{2:1} TlCl + (R^f_3Ge)_2Hg \end{cases}$$

Zinc iodide (which is in the same subgroup as Hg) in any ratio with I gives exclusively products of alcoholysis. Both the ionic intermediate $[(R^f_3Ge)_3Hg]_2Zn$ and the germylzinc $(R^f_3Ge)_2Zn$ formed may be cleaved by alcohol. The same route is observed in the reactions of I with Ph_3SbBr_2 and Cp_2NbCl_2, where, along with TlX and $(R^f_3Ge)_2Hg$, a high yield of tris(pentafluorophenyl)germane is obtained. In this case niobium is reduced to Nb^{III}, which is evidenced by disappearance of the ESR signal of Nb^{IV}. The niobium-containing residue was not investigated in more detail.

The reaction with $CuCl_2$ is characterized by an absence of alkoxy derivatives and the presence of digermane in the reaction products. The composition of the reaction mixture is similar to that of the mixture formed in the reaction of cupric chloride with $R^f_3GeGeEt_3$, for which a scheme was proposed involving the formation of $R^f_3Ge\cdot$ radicals [11]. Other halides (Cp_2TiCl_2, $MnCl_2$, $NiCl_2$, $CoCl_2$) in the reaction with I give ionic products from halogen/$Hg(GeR^f_3)_3$ exchange. Incidentally, nickel and cobalt complexes undergo partial alcoholysis with formation of hydrogermane and bis[tris(pentafluorophenyl)germyl]mercury, which makes the isolation of individual ionic products from the reaction mixture difficult.

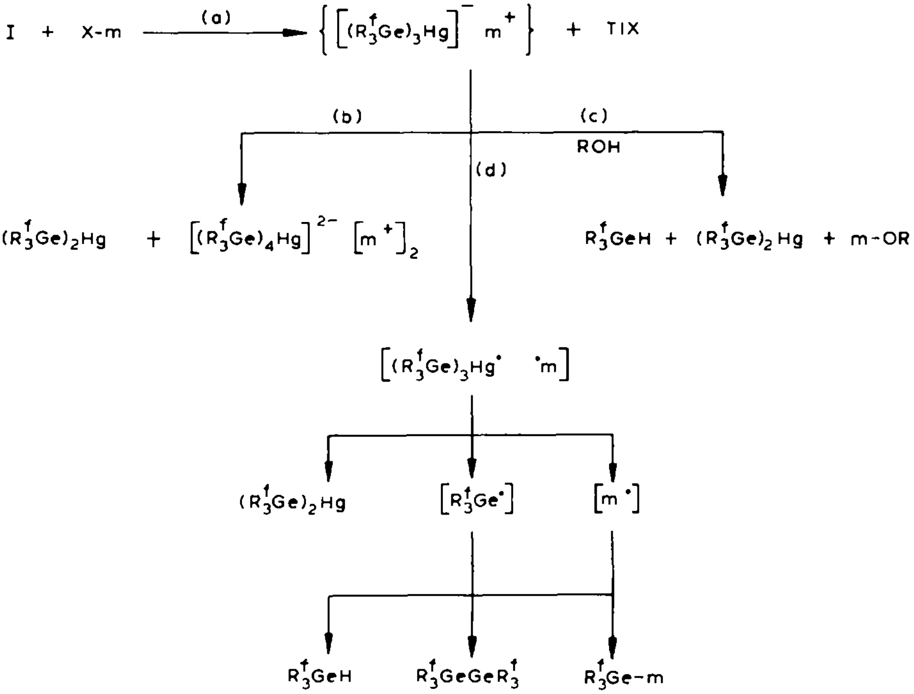
$$2\mathrm{I} + Cp_2TiCl_2 \xrightarrow[20^\circ C]{DME/EtOH} \underset{(VI)}{[(Rf_3Ge)_3Hg]_2TiCp_2} + 2TlCl$$

$$2\mathrm{I} + MnCl_2 \xrightarrow[20^\circ C]{DME/EtOH} \underset{(VII)}{[(R^f_3Ge)_3Hg]_2Mn \cdot 1.5DME} + 2TlCl$$

The properties of the light yellow complex VI and of the light pink complex VII are similar to those of the analogous complexes of thallium, lanthanides and dibenzenechromium. They are very soluble in DME and THF. In the solid state they are slowly hydrolyzed in moist air. The manganese derivative has no ESR signal in DME.

The IR spectra of all compounds with $(R^f_3Ge)_3Hg^-$ or $(R^f_3Ge)_4Hg^{2-}$ anions show a distinctive narrow band of medium intensity at 805–810 cm^{-1}. This band is readily distinguished from the other bands of organometallic pentafluorophenyl derivatives. Thus, IR spectra of the mixture of solid reaction products give effective evidence for the formation and relative yields of the ionic complexes.

Even though there are some differences in the compositions of the products, we believe that all the reactions of I with halides and organometallic halides start with $X/Hg(GeR^f_3)_3$ exchange (Scheme 2).



SCHEME 2

The ionic complex $\{[(R^f_3Ge)_3Hg]^- m^+\}$ formed may undergo the following conversions:

(a) It may be quite stable and be isolated as individual compounds (reactions with $MnCl_2$, Cp_2TiCl_2).

(b) It may undergo disproportionation reaction to give a more stable product with a doubly charged anion $(R^f_3Ge)_4Hg^{2-}$ (reaction with $ICr(C_6H_6)_2$).

(c) It may undergo alcoholysis or hydrolysis (reactions with $ZnCl_2$, Ph_3SbBr_2, Cp_2NbCl_2).

(d) When the metal "m" has a high ionization potential and a high electron affinity, electron transfer from the mercury anion to the cation may take place. Electroneutral moieties m· and $(R^f_3Ge)_3Hg\cdot$ are formed in this case. The mercury moieties decompose immediately to generate $R^f_3Ge\cdot$ radicals, the behaviour of which was studied previously [11]. They are able to abstract hydrogen from the solvent, to recombine or to add to the metal (without leaving the "cage") with formation of covalent compound, R^f_3Ge–m. The last variant is obviously realized in the reaction of I with mercury chloride and in the reaction with R^f_3GeBr described earlier [1]. It should be noted that the formation of small amounts of hydride R^f_3GeH in both cases has been explained by the presence of traces of moisture in the reaction mixture [1]. However, in view of the general Scheme 2, the formation of R^f_3GeH is more likely to be explained by the interaction of $R^f_3Ge\cdot$ radicals (which are partly free of the "cage") with the solvent. In the reaction with $CuCl_2$ this route, i.e. the formation of digermane and hydride, is considered to be the exclusive.

It may well be that the interaction of I with ZnI_2, Ph_3SbBr_2 also leads to covalent products of R^f_3Ge–m type, and that they rather than the ionic intermediate undergo alcoholysis. Unfortunately, from the data obtained it is not possible to determine at what stage of the reaction the formation of alkoxides occurs.

Experimental

All reactions were carried out in evacuated sealed ampoules. GLC analyses of products were carried out on a Tsvet-104 chromatograph with a catarometer detector, using a 100 × 0.4 cm and a 50 × 0.4 cm column packed with OV-17 (7%) on Chromaton N-AW-DMCS ($T = 200°C$), with helium as the carrier gas. LSC analyses were carried out on a Tsvet-304 liquid chromatograph with UV detector (254 nm) using a column (190 × 4 cm) made of steel packed with Silosorb 600 (5 μm), hexane-ether eluent, $T = 23°C$. IR spectra were recorded on a Perkin-Elmer-577 spectrophotometer. ESR data were obtained with an RE 1301 spectrometer. Melting points (given without corrections) were determined using evacuated capillaries.

Reaction of tris[tris(pentafluorophenyl)germyl]thallium mercurate with dibenzenechromium

A solution of $(R^f_3Ge)_3HgTl\cdot 1.5$ DME (0.62 g, 0.27 mmol) in 5 ml of DME was added to sublimed dibenzenechromium (0.085 g, 0.41 mmol). Thallium (0.050 g, 88%) and mercury (0.014 g, 100%) isolated after 1 h at 20°C were removed from the reaction mixture by centrifugation. The organic layer was decanted from the precipitate, DME was evaporated in vacuo and the residue was recrystallized from toluene to give 0.502 g (82%) of $[(R^f_3Ge)_4Hg][Cr(C_6H_6)_2]_2$, m.p. 210°C (dec.). Found: C, 38.45; H, 0.86; F, 39.45. $C_{96}H_{24}F_{60}Ge_4HgCr_2$ calcd.: C, 39.58; H, 0.82; F, 39.15%.

Reaction of I with dibenzenechromium iodide

To a solution of $(C_6H_6)_2CrI$ (0.242 g, 0.72 mmol) in ethanol (3 ml) was added a solution of I (1.094 g, 0.48 mmol) in DME (5 ml). The mixture was kept at 20°C for 10 min. The organic layer was decanted from the precipitate of thallium iodide (0.15 g, 95%). The mixture of the solvents was removed in vacuo, and the residue was extracted with toluene. Cooling of the toluene solution to −78°C for 3 h led to a precipitate of $[(R^f_3Ge)_2HgI][Cr(C_6H_6)_2]$ (0.403 g, 99%) (IV). Recrystallization from toluene gave a yellow compound, m.p. 165°C (dec.). Found: C, 34.93; H, 0.59; F, 33.96. $C_{48}H_{12}CrF_{30}Ge_2HgI$ calcd.: C, 34.25; H, 0.72; F, 33.86%. The residue insoluble in toluene at 20°C was recrystallized from toluene at 80–90°C. Complex II (0.7 g, 90%), m.p. 210°C (dec.) was isolated. ESR and IR spectra together with LSC data showed the identity of this product with that obtained in the previous test.

Reaction of II with hydrogen chloride

To a solution of complex II (0.972 g, 0.33 mmol) in 5 ml of DME was added hydrogen chloride (0.064 g, 1.8 mmol). Dibenzenechromium chloride (0.041 g, 50%) precipitated at 20°C in 10 min. It was removed by centrifugation. When the organic layer was decanted from the precipitate and the solvent was changed for toluene, $[Cl_3Hg][Cr(C_6H_6)_2]$ (0.127 g, 74%) precipitated. After isolation of the complex and removal of the solvent from the mother liquid, sublimation of the solid residue in vacuo (160°C/0.01 mmHg) gave R^f_3GeH (0.521 g, 68%) and R^f_3GeCl (0.020 g, 10%), which were identified by GLC.

Reaction of complex V with hydrogen chloride

To a solution of complex V (0.484 g, 0.22 mmol) was added hydrogen chloride (0.008 g, 0.22 mmol). The solvent was removed by vacuo evaporation. Gradual sublimation of the residue gave R^f_3GeH (0.116 g, 93%) and $(R^f_3Ge)_2Hg$ (0.262 g 90%), m.p. 228°C. On mixing with an authentic sample no depression of melting point was observed. Based on emission spectra data, the unsublimed residue was found to contain 0.006 g of lithium chloride.

Reaction of bis[tris(pentafluorophenyl)germyl]mercury with dibenzenechromium iodide

To a solution of $(R^f_3Ge)_2Hg$ (0.8 g, 0.59 mmol) in DME (4 ml) was added a solution of $(C_6H_6)_2CrI$ (0.198 g, 0.59 mmol) in ethanol (3 ml). After 10 min the solvents were removed in vacuo. The residue was washed with hexane and recrystallized from toluene. The yield of $[(R^f_3Ge)_2HgI][Cr(C_6H_6)_2]$ (IV) was 0.792 g (81%), m.p. 165°C. Its IR and ESR spectra were similar to those of the compound in the previous test. The identity was also confirmed by liquid chromatography.

Reaction of bis[tris(pentafluorophenyl)germyl]mercury with dibenzenechromium

To a solution of $(R^f_3Ge)_2Hg$ (1.302 g, 0.97 mmol) in DME (5 ml) was added a solution of $(C_6H_6)_2Cr$ (0.2 g, 0.97 mmol) in DME (5 ml). The reaction mixture was kept at 20°C for 1 h. Mercury precipitated (0.093 g, 96%) was removed by centrifugation. After removal of DME from the reaction solution, the solid residue was recrystallized from toluene to give 1.25 g (88%) of complex II, m.p. 210°C (dec.). IR and ESR spectra together with LSC data confirmed the identity of the product with the compound formed in the previous experiments.

Reaction of complex I with metallic lithium

A solution of complex I (1.7 g, 0.75 mmol) in DME (6 ml) was added to 0.02 g (2.85 mmol) of finely divided lithium. The mixture was shaken at 20°C for 10 min. The organic layer was decanted from the precipitate of thallium (0.146 g, 93%) and the excess of lithium. The solvent was removed by evaporation under vacuum and the residue was recrystallized from toluene. 1.33 g (80%) of $(R^f_3Ge)_3HgLi \cdot 3DME$, m.p. 186–188°C (dec.) was obtained. Found: C, 36.45; H, 1.19; F, 38.22. $C_{66}H_{30}F_{45}Ge_3HgLiO_6$ calcd.: C, 36.05; H, 1.37; F, 38.86%.

Thermolysis of $(R^f_3Ge)_3HgLi \cdot 3DME$

0.466 g (0.21 mmol) of the complex was placed into an evacuated tube (1×10^{-2}mmHg) and heated slowly to 230°C. The volatile products were removed constantly. At 150°C volatile solid products condensed on the cold part of the tube, the amount of those increasing with increasing temperature. The compound was held at 230°C for 1 h. The mixture of the products sublimed was extracted with hot toluene. The insoluble residue was sublimed again (220°C/1 × 10^{-2}mmHg) to give 0.09 g (74%) of digermane $R^f_6Ge_2$, m.p. (mixed) 310–312°C. GLC analysis of the toluene solution revealed the presence of traces of tris(pentafluorophenyl)germane. The toluene was evaporated off, and the residue was washed with hexane and dried in vacuo to give 0.27 g (95%) of $(R^f_3Ge)_2Hg$. After recrystallization from toluene the sample had m.p. 228°C. Thermal decomposition of complex I was carried out in a similar way.

Reaction of complex I with dicyclopentadienyltitanium dichloride

To a mixture of complex I (1.85 g, 0.82 mmol) and Cp_2TiCl_2 (0.102 g, 0.41 mmol) was added DME (4 ml) and ethanol (4 ml). After 30 min at 20°C the organic layer was decanted from the thallium chloride formed (0.19 g, 100%). The mixture of the solvents was removed in vacuo. At the end of the process foaming of the residue is observed, which is characteristic of complexes containing the anions $(R^f_3Ge)_3Hg^-$ or $(R^f_3Ge)_4Hg^{2-}$. The foam solidifies quickly and forms a light yellow powder when shaken. The powder was washed with toluene several times to give 1.2 g (73%) of $[(R^f_3Ge)_3Hg]_2TiCp_2$, m.p. 219°C (dec). Found: C, 34.96; H, 1.05; F, 42.55. $C_{118}H_{10}F_{90}Ge_6Hg_2Ti$ calcd.: C, 35.24; H, 0.25; F, 42.51%.

Reaction of complex I with $CuCl_2$

To a solution of $CuCl_2$ (0.014 g, 0.09 mmol) in 3 ml of DME was added a solution of 0.405 g (0.18 mmol) of complex I in 3 ml of DME at 20°C. After 15 min $R^f_6Ge_2$, Cu_2Cl_2 and TlCl precipitated were removed by centrifugation. The organic layer was decanted from the precipitate and the solvent was removed. R^f_3GeH (0.058 g, 78%) and $(R^f_3Ge)_2Hg$ (0.237 g, 95%) were isolated by gradual sublimation of the precipitate. The mixture of the insoluble products was sublimed in vacuo (220°C/0.01 mmHg) to isolate digermane $R^f_6Ge_2$ (0.021 g, 14%). TlCl and Cu_2Cl_2 were separated by extraction of their mixture with NH_4OH; 0.015 g (86%) of Cu_2Cl_2 appeared to be soluble, 0.036 g (85%) of TlCl remained insoluble.

Reaction of I with $MnCl_2$

To a solution of $MnCl_2$ (0.014 g, 0.11 mmol) in 2 ml of ethanol was added a solution of I (0.561 g, 0.22 mmol) in 4 ml of DME. After 5 min 0.06 g (100%) of TlCl precipitated. The organic layer was decanted from the precipitate, the mixture of solvents was removed in vacuo to isolate a light pink product. The latter was washed with toluene several times. The yield of $[(R^f_3Ge)_3Hg]_2Mn \cdot DME$ was 0.312 g (85%), m.p. 140°C (dec.). Found: C, 33.55; H, 0.95; F, 42.16. $C_{114}H_{15}F_{90}Ge_6Hg_2Mn$ calcd.: C, 33.39; H, 0.37; F, 42.39%.

Reaction of I with mercury chloride

To a solution of 0.052 g of $HgCl_2$ in 2 ml of DME was added a solution of 0.837 g of complex I in 5 ml of DME. After 5 min the reaction mixture was decanted from the precipitate (TlCl, 0.087 g, 96%). DME was replaced by toluene and the solid obtained was recrystallized from this solvent. The yield of bis[tris(pentafluorophenyl)germyl]mercury is 0.72 g (92%), m.p. (mixed) 228-229°C. The compound was found to contain no impurities by liquid chromatography.

Reaction of I with Ph_3SbBr_2

To 2.218 g (0.98 mmol) of complex I and 0.25 g (0.49 mmol) of Ph_3SbBr_2 was added 7 ml of a DME-EtOH mixture (in the ratio 5 : 2). After 5 min at 20°C, 0.28 g (100%) of TlBr precipitated, which was isolated as above. The mixture of the solvents was removed. The residue was washed with hexane at 0°C to give 1.32 g (98%) of bis[tris(pentafluorophenyl)germyl]mercury. After recrystallisation from toluene the product has m.p. 228–229°C. On mixing with an authentic sample no depression of the melting point is observed. 0.54 g (96%) of tris(pentafluorophenyl)germane precipitated from the mother liquid at −78°C over 24 h (identified by GLC). The isolation of the precipitate R^f_3GeH and removal of hexane yielded 0.17 g (80%) of $Ph_3Sb(OEt)_2$. In addition to liquid chromatography, the product was identified by the reaction with hydrogen chloride, which gave Ph_3SbCl_2 and ethanol.

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