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Reactivity of germylmercurate complexes

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Abstract

The selective insertion of sulfur into the Ge–Hg bond in the ionic complex $\{[(C_6F_5)_3Ge]_3Hg\}^-Cp_2Co^+$ results in the formation of mono-, di- and trithiolate derivatives. The compounds have been characterized by elementary analysis, IR, ^{19}F and ^{199}Hg NMR spectroscopy. The molecular structure of $\{Hg[SGe(C_6F_5)_3]_3\}^-$-$Cp_2Co^+$ has been determined by X-ray analysis. Sulfur-containing complexes are donors of chalcogen atoms in the reaction with covalent and ionic polynuclear organometallic compounds. Ytterbium dicyclopentadienide and vanadocene displace cobaltocene from $\{[(C_6F_5)_3Ge]_3Hg\}^-Cp_2Co^+$, and Cp_2Co removes thallium from its germylmercurate complex. A general scheme for the reaction of vanadocene with cobalticinium germylmercurate has been proposed. The zerovalent triphenylphosphine complex of platinum $Pt(PPh_3)_4$ destroys the ionic structure of $\{[(C_6F_5)_3Ge]_2HgI\}^-(C_6H_6)_2Cr^+$ to give dibenzenechromium iodide and a polynuclear compound with Ge–Hg–Pt–Ge chain.

Introduction

Chemical properties of covalent polynuclear compounds containing Ge–Hg group have been investigated [1]. By contrast, the reactivity of ate-complexes obtained recently [2,3], the anions of which contain similar heteroelement groups, have not yet been studied. In order to fill this gap we investigated the reaction of germylmercurate complexes $[(R^f_3Ge)_3Hg]^-Cp_2Co^+$ ($R^f = C_6F_5$) with $Pt(PPh_3)_4$, chalcogens and various metallocenes.

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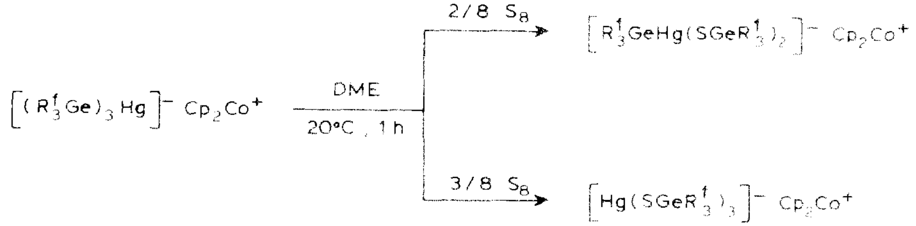
Results and discussion

The insertion of elemental sulfur into the Ge–Hg bond in the ionic complex $[(R^f_3Ge)_3Hg]^-Cp_2Co^+$ is found to occur at 20 °C. Mixing equimolar amounts of the reagents in DME solution (DME = 1,2-dimethoxyethane) gives the monothiolate derivative in 87% yield.

$$\left[(R^f_3Ge)_3Hg\right]^-Cp_2Co^+ + 1/8S_8 \xrightarrow[20\,°C,\ 1\ h]{DME} \left[(R^f_3Ge)_2HgSGeR^f_3\right]^-Cp_2Co^+$$

Reaction of the neutral compounds $(R_3Ge)_2Hg$ with S_8 gives only the monothiolate products $R_3GeSHgGeR_3$ [4–6]. By contrast, anion $[(R_3Ge)_3Hg]^-$ readily adds two or three atoms of sulfur.



The formation of di- and trithiolate complexes (in 90% and 85% yields), respectively, points to the fact that the reductive properties of cobalticinium derivatives are higher than those of 3-nuclear neutral compounds $R_3Ge–Hg–GeR_3$.

The sulfur-containing compounds obtained are light-yellow crystals which are stable in air for several weeks and decompose at 120°, 154° and 169 °C, respectively. Like the initial complex $[(R^f_3Ge)_3Hg]^-Cp_2Co^+$, these compounds are very soluble in DME, THF and acetone. Disulfur and trisulfur complexes are soluble in benzene and toluene whereas the S_1 complex and the starting compound $[(R^f_3Ge)_3Hg]^-Cp_2Co^+$ are not. The difference in solubility permits one to separate and isolate the reaction products from the initial compound by crystallization.

IR spectra of the compounds prepared show bands characteristic of $(C_6F_5)_3Ge$ and $(\eta^5\text{-}C_5H_5)_2Co$ fragments (Fig. 1). The ν(Ge–C) band is shifted by 20 cm^{-1} to lowfield, which is true for the same band for most of the other ionic complexes of this type [7].

The absorption band of the Ge–S bond is at at 430 cm^{-1}. Its intensity increases from mono- to di- and trithiolate complexes.

The ^{19}F and ^{199}Hg NMR spectra (Table 1) confirm the structure of the anions in the thiolate complex $[(R^f_3Ge)_3S_nHg]^-Cp_2Co^+$, $n = 1–3$.

Monothiolate complex is unstable in solution, so to record the ^{199}Hg NMR spectrum, supplementary additions were required; this led to three signals being observed with an intensity ratio of 1 : 1 : 2. A broad signal at -169 ppm (linewidth $\Delta\nu_{1/2} \approx 200$ Hz) is due to the monothiolate complex. Two other signals, at 95 ppm and -323 ppm, are due to much more stable complexes, the initial compound and the dithiolate complex, respectively.

The ^{199}Hg NMR spectrum of the dithiolate product which gives a weakly resolved multiplet with $^4J(Hg–F) = 57 \pm 4$ Hz, also showed a signal from the symmetrical anion $[Hg(SGeR^f_3)_3]^-$ (ratio 5 : 1). The signal from the complex con-

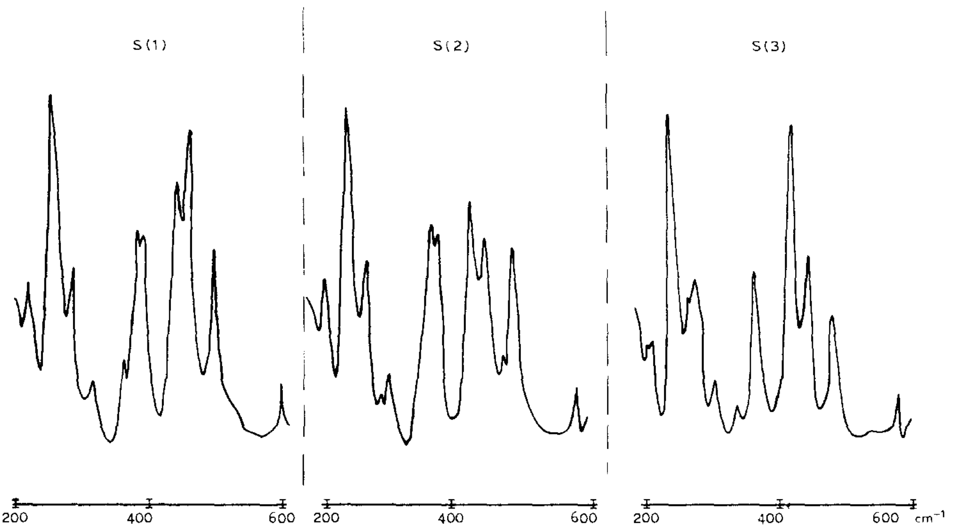


Fig. 1. IR spectra of $\{[(C_6F_5)_3Ge]_3S_nHg\}^- Cp_2Co^+$ ($n = 1, 2, 3$) (field 200–600 cm^{-1}).

taining 3 sulfur atoms in the germylmercurate anion is comparatively narrow ($\Delta\nu_{1/2} \approx 43$ Hz) with no long-range ^{199}Hg–^{19}F spin-spin coupling.

Subsequent insertion of sulphur atoms into the Ge–Hg bond of germylmercury anion leads to an increase in ^{199}Hg shielding. This result is consistent with the general trends in ^{199}Hg screening, whereby an increase in electronegativity of R-groups in R_2Hg compounds results in an shift upfield [8].

However, the insertion of the first sulphur atom (cf. data for the original complex and the monothiolate complex) is accompanied by a substantial increase in ^{199}Hg screening, which is twice as large as that which occurs on going from $(R^f_3Ge)_2Hg$ (δ Hg = −887.4 ppm [9]) to $R^f_3GeHgSGeR^f_3$ (δ Hg = −967.5 ppm). This indicates a powerful transfer of a negative charge from Hg atom in the germylmercurate complex to the $SGeR^f_3$ ligand. The degree of such charge delocalization during the

Table 1

^{19}F and ^{199}Hg chemical shifts for $[(R^f_3Ge)_3S_nHg]^-$ ($n = 1, 2, 3$) [a]

n	δ(F)(ppm)						δ(Hg) (ppm)
	$SGeR^f_3$			GeR^f_3			
	o	m	p	o	m	p	
0 [b]	–	–	–	−123.09	−159.75	−151.97	+95 34 [c]
1	−124.9	−159.5	−150.2	−123.1	−159.5	−151.2	−169
2	−124.62	−159.4	−149.90	−123.06	−159.40	−150.12	−323 57 ± 4 [c]
3	−124.32	−159.69	−149.65	–	–	–	−345 [d]

[a] ^{19}F chemical shifts are relative to CCl_3F, ^{199}Hg chemical shifts are relative to $(CH_3)_2Hg$. [b] Ref. [11]. [c] ^4J(Hg–F). [d] $\Delta\nu_{1/2} \approx 200$ Hz. [e] $\Delta\nu_{1/2} \approx 43$ Hz.

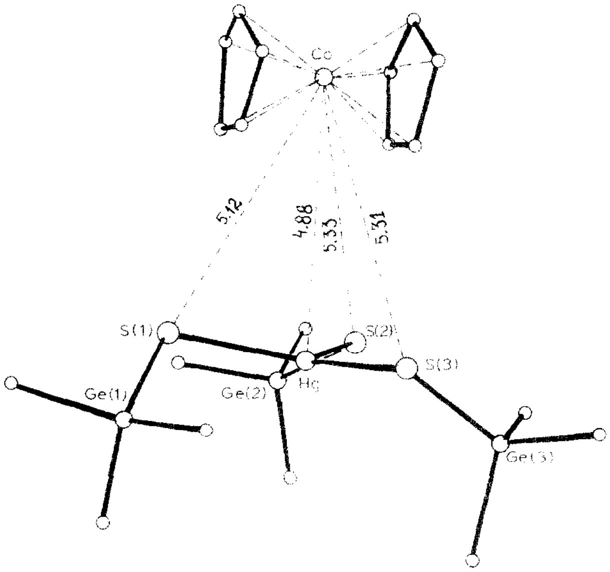


Fig. 2. General view of the ionic pair $\{Hg[SGe(C_6F_5)_3]_3\}^-$ Cp_2Co^+. Only Hg atoms of $(C_6F_5)_3$Ge-groups bonded to Ge atom are shown.

insertion of the second and third $SGeR^f_3$-groups decreases, leading to much smaller and nonadditive changes of the ^{199}Hg chemical shifts.

A change in coordination number of Hg from 2 to 3 causes a decrease in ^{199}Hg screening to 700–1000 ppm [10,11,12]. Although $(R^f_3GeS)_2Hg$ is unknown, its ^{199}Hg chemical shift can be readily estimated (1060 ± 60 ppm). Therefore, the difference in the values of δ Hg of this compound and of the trithiolate complex is also within the range of typical values (700 ppm).

It is noteworthy that an increase in ^4J(Hg–F) which is observed on going from the original complex to the dithiolate, an increase in s-character of the Ge–Hg bond is shown by the latter. This confirms that electron pair delocalization is possible in the $SGeR^f_3$ ligand.

An X-ray diffraction study * has revealed that crystals of the trithiolate complex have an ionic structure containing the anion $\{Hg[SGe(C_6F_5)_3]_3\}^-$ and the cation Cp_2Co^+, which are combined into ionic pairs (Fig. 2). The Hg ··· Co distance (4.88(1) Å) in the pair is much shorter than that between the Hg and Co atoms in different pairs. The Hg and Co atoms form a line which is approximately normal to the plane of the three S atoms bonded to the Hg atom. This is evidenced by the close values of the Co ··· S (1,2,3) distances (5.12, 5.33 and 5.31 Å) and the Co ··· Hg–S (1,2,3) angles (81.5, 86.5, and 86.4°).

The central $(GeS)_3Hg$ fragment in the anion is not planar because it has nearly C_{3v} symmetry. The Hg and Ge(1), Ge(2), Ge(3) atoms lie to one side of the plane of three S atoms and deviate from it by 0.22 and 1.02, 1.12, 1.35 Å, respectively (Fig. 2). In anion $[Hg(SGeR^f_3)_3]^-$ the deviation of the Hg atom from the plane of three S atoms bonded to it is the same as that in anion $[(R^f_3Ge)_3Hg]^-$ – 0.2 Å [11], but is

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* Full X-ray data are given in [13].

significantly greater than that in the anions $[(PhS)_3Hg]^-$ - 0.02 Å [14] and $[(PhTe)_3Hg]^-$ - 0.09 Å [15] with similar structures. The S–Hg–S valence angles (120.1(2), 120.4(2) and 117.0(2)°) are considerably less distorted (from 120°) than observed in the anions $[(PhS)_3Hg]^-$ (120.0, 137.1 and 102.9 [14]) and $[(PhTe)_3Hg]^-$ (123.8, 125.2 and 110.0) [15]). The Hg–S (2.435(7), 2.468(7) and 2.427(7) Å and Ge–S bond lengths (2.154(7), 2.176(7) and 2.168(8) Å) are actually equal. The average Hg–S bond length, 2.443 Å, is close to that in the anion $[(PhS)_3Hg]^-$, 2.448 Å [14].

The Cp_2Co^+ cation has a sandwich structure with eclipsed conformation. The angle between the normals to the planes of Cp-rings is 2°. The average Co–C bond distance, 1.98 Å, is a little shorter than that in similar cations e.g. $[(R^f_3Ge)_3Hg]^-$ Cp_2Co^+, 2.02 Å [11] and in the structures with an 18-electron shell at the Co atom, (2.036(9) Å, in $(C_5H_5)(C_5H_4)Co$ [16]), and notably less than the values in neutral Cp_2Co, 2.096(8) and 2.119(3) Å, obtained by X-ray analysis [17] and gas electron diffraction [18], respectively.

Hydrochlorination of monothiolate complex for 1 h (20 °C) yields hydrogen sulfide (79%), germanthiol (21%), $(R^f_3Ge)_2Hg$ (20%), R^f_3GeH (23%), R^f_3GeCl (47%) and an unidentified cobalt-containing compound, probably $[Cp_2CoCl]$:

$$\left[(R^f_3Ge)_2HgSGeR^f_3\right]^- Cp_2Co^+ + HCl \xrightarrow[20\,^\circ C,\ 1\ h]{DME}$$

$$H_2S + R^f_3GeSH + R^f_3GeH + R^f_3GeCl + (R^f_3Ge)_2Hg + [Cp_2CoCl]$$

The reaction of S_3 complex with a monothiolate complex under mild conditions results in the formation of an S_2 derivative $[R^f_3GeHg(SGeR^f_3)_2]^-Cp_2Co^+$:

$$\left[Hg(SGeR^f_3)_3\right]^- Cp_2Co^+ + \left[(R^f_3Ge)_2HgSGeR^f_3\right]^- Cp_2Co^+ \xrightarrow[20\,^\circ C,\ 1\ h]{THF}$$

$$2\left[R^f_3GeHg(SGeR^f_3)_2\right]^- Cp_2Co^+$$

No products were isolated in the reaction of S_3 complex with $[(R^f_3Ge)_3Hg]^-$-Cp_2Co^+. But after several hours (20 °C) ^{199}Hg NMR spectra revealed that $[(R^f_3Ge)_2HgSGeR^f_3]^-Cp_2Co^+$ and $[R^f_3GeHg(SGeR^f_3)_2]^-Cp_2Co^+$ were present in appreciable quantities. Such processes are likely to occur during the synthesis of polysulfur complexes from $[(R^f_3Ge)_3Hg]^-Cp_2Co^+$ and sulfur. Sulfur migration from S_3 derivative into neutral bis[tris(pentafluorophenyl)germyl]mercury may also occur:

$$\left[Hg(SGeR^f_3)_3\right]^- Cp_2Co^+ + (R^f_3Ge)_2Hg \xrightarrow[20\,^\circ C,\ 1\ h]{DME}$$

$$\left[R^f_3GeHg(SGeR^f_3)_2\right]^- Cp_2Co^+ + R^f_3Ge{-}S{-}Hg{-}GeR^f_3$$

Unlike sulfur, selenium does not react with cobalticinium germyl-mercurate (100 °C, 10 h).

The oxidative addition of zerovalent triphenylphosphine complexes of platinum, palladium and nickel into M–C or M–M bond is known to be characteristic of mono- and polynuclear organometallics [19]. Cobalticinium germylmercurate and its dithiolate complex are inert to PtL_4 ($L = PPh_3$).

The lack of reaction in this case probably because of steric hindrance by the three $(C_6F_5)_3Ge$ groups, which shield the Ge–Hg bond.

In contrast to this, the iodine germylmercurate complex $[(R^f_3Ge)_2HgI]^-$ $(C_6H_6)_2Cr^+$ (the structure of which has only recently been confirmed by X-ray diffraction *), is less sterically hindered and reacts readily with PtL_4. But instead of the expected product of insertion of PtL_2 into the Ge–Hg bond, we obtained $(C_6H_6)_2CrI$ and the known compound with Ge–Hg–Pt–Ge chain [20]. In our opinion it proves that the reaction between PtL_4 and $[(R^f_3Ge)_2HgI]^-(C_6H_6)_2Cr^+$ proceeds by the insertion of PtL_2 into one of the Ge–Hg bonds. The unstable intermediate formed is destroyed rapidly to give final products (Scheme 1).

Another mechanism is also possible: the initial stage including dissociation of ate-complex into neutral germylmercury and $(C_6H_6)_2CrI$. The first is known to react readily with PtL_4 to form $R^f_3GeHgPtL_2GeR^f_3$ [20]. But this is less likely since no signals from free $(R^f_3Ge)_2Hg$ were detected in the ^{199}Hg NMR spectrum of the iodine-germylmercurate complex of bis(benzene)chromium (δ $^{199}Hg = -357$ ppm).

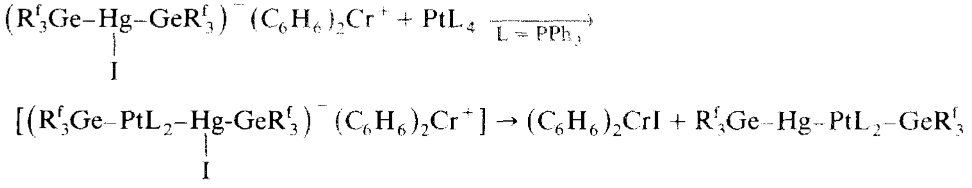
The reaction of Cp_2Co and Cp_2Yb with germylmercurate complexes proceeds by direct cation reduction without destruction of the polynuclear anion:

$$[(R^f_3Ge)_3Hg]^-Tl^+ + Cp_2Co \xrightarrow[0\,^\circ C,\ 5\ min]{DME} [(R^f_3Ge)_3Hg]^-Cp_2Co^+ + Tl$$

$$[(R^f_3Ge)_3Hg]^-Cp_2Co^+ + Cp_2Yb \xrightarrow[0\,^\circ C,\ 5\ min]{DME} [(R^f_3Ge)_3Hg]^-Cp_2Yb^+ \cdot DME + Cp_2Co$$

Ferrocene and nickelocene react neither with $[R^f_3Ge)_3Hg]^-Cp_2Co^+$ nor with neutral $(R^f_3Ge)_2Hg$. Thus, the reducing agents investigated can be arranged in the order $Cp_2Yb > Cp_2Co > Tl > Cp_2Fe \sim Cp_2Ni$ according to their decreasing activity.

The interaction between cobaltocinium germylmercurate and vanadocene proceeds in a different way. Here the anion is destroyed to form $Cp_2VGeR^f_3$. To explain the mechanism of reaction, direct Cp_2Co^+/Cp_2V exchange should probably be ruled out, since Cp_2V is a weaker electron donor than cobaltocene [21] (the latter replaces Cp_2V in $Cp_2VGeR^f_3$). The first stage of the reaction is believed to be the insertion of Cp_2V into one of Ge–Hg bonds in polynuclear anion (stage *a*, Scheme 2). The resulting 6-nuclear complex obtained is unstable, it decomposes (stage *b*) to form $Cp_2VGeR^f_3$ and an intermediate containing an anion radical fragment $[(R^f_3Ge)_2Hg^{\dot{-}}Cp_2Co^+]$. An anion radical reduces the cobalticinium cation (stage *c*) with the formation of neutral $(R^f_3Ge)_2Hg$ and Cp_2Co which readily react with each other (stage *d*) [11] yielding metallic mercury and the initial complex $[(R^f_3Ge)_3Hg]^-Cp_2Co^+$. The reaction is complete at this stage, if initial reactants are present in equimolar quantities, but if an excess of Cp_2V is added, the stages result in the final products – cobaltocene, Hg and $Cp_2VGeR^f_3$ (stage *e*).



$$(R^f_3Ge\text{–}\underset{\underset{I}{|}}{Hg}\text{–}GeR^f_3)^-(C_6H_6)_2Cr^+ + PtL_4 \xrightarrow[L = PPh_3]{}$$

$$[(R^f_3Ge\text{–}PtL_2\text{–}\underset{\underset{I}{|}}{Hg}\text{-}GeR^f_3)^-(C_6H_6)_2Cr^+] \rightarrow (C_6H_6)_2CrI + R^f_3Ge\text{–}Hg\text{–}PtL_2\text{–}GeR^f_3$$

Scheme 1

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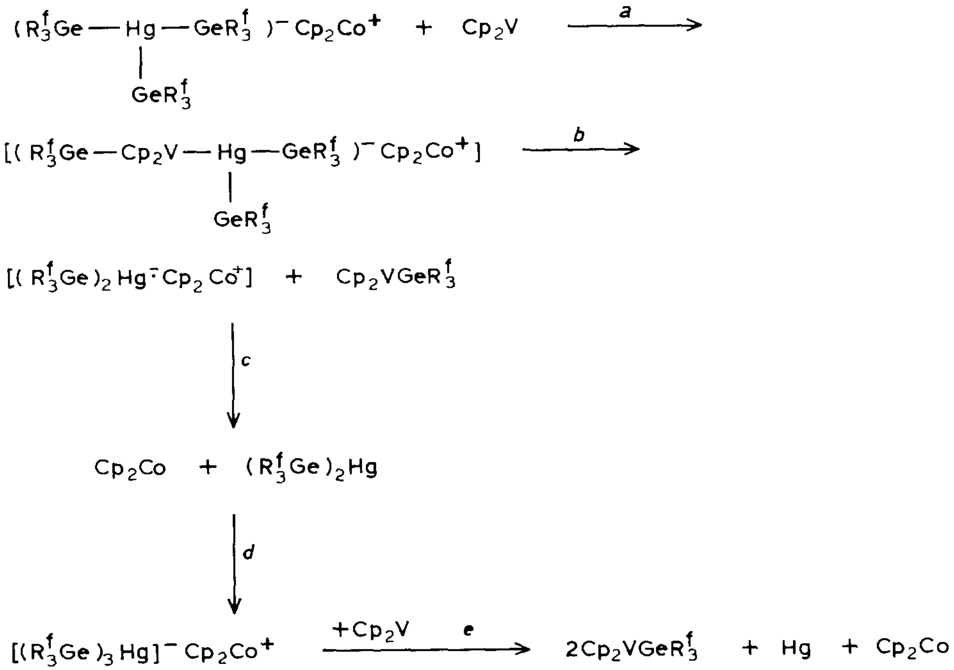
* Results to be published separately.



Scheme 2

The interaction of $[Hg(SGeR^f_3)_3]^-Cp_2Co^+$ and vanadocene in a 1 : 3 molar ratio proceeds similarly to give metallic mercury, cobaltocene and a compound with a V–S–Ge grouping:

$$\left[Hg\left(SGeR^f_3\right)_3\right]^- Cp_2Co^+ + 3Cp_2V \rightarrow 3Cp_2VSGeR^f_3 + Hg + Cp_2Co$$

With equimolar quantities of the monothiolate complex $[(R^f_3Ge)_2HgSGeR^f_3]^-$ Cp_2Co^+ and Cp_2V we obtained Hg, cobaltocene, $Cp_2VSGeR^f_3$ and $[(R^f_3Ge)_3Hg]^-Cp_2Co^+$ in high yields. We suggest that in this case the stages presented in Scheme 2 are realized at once. The formation of $Cp_2VSGeR^f_3$ indicates insertion of Cp_2V into the S–Hg bond and not into Ge–Hg bond.

$$3\left[\left(R^f_3Ge\right)_2HgSGeR^f_3\right]^- Cp_2Co^+ + 3\,Cp_2V \xrightarrow[20\,^\circ C,\ 5\ min]{DME} Cp_2Co$$
$$+ 3\,Cp_2VSGeR^f_3 + 2\left[\left(R^f_3Ge\right)_3Hg\right]^- Cp_2Co^+ + Hg$$

Germylthiovanadocene $Cp_2VSGeR^f_3$ is isolable as crystals which are unstable in air, m.p. 140 °C. They are very soluble in THF, aromatic hydrocarbons and alkanes. Like most Cp_2VR complexes (R = organic or elementoorganic radical) $Cp_2VSGeR^f_3$ is readily oxidized by $CuCl_2$, AgCl to the vanadium(IV) derivative:

$$Cp_2VSGeR^f_3 + MCl \xrightarrow[\substack{20\,^\circ C,\ 3\ min.\\ M = CuCl,\ Ag}]{THF} Cp_2V(Cl)SGeR^f_3 + M$$

ESR spectrum of $Cp_2V(Cl)SGeR^f_3$: $A_i\,^{51}V = 67$ G, $g_i = 1.9935$.

Experimental

All reactions were carried out in evacuated sealed ampoules. IR spectra were recorded on a Perkin–Elmer-577 spectrophotometer. The ^{19}F and ^{199}Hg NMR spectra were measured on a JEOL FX-100 spectrometer at 93.7 and 17.8 MHz, respectively. The samples were saturated solutions of the complexes in THF. X-Ray crystallography was carried out with a Syntex $P2_1$ automatic diffractometer. ESR spectra were recorded on a Bruker ER-200 D SCR spectrometer. Chromatographic analyses of the products were carried out on Tsvet-104 and Tsvet-304 instruments. $(C_6F_5)_3Ge$ derivatives were prepared by published methods [4,11,22].

Reaction of $[(R^f_3Ge)_3Hg]^-Cp_2Co^+$ with sulfur (1 : 1) in DME

0.022 g (0.673 mmol) of sulfur was placed in an ampoule. To it was added a solution containing 1.42 g (0.673 mmol) of $[(R^f_3Ge)_3Hg]^-Cp_2Co^+$ in DME (10 ml). The mixture was shaken at 20 °C for 1 h until the sulfur had completely dissolved. The solvent was partially evaporated in vacuo and hexane was added to yield 1.25 g (87%) of $[(R^f_3Ge)_2HgSGeR^f_3]^-Cp_2Co^+$ (yellow crystals), m.p. 120 °C (dec.). Found: C, 34.89; H, 0.60; F, 39.75. $C_{64}H_{10}CoF_{45}Ge_3HgS$ calc: C, 35.86; H, 0.40; F, 39.89%.

Reaction of $[(R^f_3Ge)_3Hg]^-Cp_2Co^+$ with sulfur (1 : 2) in DME

To a solution of $[(R^f_3Ge)_3Hg]^-Cp_2Co^+$ (0.605 g, 0.287 mmol) in DME (10 ml) was added 0.018 g (0.574 mmol) of sulfur. The reaction mixture was shaken for 1 h until the sulfur had completely dissolved. The solvent was removed by evaporation under vacuum. The residue was recrystallized from hexane/toluene (5 : 1) mixture at 0 °C and dried in vacuo. 0.56 g (90%) of yellow crystalline $[R^f_3GeHg(SGeR^f_3)_2]^-Cp_2Co^+$, m.p. 154 °C (dec.) was obtained. Found: C, 35.59; H, 0.58; F, 39.89. $C_{64}H_{10}CoF_{45}Ge_3HgS_2$ calc.: C, 35.34; H, 0.46; F, 39.30%.

Reaction of $[(R^f_3Ge)_3Hg]^-Cp_2Co^+$ with sulfur in the ratio 1 : 3 was carried out in a similar way

0.531 g (0.252 mmol) of the initial cobalticinium and 0.024 g (0.756 mmol) of sulfur gave yellow crystals of $[Hg(SGeR^f_3)_3]^-Cp_2Co^+$ (0.47 g, 85%), m.p. 168–169 °C. Found: C, 34.72; H, 0.49. $C_{64}H_{10}CoF_{45}Ge_3HgS_3$ calc: C, 34.82; H, 0.46%.

Reaction of $[(R^f_3Ge)_2HgSGeR^f_3]^-Cp_2Co^+$ with hydrogen chloride

To a solution of $[(R^f_3Ge)_2HgSGeR^f_3]^-Cp_2Co^+$ (0.59 g, 0.279 mmol) in THF was added hydrogen chloride (26 ml, 1.11 mmol). The reaction mixture was kept at 20 °C for 1 h. The volatile products were found to contain 0.007 g (79%) of H_2S. After removal of the solvent and volatile products, the solid residue was washed with hexane several times. GLC and LSC analyses of the extract revealed R^f_3GeH (0.11 g, 23%), R^f_3GeCl (0.24 g, 47%) and R^f_3GeSH (0.035 g, 21%). From the IR spectra and LSC data the insoluble yellow residue appeared to contain $(R^f_3Ge)_2Hg$ and an unidentified cobalt-containing compound.

Reaction of $[Hg(SGeR^f_3)_3]^-Cp_2Co^+$ with $(R^f_3Ge)_2Hg$

To a solution of $[Hg(SGeR^f_3)_3]^-Cp_2Co^+$ (0.4 g, 0.181 mmol) in DME (5 ml) was added a solution containing 0.244 g (0.181 mmol) of $(R^f_3Ge)_2Hg$ in DME (7 ml).

The reaction mixture was kept at 20 °C for 1 h. The solvent was removed by evaporation under vacuum and the residue was extracted with hot hexane. Cooling of the hexane solution gave 0.237 g (95%) of crystalline $R^f_3GeHgSGeR^f_3$, m.p. 169 °C (lit. [4], m.p. 169–170 °C). The product was identified by LSC. The yellow residue which is insoluble in hexane was recrystallized from toluene hexane mixture. 0.315 g (80%) of $[R^f_3GeHg(SGeR^f_3)_2]^- Cp_2Co^+$, m.p. 154 °C (dec.), was obtained. IR spectra showed that this product was identical with that obtained from the reaction of $[(R^f_3Ge)_3Hg]^- Cp_2Co^+$ and two equivalents of sulfur.

Reaction of $[(R^f_3Ge)_2HgI]^-(C_6H_6)_2Cr^+$ with $Pt(PPh_3)_4$ in toluene

To a solution of $[(R^f_3Ge)_2HgI]^-(C_6H_6)_2Cr^+$ (0.92 g, 0.546 mmol) in toluene (10 ml) was added a solution of $Pt(PPh_3)_4$ (0.68 g, 0.546 mmol) in toluene (20 ml). The reaction proceeded for 15 h at 20 °C with precipitation of 0.88 g (95%) of yellow crystals of $(C_6H_6)_2CrI$, m.p. 172 °C. The product was identified as $(C_6H_6)_2CrI$ from its IR, ESR spectra and its melting point [23]. The solvent was partially evaporated in vacuo and 10 ml of hexane was added to the residue. 0.8 g (87%) of colourless crystals of $R^f_3GeHgPt(PPh_3)_2GeR^f_3$, m.p. 242–244 °C (dec.) was isolated (lit. [20], m.p. 244 °C (dec.)). The product was identified by LSC analysis and IR spectroscopy.

Reaction of $[(R^f_3Ge)_3Hg]^- Cp_2Co^+$ with Cp_2Yb in DME

To a solution of the complex (1g, 0.473 mmol) in 5 ml of DME was added a solution of Cp_2Yb (0.143 g, 0.473 mmol) in 15 ml of DME. After 5 min (20 °C), the solvent was removed in vacuo and the residue was extracted with hexane. 0.08 g (90%) of Cp_2Co was isolated by sublimation of the residue in vacuo. The solid residue was recrystallized from DME/toluene mixture to give 0.9 g (81%) of red crystals of $[(R^f_3Ge)_3Hg]^- Cp_2Yb^+ \cdot DME$, m.p. 199 °C (lit. [11], m.p. 199 °C). The IR spectrum is identical with that of the product obtained from the reaction of $(R^f_3Ge)_2Hg$ with Cp_2Yb.

The reaction of $[(R^f_3Ge)_3Hg]^- Tl^+$ with Cp_2Co was carried out in a similar way.

Reaction of $[(R^f_3Ge)_3Hg]^- Cp_2Co^+$ with Cp_2V (1 : 3) in THF

To a solution of Cp_2V (0.303 g, 1.671 mmol) in THF (5 ml) was added a solution containing 1.18 g (0.558 mmol) of $[(R^f_3Ge)_3Hg]^- Cp_2Co^+$ in THF (10 ml). After 5 h (20 °C) the ESR signal from the starting Cp_2V had disappeared and metallic mercury (0.109 g, 98%) was found to have precipitated. The organic layer was decanted, THF was evaporated off in vacuo, the residue was extracted several times with hexane. 0.093 g (88%) of Cp_2Co was isolated by sublimation of the residue in vacuo. The insoluble residue contained 1.16 g (92%) of $Cp_2VGeR^f_3$, which was deduced from its IR and ESR spectra (the oxidation by $CuCl_2$ in THF led to $Cp_2V(Cl)GeR^f_3$ [24]).

The reaction with equimolar quantities of the reactants was carried out in a similar way.

Reaction of $[(R^f_3Ge)_2HgSGeR^f_3]^- Cp_2Co^+$ with Cp_2V (1 : 1) in DME-toluene solution

To a solution of Cp_2V (0.07 g, 0.387 mmol) in toluene (5 ml) was added a solution containing 0.839 g (0.387 mmol) of $[(R^f_3Ge)_2HgSGeR^f_3]^- Cp_2Co^+$ in DME (7 ml). After 5 min (20 °C) the metallic mercury (0.026 g, 100%) which precipitated was removed by centrifugation. The organic layer was decanted, the solvents were evaporated off in vacuo, and 10 ml of hexane was added. 0.02 g (73%) of Cp_2Co was isolated by sublimation of the residue in vacuo. The insoluble residue was extracted three times with toluene. After hexane (0 °C) had been added to the toluene extract, 0.2 g (92%) of violet crystals of $Cp_2VSGeR^f_3$ was isolated. It was identified by ESR-spectroscopy after oxidation by $CuCl_2$ in THF to $Cp_2V(Cl)SGeR^f_3$ ($A_i\,^{51}V = 67$ G; $g_i = 1.9936$) and by IR-spectroscopy (ν(Ge–S) = 420 cm^{-1}). The residue which was insoluble in toluene was recrystallized from DME/toluene solution (1 : 5) to give 0.38 g (70%) of yellow crystals of $[(R^f_3Ge)_3Hg]^-Cp_2Co^-$, m.p. 175 °C (lit. [11], m.p. 175 °C). The IR spectrum was the same as that of the product obtained from the reaction of $(R^f_3Ge)_2Hg$ with Cp_2Co [11].

The reaction of $[Hg(SGeR^f_3)_3]^-Cp_2Co^+$ with Cp_2V in a molar ratio of 1 : 3 was carried out in a similar way.

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