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PREPARATION AND SOME REACTIONS OF ORGANOGERMYLMERCURYPLATINUM COMPLEXES AND RELATED COMPOUNDS

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Summary

The preparation of some stable organometallic compounds involving Ge(Sn)—Hg(Cd,Zn)—Pt(Pd)—Ge(Sn) chains is reported. Photolysis of $(C_6F_5)_3GeHgPt-(PPh_3)_2Ge(C_6F_5)_3$ and reactions of this compound with bromine, hydrogen chloride and hydrogen have been studied. The data of physico-chemical investigation of the compounds are presented.

Introduction

Zerovalent complexes of the platinum group metals are known to readily undergo oxidative addition reactions with numerous compounds including organometallic hydrides and halides [1]. Insertion of complexes into M—H or M—Hal bonds in these reactions produces compounds containing a metal—metal bond *. It has recently been shown [3–5] that complexes of platinum(0) and palladium(0) react in a similar way with organomercurials inserting into Hg—Hal or Hg—C bonds. Stability of the reaction products $R-Hg-M(PPh_3)_2-R$ (M = Pt, Pd) strongly depends on the nature of the substituents. Thus organoplatinummercurials with strong electron-acceptor groups, CF_3 or C_6F_5 , are most stable compounds [5].

It would appear interesting to investigate the reactions of triphenylphosphine complexes of platinum(0) and palladium(0) with organometallic compounds containing Hg(Cd,Zn)—Ge(Sn) groups. Pentafluorophenyl derivatives of mercury, cadmium and zinc of the type $[(C_6F_5)_3Ge]_2Hg$ were used as starting materials

* Quite recently a favoured M—C insertion of $Pt(PPh_3)_3$ has been reported for organotin and organogermanium halides [2].

TABLE 1
M.P., COLOUR AND ANALYSIS OF THE COMPLEXES PREPARED

No.	Compound	M.p. (°C)	Colour	Analysis found (calcd.) (%)		
				C	H	F
Ia	$(C_6F_5)_3GeHgPt(PPh_3)_2Ge(C_6F_5)_3$	243-244	colourless	41.86 (41.82)	1.77 (1.46)	27.14 ^a (27.56)
Ib	$(C_6F_5)_3GeCdPt(PPh_3)_2Ge(C_6F_5)_3 \cdot 2C_6H_6$	222-224 (dec.)	pale yellow	47.33 (47.24)	1.99 (1.98)	27.01 (26.68)
Ic	$(C_6F_5)_3GeZnPt(PPh_3)_2Ge(C_6F_5)_3 \cdot 2C_6H_6$	211 (dec.)	colourless	48.61 (48.30)	2.15 (2.03)	
II	$(C_6F_5)_3SnHgPt(PPh_3)_2Sn(C_6F_5)_3 \cdot C_6H_6$	170-171	pale yellow	42.32 (41.89)	1.71 (1.62)	25.15 (25.47)
III	$(C_6F_5)_3GeHgPd(PPh_3)_2Ge(C_6F_5)_3$	134 (dec.)	yellow-green	43.82 (43.70)	1.66 (1.53)	29.02 (28.80)
IV	$(C_6F_5)_3GePtHgEt \cdot C_6H_6$	153-155	pale yellow	46.42 (46.51)	2.65 (2.58)	17.83 (17.80)
V	$(C_6F_5)_3GeHgPt(PPh_3)_2Sn(C_6F_5)_3 \cdot 2C_6H_6$	216-218	colourless	44.01 (44.49)	1.86 (1.86)	25.74 (25.11)
VI	$(C_6F_5)_3GePt(PPh_3)_2H$	213-215	colourless	50.51 (51.10)	2.53 (2.41)	21.99 (22.01)
VIII	$(C_6F_5)_3GePt(PPh_3)_2Br$	243-248	colourless	48.58 (47.23)	2.26 (2.20)	20.32 (20.75)

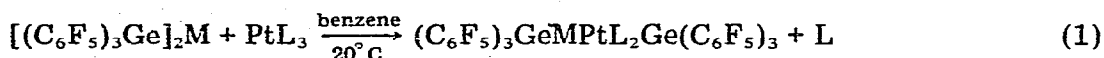
^a Found: P, 2.90; calcd.: P, 2.81%.

[6–8]. We hoped that an enhanced stability of these derivatives would allow us to obtain stable complexes of platinum and palladium with polymetallic chains by this route.

Results and discussion

Preparation

We found * the reactions of PtL_3 (here and below L is PPh_3) with bis[tris(pentafluorophenyl)germyl]mercury and its zinc and cadmium analogues occur easily in benzene solution at room temperature and give stable polymetallic compounds.



(a, M = Hg; b, M = Cd; c, M = Zn)

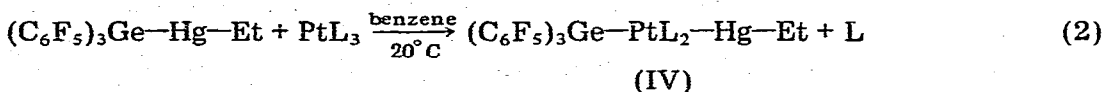
Of particular interest is the fact that PtL_2 carbenoid inserts into germanium–cadmium and germanium–zinc bonds to give compounds with unprecedented Pt–Cd and Pt–Zn bonds. Insertion of triphenylphosphine platinum complex into Sn–Hg bonds in bis[tris(pentafluorophenyl)stannyl]mercury proceeds with a similar readiness to give compound II (see Table 1) with a Sn–Hg–Pt–Sn chain.

This method can be used for the synthesis of polymetallic palladium complexes. Thus the reaction of $[(\text{C}_6\text{F}_5)_3\text{Ge}]_2\text{Hg}$ with the zerovalent palladium complex under similar conditions gives the germylmercurypalladium compound III. As we know this surprisingly stable product is the first complex with a Pd–Hg bond.

The PtL_3 reacts with bis(triethylgermyl)mercury with extreme readiness. It is natural to assume that insertion of platinum into the Ge–Hg bond should occur in this case as well. However the absence of stabilizing C_6F_5 -substituents at the germanium results, as should be expected, in the immediate decomposition of the polymetallic product with elimination of mercury.

It is interesting to note that no diplatinum derivative, $[(\text{C}_6\text{F}_5)_3\text{GePtL}_2]_2\text{Hg}$, is produced when an excess of the platinum(0) complex is used in the synthesis of compound Ia according to reaction (1) or when the compound Ia is heated with an equimolar quantity of PtL_3 in benzene solution to 80°C for 2 h.

Two isomers with Ge–Pt–Hg or Ge–Hg–Pt groupings may be expected from the reaction of the unsymmetrical compound $(\text{C}_6\text{F}_5)_3\text{GeHgEt}$ with PtL_3 . We believe $(\text{C}_6\text{F}_5)_3\text{GePtHgEt}$ (IV) to be the main reaction product (76% yield) since PtL_2 insertion into the Hg–C bond in dialkylmercury was not observed under these conditions.

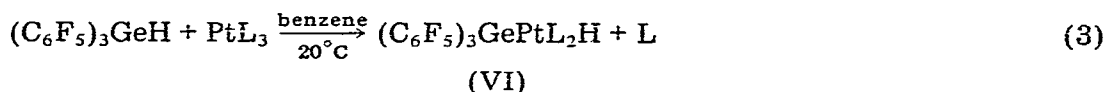


A simultaneous attack of the platinum carbenoid in two directions, viz., Ge–Hg or Hg–Sn bonds, seems more probable in the case of another unsymmetrical

* A preliminary communication [9].

compound, $(C_6F_5)_3GeHgSn(C_6F_5)_3$, since reactions with $[(C_6F_5)_3Ge]_2Hg$ and with $[(C_6F_5)_3Sn]_2Hg$, as it is noted above, proceed under the same conditions.

We have recently shown that unlike unfluorinated organodigermanes the Ge—Ge bond in the pentafluorophenyl digermanes possesses high reactivity [10]. Thus sulphur, selenium and tellurium interact with such compounds to form corresponding chalcogenides $(C_6F_5)_3GeXGeR_3$ under mild conditions. Redox reactions of pentafluorophenyl digermanes with some salts of metals also proceed easily. However an attempt to obtain bis(germyl)platinum complex $[(C_6F_5)_3Ge]_2PtL_2$ by interaction of $(C_6F_5)_6Ge_2$ with PtL_3 failed. The reaction proceeds neither in benzene nor in THF solution even on prolonged heating at $80^\circ C$. The small amount of platinum hydride $(C_6F_5)_3GePtL_2H$ (VI) formed in the reaction was probably due to hydrolysis of the initial digermane by traces of moisture and to subsequent interaction of the thus formed tris(pentafluorophenyl)germane with PtL_3 . A separate experiment showed such a reaction occurs easily at room temperature (eq. 3).



Properties and reactivity

All the complexes prepared are colourless or light yellow crystalline solids (see Table 1). In the solid state all of them are air stable except Zn- and Cd-derivatives. The compounds crystallize from hexane/benzene solution with one or two molecules of benzene which are easily separated by heating the complexes to $45\text{--}50^\circ C$ under reduced pressure.

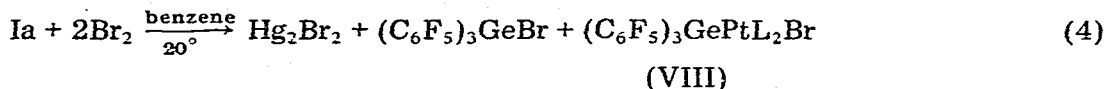
Reactivity of the compounds was studied using complex Ia. At room temperature the compound does not react with Et_3SiH , CF_3COOH nor the methanol solution of KOH. Decomposition of Ia with mercury elimination occurs only when its CF_3COOH solution is heated for some hours. Compounds Ib, Ic, II and V are more sensitive to trifluoroacetic acid.

Photolysis of Ia in toluene with UV irradiation affords mercury and a complex mixture of products from which tris(pentafluorophenyl)germane, traces of hexakis(pentafluorophenyl)digermane * and the platinum complex VII were isolated. Carbon, hydrogen and fluorine contents in VII correspond to the formula of the hydride, $(C_6F_5)_3GePtL_2H$, which may be expected from the reaction. However LSC analysis did not confirm the identity of VII with hydride VI obtained according to reaction 3. Moreover, the IR spectrum of VII does not show absorption bands in the region $1900\text{--}2300\text{ cm}^{-1}$ which is characteristic of the Pt—H stretching modes [11]. It may therefore be assumed that compound VII is a cluster $[(C_6F_5)_3GePtL_2]_n$. Existence of platinum cluster compounds is an established fact [12]. At the same time it should be noted that Cross and Glockling have obtained a certain compound in the reaction of I_2PtL_2 with triphenylgermyllithium which had an elemental analysis and molecular weight corresponding to the diplatinum complex $Ph_3GePtL_2\text{--}PtL_2GePh_3$. A detailed X-ray investigation however did not confirm this structure [13]. Therefore the final

* Photochemical decomposition of $[(C_6F_5)_3Ge]_2Hg$ in toluene affords the same products (i.e. Hg , $(C_6F_5)_6Ge_2$ and $(C_6F_5)_3GeH$) [5]. Moreover, dibenzyl and $(C_6F_5)_3GeCH_2C_6H_5$ are also formed which were not found among photolysis products of Ia.

conclusion about the structure of VII will become possible only after additional investigations. The products obtained from the photolysis of Ia show that it proceeds via cleavage of the Ge—Hg—Pt grouping while the Pt—Ge bond is destroyed to a lesser degree.

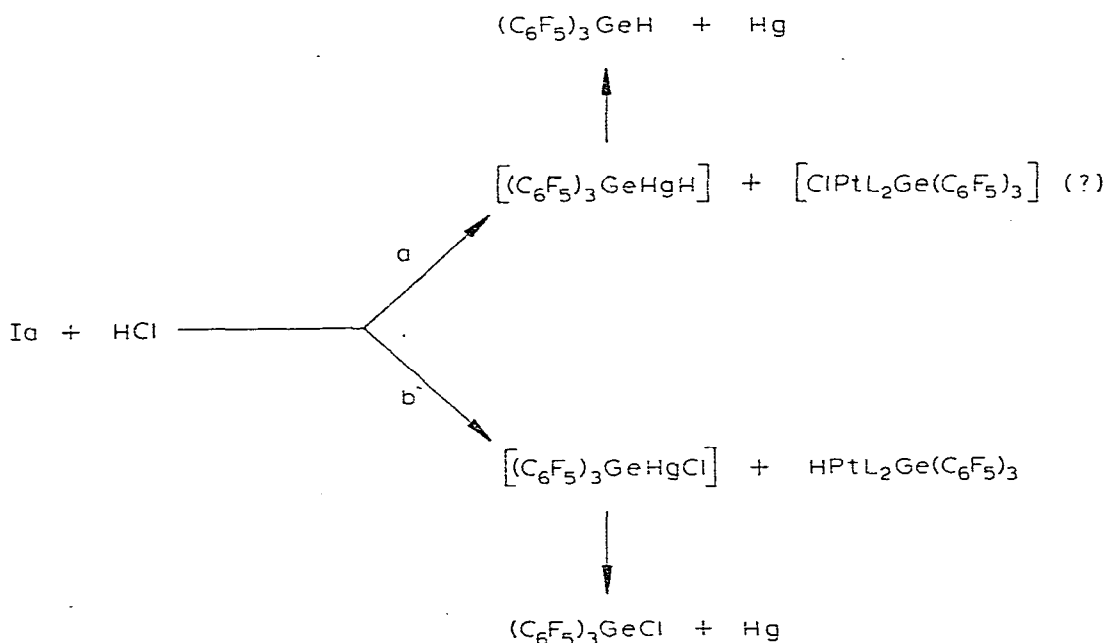
Complex Ia reacts with Br₂ in benzene at room temperature according to eq. 4.



Excess of bromine can cause cleavage of the germanium—platinum bond in VIII but this reaction proceeds much slower under these conditions.

Complex Ia reacts slowly with hydrogen chloride under reflux in benzene. Mercury precipitates and (C₆F₅)₃GeCl (68%), (C₆F₅)₃GeH (28%) and platinum hydride (C₆F₅)₃GePtL₂H (42%) are formed. According to LSC data the reaction mixture contains a small amount of one more compound, presumably platinum chloride (C₆F₅)₃GePtL₂Cl. But we failed to isolate this product in a pure state. Since its yield of germanium chloride and platinum hydride are considerably higher than the corresponding products of route (a) in Scheme I, route (b) is

SCHEME 1



more favourable. It should be noted that the absorption band of Pt—H in the IR spectra of the platinum hydride obtained in this reaction is shifted to longer wavelengths by 20 cm⁻¹ in comparison with those of the hydride prepared in reaction 3. This fact is due to the difference in the geometrical configuration of hydrides obtained in reaction 3 and in the reaction of Ia with hydrogen chloride. It is known [11] that *cis*-hydrides of platinum have a lower value of ν(Pt—H) than *trans*-isomers.

Insertion of chalcogens into metal-metal bonds is typical for organometallic compounds containing such bonds. Thus sulphur and selenium insert into $\text{Ge}(\text{Sn}, \text{Pb})-\text{Li}$ [14], $\text{Sn}-\text{Sn}$ [15], $\text{Ge}-\text{Hg}$ [16] and $\text{Ge}-\text{Cd}$ [17]. We believed that complexes prepared in this work would react with chalcogens in a similar manner since they contain polymetallic chains. However an attempt to carry out such a reaction was unsuccessful. The reaction between complex Ia and sulphur in benzene does not occur even at heating to 50°C . In THF the reaction of Ia with one equivalent of sulphur is completed within 20 h at room temperature (according to LSC analysis). Free sulphur disappears and the colour of the solution changes from pale yellow to brown. The IR spectra of the product is practically identical with the spectrum of the initial complex. The absence of the $\text{Ge}-\text{S}$ absorption bands at $400-450\text{ cm}^{-1}$ characteristic of pentafluorophenyl germanium sulphides [16] indicates that sulphur does not insert either into the $\text{Ge}-\text{Hg}$ or the $\text{Pt}-\text{Ge}$ bonds. We assumed that the reaction led to sulphur attaching to phosphorus atoms in triphenylphosphine ligands. A confirmation of such a supposition is the appearance in the IR spectra of the product of only a new low intensity band with a frequency of about 650 cm^{-1} specific to the stretching modes of the $\text{P}-\text{S}$ bond [18].

It was earlier shown [19] that germylplatinum complex $(\text{Ph}_3\text{Ge})_2\text{PtL}_2$ readily reacts with hydrogen to give Ph_3GeH and $\text{Ph}_3\text{GePtL}_2\text{H}$. Hydrogenolysis of Ia proceeds less readily. Less than 50% of the starting complex had reacted after bubbling hydrogen through a boiling benzene solution of Ia for 11 h. Only 9% of metallic mercury was found. Analysis of the reaction mixture by the LSC method showed that five more components were present in it apart from the starting complex Ia. Among those identified were tris(pentafluorophenyl)germane, platinum hydride (VI) and compound IX, which was isolated as an individual compound. This compound crystallizes from benzene as beautiful yellow crystals which reversibly change their colour to bright orange on heating to $130-150^\circ\text{C}$. The compound decomposes at $224-225^\circ\text{C}$. It gave on analysis data corresponding to a general formulae $(\text{C}_6\text{F}_5)_7\text{Ge}_2\text{Pt}_2\text{L}$. The IR spectra of IX exhibit the same absorption bands as the starting complex Ia, but with a certain redistribution of intensities of bands belonging to the $(\text{C}_6\text{F}_5)_3\text{Ge}$ moiety and triphenylphosphine groups. The structure of IX remains unclear.

Structure

A preliminary X-ray investigation * of complex V showed it to have a planar square configuration with *cis*-triphenylphosphine ligands, and presumably to contain both isomers: one with $\text{Ge}-\text{Hg}-\text{Pt}-\text{Sn}$ and the other with $\text{Ge}-\text{Pt}-\text{Hg}-\text{Sn}$ groupings. Complex Ia also has a *cis*-configuration which is confirmed by its ^{31}P NMR spectrum comprising two doublets $\delta_p = +23.5\text{ ppm}$ ($J(\text{P}-\text{Pt})\ 2667\text{ Hz}$) and $+36.9\text{ ppm}$ ($J(\text{P}-\text{Pt})\ 2870\text{ Hz}$). Since an earlier investigation showed [20] the mercurplatinum compound $\text{CF}_3\text{Hg}-\text{PtL}_2-\text{CF}_3$ to have *cis*-configuration as well it may therefore be suggested that formation of *cis*-complexes should prevail with the insertion of the PtL_2 moiety into a mercury-element bond.

* The X-ray analysis has been carried out by Yu. T. Struchkov and L.G. Kuzmina; the results will be published separately.

IR spectra

IR spectra of the compounds Ia–c, II–VIII exhibit a number of bands (see Experimental section) specific to the $(C_6F_5)_3M$ moieties ($M = Ge, Sn$) [6,21] and triphenylphosphine groups bonded to platinum or palladium. In addition complexes containing benzene of crystallization show a band at 680 cm^{-1} which disappears after the benzene is removed. The stretching modes of the Pt–H bond in the spectrum of VI is observed at about 2122 cm^{-1} . As was mentioned above this band in the spectrum of the platinum hydride obtained upon hydrochlorination of Ia is shifted and observed at 2102 cm^{-1} .

Experimental

All reactions were carried out under argon or in evacuated sealed ampoules. GLC analyses of volatile products were carried out on a Tsvet-104 chromatograph with a catarometer detector; helium was used as a gas-carrier. A $100 \times 0.4\text{ cm}$ column packed with OV-17 (7%) on chromaton N-AW-DMCS was used. LSC analyses were carried out on a Tsvet-304 liquid chromatograph with a detector of absorption in the UV region (254 nm). A $35 \times 0.4\text{ cm}$ column packed with C-80 silochrome ($\sim 15\text{ }\mu$) was used; n-hexane/ether mixture (32 : 1) served as a mobile phase. IR spectra were recorded on a UR-20 spectrometer. The $^{31}\text{P}\{^1\text{H}\}$ spectra were recorded on a Bruker HX-90 spectrometer in the Fourier transformation regime.

Starting complexes of mercury, cadmium and zinc were prepared by the methods described elsewhere [6–8]. Zerovalent complexes of platinum and palladium were obtained by known procedures [22,23].

$(C_6F_5)_3GeHgPtL_2Ge(C_6F_5)_3$ (Ia)

1.04 g (0.77 mmol) of bis[tris(pentafluorophenyl)germyl]mercury were added to a solution of $Pt(PPh_3)_3$ (0.76 g, 0.77 mmol) in 30 ml of benzene. The mixture was allowed to stand for 2 h at room temperature and then passed through a 2 cm layer of silica gel (L 100/140 μ). The filtrate was evaporated and pentane was added to the residue to deposit crystals. The crystals were separated, reprecipitated with pentane from benzen solution and dried in vacuo ($40\text{--}50^\circ\text{C}/1\text{ mmHg}$). 1.42 g (89%) of complex Ia was obtained, m.p. $243\text{--}244^\circ\text{C}$. IR spectrum: 1640, 1518, 1470, 1380, 1280, 1085, 970, 810, 750, 695, 620, 536, 525, 514, 503, 450 cm^{-1} .

$(C_6F_5)_3GeCdPtL_2Ge(C_6F_5)_3 \cdot 2C_6H_6$ (Ib)

A solution of tris(triphenylphosphine)platinum (1.18 g, 1.2 mmol) and $[(C_6F_5)_3Ge]_2Cd$ (1.51 g, 1.19 mmol) in 50 ml of benzene was kept for 20 h at 20°C . The product was isolated as described above and dried at room temperature to obtain 1.28 g (54%) of complex Ib, m.p. $222\text{--}224^\circ\text{C}$ (dec.). IR spectrum: 1640, 1518, 1470, 1380, 1280, 1085, 970, 808, 750, 725, 695, 680, 623, 536, 522, 512, 503, 450 cm^{-1} .

$(C_6F_5)_3GeZnPtL_2Ge(C_6F_5)_3 \cdot 2C_6H_6$ (Ic)

This complex was prepared by the procedure similar to the one described for Ib; 1 g (1.02 mmol) of $Pt(PPh_3)_3$ and 1.3 g (1.07 mmol) of bis[tris(pentafluoro-

0.046 g (76%) of Hg_2Br_2 remained unsolved. 0.14 g (98%) of $(\text{C}_6\text{F}_5)_3\text{GeBr}$ was found in the hexane extracts by GLC and LSC methods. The benzene extracts were concentrated, a part of the solvent was removed by an air flow, and hexane was added to the residue. The resulting colourless precipitate was again reprecipitated with hexane from benzene solution. 0.2 g (67%) yield of compound VIII was obtained, m.p. 243–248°C. IR spectrum: 1640, 1518, 1470, 1380, 1275, 1075, 972, 801, 753, 725, 697, 618, 545, 528, 512, 503, 460 cm^{-1} .

Reaction of Ia with hydrogen chloride

Dry HCl was bubbled through a solution of Ia (0.498 g, 0.24 mmol) in 8 ml of benzene for 2 h at 80°C. Metallic mercury precipitated (0.042 g, 88%). After separating the mercury the solution was concentrated and 15 ml of hexane were added to it. The solution was filtered and left overnight at 20°C to give a residue of platinum hydride $(\text{C}_6\text{F}_5)_3\text{GePtL}_2\text{H}$ and small quantities (according to LSC analysis) of an unidentified impurity, $[(\text{C}_6\text{F}_5)_3\text{GePtL}_2\text{Cl} (?)]$. A repeated recrystallization from benzene/hexane gave 0.132 g (42%) of compound VI, m.p. 212–213°C. The product was identified by the LSC method. IR spectrum: 2102, (~2122 (sh)), 1640, 1518, 1470, 1380, 1275, 1080, 970, 802, 780, 748, 725, 697, 623, 540, 520, 498, 455, 425 cm^{-1} . GLC and LSC analyses showed the presence of 0.026 g (19%) of tris(pentafluorophenyl)germane and 0.1 g (68%) of $(\text{C}_6\text{F}_5)_3\text{GeCl}$ in the hexane mother liquor.

Reaction of Ia with hydrogen

Hydrogen was bubbled through a solution of Ia (1.26 g, 0.61 mmol) in 15 ml of benzene at 80°C to deposit 0.01 g (9%) of mercury and to develop a yellow-brown colour of the solution. After separating the mercury the solution was kept at 20°C for 15 h. Precipitated yellow crystals of compound IX (0.11 g) were separated and again recrystallized from benzene, m.p. 230–231°C (dec.). When heated to 130–150°C compound IX becomes bright yellow, and on subsequent cooling it recovers its original yellow colour. (Found: C, 33.28, 33.02, 33.10; H, 1.05, 1.16, 1.09; F, 30.08, 29.88. $(\text{C}_6\text{F}_5)_7\text{Ge}_2\text{Pt}_2\text{PPh}_3$ calcd.: C, 33.33; H, 0.70; F, 30.75%. IR spectrum: 1640, 1520, 1470, 1380, 1285, 1090, 870, 815, 755, 730, 700, 620, 530, 520, 495, 460 cm^{-1} . After compound IX was removed the reaction mixture was concentrated and 0.66 g (52%) of the starting complex Ia was deposited with hexane. LSC analysis showed the presence of compound IX, the initial complex Ia, platinum hydride VI, tris(pentafluorophenyl)germane and traces of two unidentified components in the mother liquor.

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