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SYNTHESIS, STRUCTURE AND REACTIVITY OF $[(CF_3)_3GePt(PPh_3)_2]_2Hg$

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Summary

The reaction of $Pt(PPh_3)_n$ ($n = 3$ or 4) with $[(CF_3)_3Ge]_2Hg$ or $(CF_3)_3GeHgPt(PPh_3)_2Ge(CF_3)_3$ (I) gives a stable diplatinum complex $[(CF_3)_3GePt(PPh_3)_2]_2Hg$ (II). X-Ray analysis has established that compound II contains a Ge–Pt–Hg–Pt–Ge chain of C_2 symmetry. Both of the Pt atoms have distorted square-planar coordinations. The bond lengths are: Pt–Hg, 2.630(2) and 2.665(2) Å; Ge–Pt, 2.410(4) and 2.407(4) Å.

Compound II reacts with dihydrogen in THF solution under mild conditions to give mercury and the hydride $(CF_3)_3GePt(PPh_3)_2H$. On interaction of II with R_2Hg organomercurials ($R = Cl$, Et, $GeEt_3$, $Ge(CF_3)_3$, $Ge(C_6F_5)_3$) an unknown reaction takes place: $Pt(PPh_3)_2$ moieties migrate from the polymetallic grouping into the substrate with the formation of the corresponding $RHgPt(PPh_3)_2R$ complexes or their demercuration products, $R_2Pt(PPh_3)_2$ ($R = Cl$, Et). The latter react further with complex I formed in the first step of the process to give Hg and $(CF_3)_3GePt(PPh_3)_2R$. The reaction schemes are discussed.

Introduction

As shown earlier [1–3], the germylmercury compounds $R_3GeHgGeR_3$ readily undergo an oxidative addition reaction with a triphenylphosphine complex of platinum, PtL_3 ($L = PPh_3$). Stable, light-coloured 4-nuclear $R_3GeHgPtL_2GeR_3$ complexes are formed when R is C_6H_5 or C_6F_5. All attempts to insert PtL_2 carbenoid into the remaining Ge–Hg bond failed. $(R_3Ge)_2Cd$, $(R_3Ge)_2Zn$ and $R_3GeHgSnR_3$ ($R = C_6F_5$) react in a similar way [2]. In contrast, the alkyl derivatives $(Et_3Ge)_2M$ (M = Cd, Hg) do not form stable addition products of PtL_2.

In this paper we report on the interaction of triphenylphosphine complexes of platinum(0) with the alkyl perfluorinated compound $[(CF_3)_3Ge]_2Hg$ [4] and some of the reactions of the products obtained.

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Results and discussion

We have found that bis[tris(trifluoromethyl)germyl]mercury, like other compounds of the $(R_3Ge)_2Hg$ row, reacts readily with PtL_n ($n = 3,4$). The resulting complex $[(CF_3)_3Ge]_2HgPtL_2$ has composition and properties similar to those of its phenyl and pentafluorophenyl analogues. It is likely that the product has the same hetero-element framework structure, i.e. the Ge–Hg–Pt–Ge chain [5]. However, as was noticed in the preliminary communication [6], these reactions, unlike those of $(Ph_3Ge)_2Hg$ and $[(C_6F_5)_3Ge]_2Hg$, include the formation of an intensively coloured intermediate. On addition of a colourless solution of $[(CF_3)_3Ge]_2Hg$ to the yellow-orange PtL_4 or PtL_3 in toluene solution, the mixture immediately turns dark-red. With an equimolar ratio of the initial reagents, the colour disappears gradually becoming light-yellow in 20–25 h due to the formation of product I.

$$[(CF_3)_3Ge]_2Hg + PtL_4 \rightarrow \underset{(I)}{(CF_3)_3GeHgPtL_2Ge(CF_3)_3} \qquad (1)$$

When PtL_4 is present in double excess, no colour change is observed. In this case, air-stable, red-brown crystals precipitate after 10–20 h. Their elemental analysis and IR spectra correspond to the formula $[(CF_3)_3GePtL_2]_2Hg$ (II). Product II is moderately soluble in THF and 1,2-dimethoxyethane, and is practically insoluble in aromatic and aliphatic hydrocarbons. On heating above 170 °C the compound melts and decomposes.

$$[(CF_3)_3Ge]_2Hg + 2PtL_4 \rightarrow \underset{(II)}{[(CF_3)_3GePtL_2]_2Hg} \qquad (2)$$

X-Ray analysis has established that the molecule of II contains the Ge–Pt–Hg–Pt–Ge chain. Thus, it confirmed the supposed insertion of two PtL_2 moieties into the Hg–Ge bonds in the molecule $(CF_3)_3Ge–Hg–Ge(CF_3)_3$. The polymetallic chain of the molecule of II with the main bond lengths and valence angles is shown in Fig. 1.

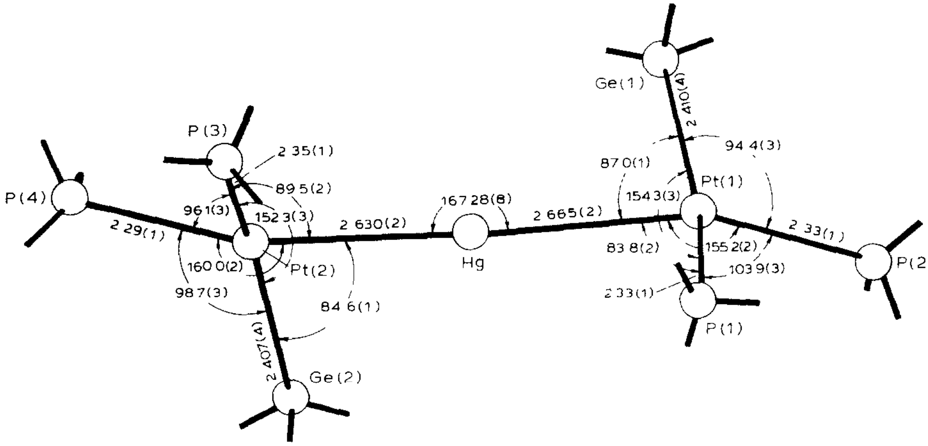


Fig. 1. Polymetallic chain of the molecule of II.

The non-crystallographical symmetry of the molecule of II is similar to C_2. One $(Ph_3P)_2(CF_3)_3GePt$ fragment of the molecule rotates relative to the other so that the Ge(1)Pt(1)...Pt(2)Ge(2) torsion angle is equal to 101.5°. The valence angle at the Hg atom, 167.28(8)°, is significantly distorted from the ideal value of 180°. The Hg–Pt bond lengths in the molecule of II (2.630(2) and 2.665(2) Å) exceed those in the structurally investigated compounds with one PtL_2 fragment inserted into the Hg–X bond (X = Sn, C, Br): 2.617(1) Å in $(C_6F_5)_3Ge–Hg–PtL_2–Sn(C_6F_5)_3$ [5]; 2.569(2) Å in $F_3C–Hg–PtL_2–CF_3$ [7]; 2.499(2) Å in $PhCH[HgPt(Ph_3P)_2Br]COOC_{10}H_{19}$ [8]. The Pt(1)–Ge(1) and Pt(2)–Ge(2) bond lengths (2.410(4) and 2.407(4) Å, respectively) are slightly shorter than the length of this bond (2.466(5) Å) in $[(C_6F_5)_2Ge]_3Bi_2Pt(PPh_3)_2$ [9].

The coordination of the Pt atoms in the molecule of II is considerably distorted from square-planar geometry due to the steric repulsion of the $(PPh_3)_2(CF_3)_3GePt$ fragments. The sums of the valence angles at the Pt(1) and Pt(2) atoms are equal to 369.1° and 368.9°, respectively (Fig. 1); the angles between the normals to HgPt(1)Ge(1), Pt(1)P(1)P(2) and HgPt(2)Ge(2), Pt(2)P(3)P(4) planes are equal to 31.5° and 32.6°, respectively. In this the molecule of II differs from those with one PtL_2 fragment, in which the coordination of the Pt atom is much more similar to square-planar coordination, though in the last case the valence angles at the Pt atom are also distorted from the ideal value of 90° due to steric effects [5,7,8]. In particular, there is an increase in the HgPt(1)Ge(1) (87.0°), HgPt(2)Ge(2) (84.6°), HgPt(1)P(1) (83.8°) and HgPt(2)P(3) (89.5°) valence angles observed in the molecule of II compared to the corresponding HgPtSn (77.8°) and HgPtP(1) (81.3°) angles in $(C_6F_5)_3Ge–Hg–PtL_2–Sn(C_6F_5)_3$, as well as a significant decrease in the HgPt(1)P(2) (155.2°) and HgPt(2)P(4) (160.0°) angles compared to the corresponding HgPtP(2) (177.5°) angle in the $(C_6F_5)_3Ge–Hg–PtL_2–Sn(C_6F_5)_3$ molecule.

Steric strain in the molecule of II is also demonstrated (together with the distorted coordinations of the Hg and Pt atoms) by the significant distortion of the tetrahedral coordination of the Ge atoms (the PtGeC valence angles are in the range 111 to 130°, with an average value of 122(1)°) and by the similarity of the intramolecular distances between the $Ge(CF_3)_3$ and PPh_3 groups bonded to the same (for example, F(2)...C(37) 3.00 Å, F(13)...C(66) 3.06 Å) or to different (for example, F(15)...C(9) 3.06 Å, F(6)...C(45) 3.16 Å) Pt atoms and the sum of the Van der Waals radii of F and C atoms (3.10 Å) [10].

Except for the distortions of the valence angles at the Ge atoms mentioned above, the geometries of the $Ge(CF_3)_3$ and PPh_3 groups in the molecule of II are usual: the average lengths of the Ge–C and Pt–P bonds are equal to 2.00(4) and 2.33(1) Å, respectively. The average length of the Pt–P bond in the molecule of II is similar to that in the molecule with one PtL_2 fragment: 2.31 Å in $(C_6F_5)_3Ge–Hg–PtL_2–Sn(C_6F_5)_3$ [5]; 2.32 Å in $F_3C–Hg–PtL_2–CF_3$ [7] and 2.31 Å in $PhCH[HgPt(Ph_3P)_2Br]COOC_{10}H_{19}$ [8].

The crystals investigated contain solvated toluene molecules together with molecules of II. The intermolecular distances between the molecules of II and solvated toluene are usual.

On close investigation of the processes of I and II formation, we established that the 4-nuclear complex I readily adds a PtL_2 moiety to give diplatinum complex II. Under comparable conditions the latter can interact with $[(CF_3)_3Ge]_2Hg$ to give again product I in more than 90% yield.

$$\underset{(I)}{(CF_3)_3GeHgPtL_2Ge(CF_3)_3} + PtL_4 \rightarrow \underset{(II)}{(CF_3)_3GePtL_2HgPtL_2Ge(CF_3)_3} \qquad (3)$$

$$\underset{(II)}{(CF_3)_3GePtL_2HgPtL_2Ge(CF_3)_3} + [(CF_3)_3Ge]_2Hg \rightarrow$$

$$2\underset{(I)}{(CF_3)_3GeHgPtL_2Ge(CF_3)_3} \qquad (4)$$

Thus, the interaction of $[(CF_3)_3Ge]_2Hg$ with a triphenylphosphine complex of platinum may be represented by eq. 5.

$$RHgR \xrightarrow{PtL_2} RHgPtL_2R \underset{R_2Hg}{\overset{PtL_2}{\rightleftharpoons}} RPtL_2HgPtL_2R \qquad (5)$$

$(R = Ge(CF_3)_3)$

As far as we know, the addition of a second equivalent of PtL_2 to the platinum-containing complex with formation of the stable grouping Pt–Hg–Pt has been observed for the first time, as has reaction 4, which may be regarded as a disproportionation reaction between 5- and 3-nuclear derivatives or as a migration process of PtL_2 from the 5-nuclear compound to the 3-nuclear one.

In toluene solution the addition of the first and second moles of PtL_2 proceeds more rapidly (0 °C, 1–2 min) than the interaction of II with $[(CF_3)_3Ge]_2Hg$ (20 °C, 25–30 h). Therefore the mixing of bis[tris(trifluoromethyl)germyl]mercury and PtL_4 in all proportions results in the formation of red product II. With equimolar amounts of the starting reagents, the colour of the solution gradually turns yellow due to the formation of complex I by reaction 4. In THF all the reactions (eq. 1, 2 and 3) proceed with roughly equal facility and the composition of the products is determined only by the PtL_4 and $[(CF_3)_3Ge]_2Hg$ ratio.

It should be noted that the process seems to be affected by the binding of some germylmercury into triphenylphosphine complex $[(CF_3)_3Ge]_2Hg \cdot 2PPh_3$ [4]. In separate experiments we established that this complex is less active towards PtL_4 than free bis[tris(trifluoromethyl)germyl]mercury.

To ascertain the final step of reaction 4, we investigated the interaction of complex II with different mercury compounds. It was found that the reaction of II with bis[tris(pentafluorophenyl)germyl]mercury gives two "symmetrical" complexes, $(CF_3)_3GeHgPtL_2Ge(CF_3)_3$ and $(C_6F_5)_3GeHgPtL_2Ge(C_6F_5)_3$, instead of the disproportionation product $(CF_3)_3GePtL_3HgGe(C_6F_5)_3$, i.e. in this case complex II acts as a formal donor of the PtL_2 moiety.

$$II + [(C_6F_5)_3Ge]_2Hg \xrightarrow[20\,°C]{THF} (CF_3)_3GeHgPtL_2Ge(CF_3)_3 + (C_6F_5)_3GeHgPtL_2Ge(C_6F_5)_3 \qquad (6)$$

It is likely that the reactions of complex II with other compounds of the R_2Hg row ($R = GeEt_3$, Et, Cl) proceed in a similar way, i.e. with transfer of the PtL_2 fragment.

$$II + R_2Hg \rightarrow (CF_3)_3GeHgPtL_2Ge(CF_3)_3 + RHgPtL_2R \qquad (7)$$

However, the $RHgPtL_2R$ products formed in this case are not stable [2,13,14]. Decomposition of triethylgermyl derivatives leads to mercury, hexaethyldigermane and free PtL_2. The latter adds to the 4-nuclear product I formed in the first stage to give the starting complex II, i.e. catalytic demercuration of $(Et_3Ge)_2Hg$ takes place.

$$Et_3GeHgPtL_2GeEt_3 \rightarrow Et_6Ge_2 + Hg + PtL_2 \qquad (8)$$

$$I + PtL_2 \rightarrow II \qquad (9)$$

With a great excess of bis(triethylgermyl)mercury, the main route of the process is affected by side reactions which lead to a complex, intractable mixture of products.

Decomposition of $EtHgPtL_2Et$ and $ClHgPtL_2Cl$ is known [13] to result in the demercurated complexes Et_2PtL_2 and Cl_2PtL_2. In reaction 8 (R = Et, Cl) these complexes were not observed but in addition to metallic mercury (100%), $(CF_3)_3GePtL_2R$ compounds were obtained in high yields. They were apparently demercurated products of I and the R_2PtL_2 exchange.

$$I + R_2PtL_2 \rightarrow 2(CF_3)_3GeHgPtL_2R \rightarrow Hg + 2(CF_3)_3GePtL_2R \qquad (10)$$

(R = Et, Cl)

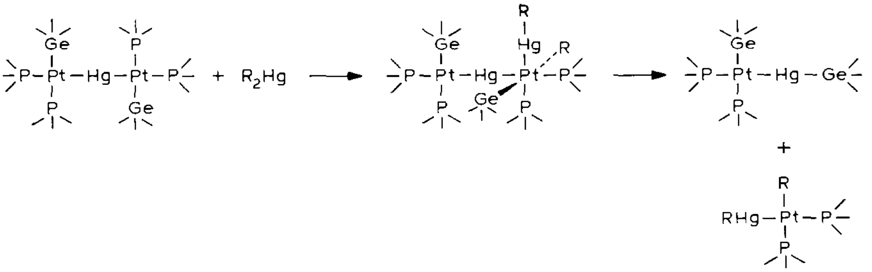
In separate experiments we found that Cl_2PtL_2 and Et_2PtL_2 do react with the 4-nuclear complex I at room temperature to give the products mentioned above in high yields.

It is not improbable that the precipitation of mercury in reaction 10 occurs at the step of the reaction complex without formation of the supposed unstable intermediate $(CF_3)_3GeHgPtL_2R$. The high stability of the isomer $(CF_3)_3GePtL_2HgEt$ (m.p. 155 °C) obtained by us in reaction 11 may serve as indirect proof for such a supposition.

$$(CF_3)_3GeHgEt + PtL_4 \rightarrow (CF_3)_3GePtL_2HgEt \qquad (11)$$

Unlike germylmercury compounds, mercuric chloride and diethylmercury, bis(trifluoromethyl)mercury does not react with complex II under corresponding conditions. This may be associated with the specific nature of $(CF_3)_2Hg$ in THF solution [15]. It should be noted that the absence of interaction of II with $(CF_3)_2Hg$ is an argument against possible dissociation of complex II into I and PtL_2, since $(CF_3)_2Hg$ is known [13] to react readily with PtL_2 to give the stable complex $CF_3HgPtL_2CF_3$.

Thus, the data obtained indicate that the migration of PtL_2 fragments from the diplatinum complex into R_2Hg takes place in all the reactions of II with R_2Hg. It is proposed that the process is accomplished through an octahedral transition state of one of the platinum atoms in the Ge–Pt–Hg–Pt–Ge chain (eq. 12).



(12)

It has been shown earlier [2] that the 4-nuclear pentafluorophenyl complex $(C_6F_5)_3GeHgPtL_2Ge(C_6F_5)_3$ undergoes hydrogenolysis very slowly in boiling ben-

TABLE 1

COORDINATES OF THE Hg, Pt, Ge AND P ATOMS ($\times 10^5$) AND THEIR ANISOTROPIC THERMAL FACTORS $T = \exp[-1/4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + \ldots + 2B_{23}klb^*c^*)]$ IN THE STRUCTURE OF II

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Hg	24999(6)	40000[a]	24879(5)	1.43(4)	1.54(4)	2.02(4)	−0.80(4)	0.19(3)	−0.41(4)
Pt(1)	21228(5)	37853(12)	33762(4)	1.00(4)	0.73(4)	1.31(4)	0.56(4)	0.17(3)	−0.19(4)
Pt(2)	28990(6)	37430(16)	16415(5)	1.96(5)	2.13(5)	2.14(5)	0.00(5)	−0.04(4)	0.03(6)
Ge(1)	29519(15)	25362(28)	34898(13)	1.2(2)	1.0(2)	1.9(2)	1.0(2)	−0.2(2)	−0.0(2)
Ge(2)	20411(17)	25514(33)	15504(14)	1.8(2)	2.1(2)	2.3(2)	−0.1(2)	0.1(2)	−0.3(2)
P(1)	16999(32)	54865(59)	32504(26)	0.3(3)	0.6(3)	0.7(3)	0.2(3)	0.6(3)	0.4(3)
P(2)	15386(42)	30545(74)	39720(32)	2.6(4)	1.4(4)	1.6(4)	1.2(4)	0.9(4)	0.2(4)
P(3)	33418(44)	54719(79)	16778(36)	2.2(4)	1.5(4)	2.6(4)	−0.1(4)	0.0(4)	0.7(4)
P(4)	34708(41)	31250(80)	10320(32)	1.6(4)	2.7(4)	1.4(4)	−0.4(4)	0.0(4)	0.2(4)

[a] This value is fixed to choose the initial coordinate in the y-axis

zene, in contrast to the phenyl complex $(Ph_3Ge)_2PtL_2$ which reacts readily [16,17]. Compound II reacts with dihydrogen in THF at 20 °C. In this case Hg is quantitatively precipitated and the germylplatinum hydride $(CF_3)_3GePtL_2H$ is formed in 80% yield.

$$II + H_2 \rightarrow 2(CF_3)_3GePtL_2H + Hg \qquad (13)$$

The same hydride was also obtained by oxidative addition of PtL_4 to $(CF_3)_3GeH$.

Experimental

X-Ray analysis was carried out with a Syntex $P2_1$ automatic diffractometer (λ Mo-K_α; $\theta/2\theta$-scan in the range $1 \leqslant 2\theta \leqslant 48°$; of the 6510 independent reflections, 3246 with $|F| > 4\sigma(F)$were used in the refinement). Absorption corrections were made taking into account the real crystal shape (μ 67.7 cm^{-1}) according to ref. 11.

The crystals of II · $C_6H_5CH_3$ are monoclinic, at 20 °C *a* 22.025(7), *b* 12.356(5), *c* 28.593(6) Å, β 90.58(3) °, *V* 7780.8 $Å^3$, D_c 2.01 g cm^{-3}, $Z = 4$, space group *C*2.

Experimentally observed absences with no regard for three weak ($\sim 5\sigma(F)$) impossible reflexes $h0l$ with $l = 2n + 1$ indicate the $C2/c$ group. We failed to define the structure in this symmetry group. Therefore, further structure determination was made in the *C*2 group. The linear heavy-atom Pt–Hg–Pt fragment was found by Patterson function. The arrangement of these fragments in the crystal conforms to $C2/c$ symmetry, which is responsible for the above-mentioned pseudo-absences. All the non-hydrogen atoms were found by subsequent electron density synthesis. Besides, difference synthesis revealed that the independent part of the unit cell contains two molecules of solvated toluene, each being in a general position and disordered with a half-site occupation factor on two positions, related by the two-fold crystallographic axis (one of the carbon atoms in the toluene molecule lies in this symmetry axis). The structure was refined by a block-diagonal least-squares method with anisotropic (for the Hg, Pt, Ge and P atoms) and isotropic (for the F and C atoms) thermal parameters. Atoms of the toluene molecule (with the exception of the atom situated in the symmetry axis) were included in the refinement with half weight. Hydrogen atoms of the Ph group in the molecule of II and in the molecules of solvated toluene (with the exception of the H atoms of the CH_3 groups) were taken into account in the calculations of F_{cal}, but their positions determined from general geometrical conditions (C–H 1.0 Å, C–C–H 120 °), as well as the isotropic thermal factors (adopted B_{iso} 5 $Å^2$), were not refined. Final *R*-factors $R = 0.040$ and $R_G = 0.042$ were obtained. The coordinates of the Hg, Pt, Ge, P atoms and their anisotropic thermal factors are given in Table 1. Table 2 lists the coordinates of the F and C atoms and their isotropic thermal factors. All calculations were performed with INEXTL programs [12].

All solvents were purified by standard methods. Synthesis and isolation of the compounds were performed in evacuated ampoules. Melting points (given without corrections) were determined using sealed capillaries.

Preparation of $(CF_3)_3GeHgPt(PPh_3)_2Ge(CF_3)_3$ *(I)*

0.93 g (0.747 mmol) of $Pt(PPh_3)_4$ and 0.588 g (0.774 mmol) of $[(CF_3)_3Ge]_2Hg$ were mixed in 30 ml of benzene. The dark-red solution turned yellow and yellow crystals precipitated. After 4 days, benzene was removed in vacuo, the residue was

(Continued on p. 298)

TABLE 2

COORDINATES OF THE F AND C ATOMS AND THE ISOTROPIC THERMAL FACTORS (B_{iso}, Å^2) IN THE STRUCTURE OF II

Atom	x	y	z	B_{iso}	Atom	x	y	z	B_{iso}
F(1)	2767(12)	409(24)	3772(10)	5.2(6)	C(38)	1512(16)	2814(31)	4967(13)	2.9(7)
F(2)	2692(11)	1501(22)	4333(9)	4.4(6)	C(39)	1786(18)	2971(35)	5375(15)	4.0(9)
F(3)	3563(11)	1105(22)	4122(9)	5.1(6)	C(40)	2262(17)	3605(40)	5435(14)	4.0(9)
F(4)	3672(13)	3452(26)	4219(10)	6.7(8)	C(41)	2615(21)	4110(41)	5025(17)	5(1)
F(5)	4231(13)	2919(26)	3720(10)	7.1(8)	C(42)	2313(19)	3900(48)	4583(15)	5(1)
F(6)	3713(11)	4362(22)	3648(9)	4.9(6)	C(43)	3912(13)	5736(25)	2177(11)	1.0(6)
F(7)	3797(12)	953(23)	3098(9)	4.7(6)	C(44)	4076(14)	4842(25)	2439(11)	1.0(6)
F(8)	3657(11)	2343(23)	2679(9)	4.9(6)	C(45)	4543(17)	4951(32)	2790(13)	2.7(8)
F(9)	3044(12)	1101(23)	2730(10)	5.5(7)	C(46)	4847(18)	5935(33)	2792(14)	3.3(8)
F(10)	2205(9)	393(17)	1256(7)	2.6(4)	C(47)	4696(19)	6727(37)	2600(16)	3.8(9)
F(11)	2343(9)	1504(17)	672(7)	2.6(4)	C(48)	4223(14)	6702(27)	2193(11)	1.6(7)
F(12)	1443(9)	1095(16)	916(7)	2.2(4)	C(49)	3630(12)	6045(22)	1201(10)	0.4(5)
F(13)	1333(10)	3378(18)	787(8)	3.4(5)	C(50)	4269(18)	6233(36)	1050(15)	4.2(9)
F(14)	767(9)	2941(17)	1394(7)	1.9(4)	C(51)	4389(18)	6645(35)	617(14)	3.1(9)
F(15)	1255(9)	4379(17)	1442(7)	2.4(4)	C(52)	4035(19)	6821(36)	254(15)	4.3(9)
F(16)	1128(10)	1116(18)	1845(8)	3.0(5)	C(53)	3425(13)	6713(24)	398(10)	0.9(6)
F(17)	1283(9)	2391(16)	2331(7)	2.0(4)	C(54)	3242(13)	6277(25)	799(10)	1.0(6)
F(18)	1991(10)	1166(18)	2307(8)	3.2(5)	C(55)	2763(16)	6505(30)	1796(13)	2.6(7)
C(1)	2986(14)	1255(26)	3951(11)	1.0(6)	C(56)	2871(15)	7579(29)	1835(12)	2.1(7)
C(2)	3637(19)	3214(37)	3841(15)	5(1)	C(57)	2422(17)	8355(32)	1953(13)	3.2(8)
C(3)	3376(13)	1746(25)	2979(11)	1.5(6)	C(58)	1804(12)	8128(21)	1848(9)	0.2(5)
C(4)	1986(18)	1469(35)	1087(15)	3.9(9)	C(59)	1668(17)	6980(32)	1785(14)	2.9(8)
C(5)	1300(13)	3368(23)	1255(10)	0.6(5)	C(60)	2089(15)	6268(29)	1821(12)	1.9(7)
C(6)	1567(15)	1759(28)	2024(12)	1.7(7)	C(61)	3145(14)	3441(25)	423(11)	1.6(6)
C(7)	1059(18)	5602(35)	2832(15)	3.2(9)	C(62)	3434(15)	3040(27)	38(12)	1.9(7)
C(8)	878(20)	4902(39)	2550(16)	5(1)	C(63)	3147(15)	3177(29)	−424(12)	1.8(7)

C(9)	432(21)	5103(40)	2241(17)	5(1)	C(64)	2586(17)	3769(44)	−406(13)	3.3(8)
C(10)	132(19)	5895(36)	2196(16)	4(1)	C(65)	2374(17)	4118(33)	−39(14)	3.3(8)
C(11)	238(19)	6716(37)	2560(16)	3(1)	C(66)	2634(13)	3904(29)	376(10)	1.4(6)
C(12)	691(23)	6575(46)	2823(18)	5(1)	C(67)	4261(13)	3591(28)	1001(10)	2.1(6)
C(13)	1337(18)	6018(34)	3844(14)	3.4(9)	C(68)	4576(16)	3454(31)	1393(12)	3.1(8)
C(14)	737(15)	6283(27)	3853(12)	1.5(6)	C(69)	5231(17)	3759(44)	1398(13)	4.4(8)
C(15)	488(15)	6667(29)	4255(12)	1.4(7)	C(70)	489(18)	9182(36)	1124(15)	2.1(9)
C(16)	871(16)	6914(30)	4630(13)	2.1(7)	C(71)	5141(16)	4349(29)	687(12)	2.3(7)
C(17)	1430(22)	6645(42)	4633(17)	5(1)	C(72)	4587(13)	3969(30)	663(11)	2.1(6)
C(18)	1645(20)	6214(40)	4189(16)	5(1)	C(73)	3610(17)	1601(32)	1125(13)	2.9(8)
C(19)	2302(14)	6495(26)	3178(11)	1.5(6)	C(74)	3565(17)	1250(32)	1576(13)	2.6(8)
C(20)	2840(16)	6268(30)	3345(12)	2.0(7)	C(75)	3694(15)	164(29)	1709(12)	1.9(7)
C(21)	3344(20)	7043(38)	3268(16)	4(1)	C(76)	3868(19)	−459(36)	1315(15)	4(1)
C(22)	3148(20)	7976(39)	3154(16)	5(1)	C(77)	3793(13)	−157(24)	861(10)	0.8(6)
C(23)	2595(24)	8301(46)	3100(18)	6(1)	C(78)	3723(13)	916(24)	788(10)	0.8(6)
C(24)	2133(17)	7534(32)	3006(13)	2.2(8)	C(79)[a]	0(0)	1684(47)	5000(0)	3(1)
C(25)	708(14)	3514(26)	3936(10)	1.2(6)	C(80)[a]	231(58)	1367(99)	5445(46)	7(4)
C(26)	404(16)	3365(29)	3523(12)	1.8(7)	C(81)[a]	313(27)	309(52)	5655(22)	1(1)
C(27)	−152(14)	3808(33)	3470(11)	1.6(6)	C(82)[a]	120(38)	−514(65)	5217(27)	4(2)
C(28)	−444(19)	4260(37)	3960(15)	3(1)	C(83)[a]	−88(63)	−183(76)	4911(55)	7(3)
C(29)	−225(22)	4290(43)	4306(18)	5(1)	C(84)[a]	−111(60)	904(98)	4797(40)	7(3)
C(30)	443(17)	4095(36)	4359(14)	4.0(9)	C(85)[a]	−402(42)	1144(82)	4253(33)	1(2)
C(31)	1421(15)	1643(28)	3885(12)	1.8(7)	C(86)[a]	0(0)	6623(51)	0(0)	4(1)
C(32)	1446(15)	1293(29)	3437(12)	2.2(7)	C(87)[a]	204(26)	6444(49)	463(20)	2(1)
C(33)	1332(21)	298(41)	3341(17)	5(1)	C(88)[a]	255(42)	5439(85)	577(34)	6(3)
C(34)	1193(18)	−503(32)	3694(14)	3.3(8)	C(89)[a]	158(30)	4499(54)	373(24)	2(2)
C(35)	1027(28)	17(57)	4096(23)	10(2)	C(90)[a]	−135(33)	4783(57)	−150(24)	3(2)
C(36)	1314(23)	887(44)	4324(18)	6(1)	C(91)[a]	−227(21)	5760(38)	−259(16)	0.1(8)
C(37)	1778(17)	3201(33)	4577(13)	2.5(8)	C(92)[a]	−345(60)	5841(99)	−596(48)	10(4)

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[a] Atoms of two disordered solvated toluene molecules.

washed with hexane (3 × 15 ml) and dissolved again in THF (5 ml). After addition of hexane (20 ml) to the THF solution, a microcrystalline precipitate of complex I was obtained (yield 0.831 g; 75%), m.p. 193°C(dec.). Found: C, 34.42; H, 2.31; F, 23.32. $C_{42}H_{30}F_{18}Ge_2HgP_2Pt$ calcd.: C, 34.10; H, 2.04; F, 23.11%.

Preparation of $[(CF_3)_3GePt(PPh_3)_2]_2Hg$ (II)

0.913 g (0.734 mmol) of $Pt(PPh_3)_4$ and 0.279 g (0.367 mmol) of $[(CF_3)_3Ge]_2Hg$ were mixed in toluene solution (40 ml) at room temperature. The reaction product crystallized slowly from the resulting dark-red solution. After 4 days the crystals were separated, washed with toluene (2 × 15 ml) and dried in vacuo. 0.668 g (79%) of red-brown crystals of complex II, m.p. 170°C (dec.), containing crystallized toluene, was obtained. This complex was used in subsequent reactions and X-ray structural analysis. Reprecipitation of the product obtained with hexane from THF gave a sample of II without solvated toluene; the melting point did not change. Found: C, 42.43; H, 3.04; F, 16.19; Ge, 6.28. $C_{78}H_{60}F_{18}Ge_2HgP_4Pt_2$ calcd.: C, 42.60; H, 2.76; F, 15.55; Ge, 6.60%.

Reaction of I with $Pt(PPh_3)_4$

0.5 g (0.338 mmol) of I and 0.42 g (0.388 mmol) of $Pt(PPh_3)_4$ were mixed in 40 ml of toluene. From the resulting red solution red-brown crystals precipitated. After 4 days the solution was decanted from the precipitate, the latter was washed with toluene (2 × 15 ml) and dried in vacuo. 0.632 g (81%) of II was obtained. Elemental analysis, IR spectra and melting point confirmed the identity of the product with the compound formed in the previous experiment.

Reaction of II with $[(CF_3)_3Ge]_2Hg$

To a solution of II (0.221 g, 0.096 mmol) in THF (30 ml) was added 0.072 g (0.095 mmol) of $[(CF_3)_3Ge]_2Hg$. At room temperature the reaction was completed in 24 h. The solution was evaporated under vacuum to 5 ml and hexane (30 ml) was added. Light-yellow crystals of I precipitated (0.235 g, 84%).

Reaction of II with $[(C_6F_5)_3Ge]_2Hg$

0.216 g (0.094 mmol) of II and 0.132 g (0.098 mmol) of $[(C_6F_5)_3Ge]_2Hg$ were dissolved in 25 ml of THF. The dark-red solution that formed turned light-yellow in 50 h at room temperature. The solution was evaporated under vacuum to 5 ml and 20 ml of hexane was added. Light-yellow crystals precipitated. The solution was decanted from the precipitate and was dried to give 0.103 g (74%) of I. The mother liquor was evaporated and 10 ml of hexane was added to the residue. Crystals of $(C_6F_5)_3GeHgPt(PPh_3)_2Ge(C_6F_5)_3$ (0.124 g, 64%), m.p. (mixed) 230–245°C, precipitated in 24 h. The compound was also identified by means of IR spectroscopy and LSC [18].

Reaction of II with $(Et_3Ge)_2Hg$

To a solution of II (0.246 g, 0.107 mmol) in 30 ml of toluene was added 0.058 g (0.112 mmol) of $(Et_3Ge)_2Hg$ at room temperature. In a matter of minutes metallic mercury precipitated, but the colour of the solution (dark-red) did not change. After 24 h mercury was isolated (0.021 g, 93% taking into consideration the quantity of $(Et_3Ge)_2Hg$), the solution was evaporated to 5 ml and hexane (30 ml) was added. At room temperature crystals of II precipitated (0.180 g, 77%). $(Et_3Ge)_2$ was found quantitatively in the mother liquor by GLC.

Interaction of II with Cl_2Hg

To a solution of II (0.227 g, 0.099 mmol) in THF (30 ml) was added a solution of Cl_2Hg (0.028 g, 0.103 mmol) in THF (5 ml). Immediate decoloration of the solution was observed. After 5 min the metallic mercury precipitated (0.039 g, 98%) was isolated by decantation. The solvent was evaporated in vacuo, the residue was washed with hexane and recrystallized from ether. 0.192 g (94%) of $(CF_3)_3GePt(PPh_3)_2Cl$ was obtained as a white powder, m.p. 225 °C (dec.). Found: C, 45.85; H, 3.52. $C_{39}H_{30}ClF_9GeP_2Pt$ calcd.: C, 45.27; H, 2.92%.

Interaction of II with Et_2Hg

To a solution of II (0.248 g, 0.108 mmol) in THF (30 ml) was added 0.029 g (0.112 mmol) of Et_2Hg. In 2–3 min metallic mercury appeared. The reaction proceeded for 2 h, and 0.041 g (94%) of Hg was obtained. The solvent was evaporated to 5 ml and hexane (20 ml) was added. A colourless, crystalline residue, $(CF_3)_3GePt(PPh_3)_2Et$ (0.2 g, 90%), was obtained, m.p. 203°C (dec.). Found: C, 47.95; H, 3.44. $C_{41}H_{35}F_9GeP_2Pt$ calcd.: C, 47.89; H, 3.43%.

Preparation of $(CF_3)_3GePt(PPh_3)_2HgEt$

A solution of $Pt(PPh_3)_4$ (0.29 g, 0.233 mmol) in toluene (20 ml) was added to a solution of $(CF_3)_3GeHgEt$ (0.118 g, 0.233 mmol) in 5 ml of toluene. After 2 h the solution was evaporated under vacuum to 5 ml and 20 ml of hexane was added. Light-yellow $(CF_3)_3GePt(PPh_3)_2HgEt$ (0.164 g, 68%) precipitated, m.p. 155–192°C. The compound decomposed slowly in air. Found: C, 40.69; H, 2.85. $C_{41}H_{35}F_9GeHgP_2Pt$ calcd.: C, 40.07; H, 2.87%.

Interaction of I with $Cl_2Pt(PPh_3)_2$

To a mixture of I (0.15 g, 0.101 mmol) with $Cl_2Pt(PPh_3)_2$ (0.08 g, 0.101 mmol) was added 10 ml of THF. Precipitation of metallic mercury was observed at room temperature. The mixture was shaken from time to time until $Cl_2Pt(PPh_3)_2$ had completely dissolved. 0.02 g (99%) of Hg was isolated in 8 days. THF was removed under vacuum to give 0.206 g (98%) of $(CF_3)_3GePt(PPh_3)_2Cl$, m.p. 225 °C (dec.). Its IR spectra and elemental analysis were the same as those for the compound obtained in the above reaction of II with Cl_2Hg.

Reaction of I with $Et_2Pt(PPh_3)_2$

To a mixture of I (0.229 g, 0.155 mmol) with 0.12 g (0.155 mmol) of $Et_2Pt(PPh_3)_2$ was added 10 ml of THF. Metallic mercury precipitated slowly from the solution. After 4 days the solution was decanted from Hg (0.025 g, 80%) and evaporated to 2 ml under vacuum. Hexane was added to precipitate $(CF_3)_3GePt(PPh_3)_2Et$ (0.263 g, 82%), which was identified by means of LSC and IR spectroscopy.

Reaction of II with dihydrogen

Dry dihydrogen was bubbled through a solution of II (0.214 g, 0.093 mmol) in 30 ml of THF for 2 h at room temperature. After decantation metallic mercury precipitated (0.017 g, 91%) and THF was removed under vacuum to obtain a viscous compound. Hexane was added to the residue to precipitate crystalline $(CF_3)_3GePt(PPh_3)_2H$ (0.17 g, 91%), m.p. 200–205 °C (dec.). IR ν(Pt–H): 2130 cm^{-1}. Found: C, 46.57; H, 3.32; F, 16.91. $C_{39}H_{31}F_9GeP_2Pt$ calcd.: C, 46.83; H, 3.12; F, 17.02%.

Preparation of $(CF_3)_3GePt(PPh_3)_2H$

$(CF_3)_3GeH$ (0.1 g, 0.356 mmol) was added to a solution of $Pt(PPh_3)_4$ (0.38 g, 0.305 mmol) in 15 ml of THF. Decoloration of the solution was observed at room temperature. After 1 h the $(CF_3)_3GePt(PPh_3)_2H$ that formed (0.302 g, 87%) was isolated as described above. M.p. 205 °C (dec.), IR ν(Pt–H): 2130 cm^{-1}. LSC data revealed that the product was identical to the compound obtained in the previous experiment.

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