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## STUDY OF THE REACTIONS OF PENTAFLUOROPHENYL ORGANOPOLY-METALLIC COMPOUNDS BY LIQUID-SOLID CHROMATOGRAPHY

M. N. BOCHKAREV, G. N. BORTNIKOV, N. P. MAKARENKO and L. P. MAIOROVA

*Institute of Chemistry, U.S.S.R. Academy of Science, Gorky (U.S.S.R.)*

and

A. V. KISELEV and Ya. I. YASHIN

*Department of Chemistry, M. V. Lomonosov State University of Moscow, Moscow (U.S.S.R.)*

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### SUMMARY

Liquid-solid chromatography has been used for the separation and analysis of pentafluorophenyl organopolymetallic compounds, containing groups of the type Ge-Hg-Pt-Ge, Sn-Hg-Pt-Sn, Ge-Cd-Pt-Ge and germylated hydrides of platinum and palladium. This technique provides a convenient method of monitoring the synthesis of the above compounds. Its use in the investigation of the reactivity of these compounds allows one to determine the direction of the reactions and to detect the formation of intermediate and by-products, the identification of which may be difficult by other methods. This method is also useful for the determination of the relative stability of these substances.

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### INTRODUCTION

The recently discovered ability of zerovalent triphenylphosphine complexes of platinum and palladium to insert into Hg-C and M-M' bonds (M = Hg, Cd, Zn; M' = Ge, Sn) allowed us to synthesize a series of organometallic compounds comprising polymetallic chains<sup>2</sup>. Germyl-platinum or -palladium complexes were also obtained by oxidative addition of ML<sub>3</sub> (M = Pt, Pd; L = PPh<sub>3</sub>) into the Ge-H bond in pentafluorophenylgermanium hydrides<sup>3</sup>. All these products have low volatility and thermal stability which prevents their analysis by gas chromatography. Thin-layer chromatography provides limited information and is of little use for the analysis of multi-component mixtures of such compounds<sup>1</sup>.

We have found that liquid column molecular chromatography can be used for the analysis of thermally unstable per-esters of silyl-substituted carboxylic acids<sup>4</sup> and for peroxide products of the oxidation of silyl-substituted phenols<sup>5</sup>. This paper describes the use of liquid-solid chromatography (LSC) for the analysis and identification of involatile organopolymetallic complexes of platinum and palladium.

TABLE I

REACTIONS OF PENTAFLUOROPHENYL ORGANOPOLYMETALLIC COMPOUNDS, STUDIED BY LSC

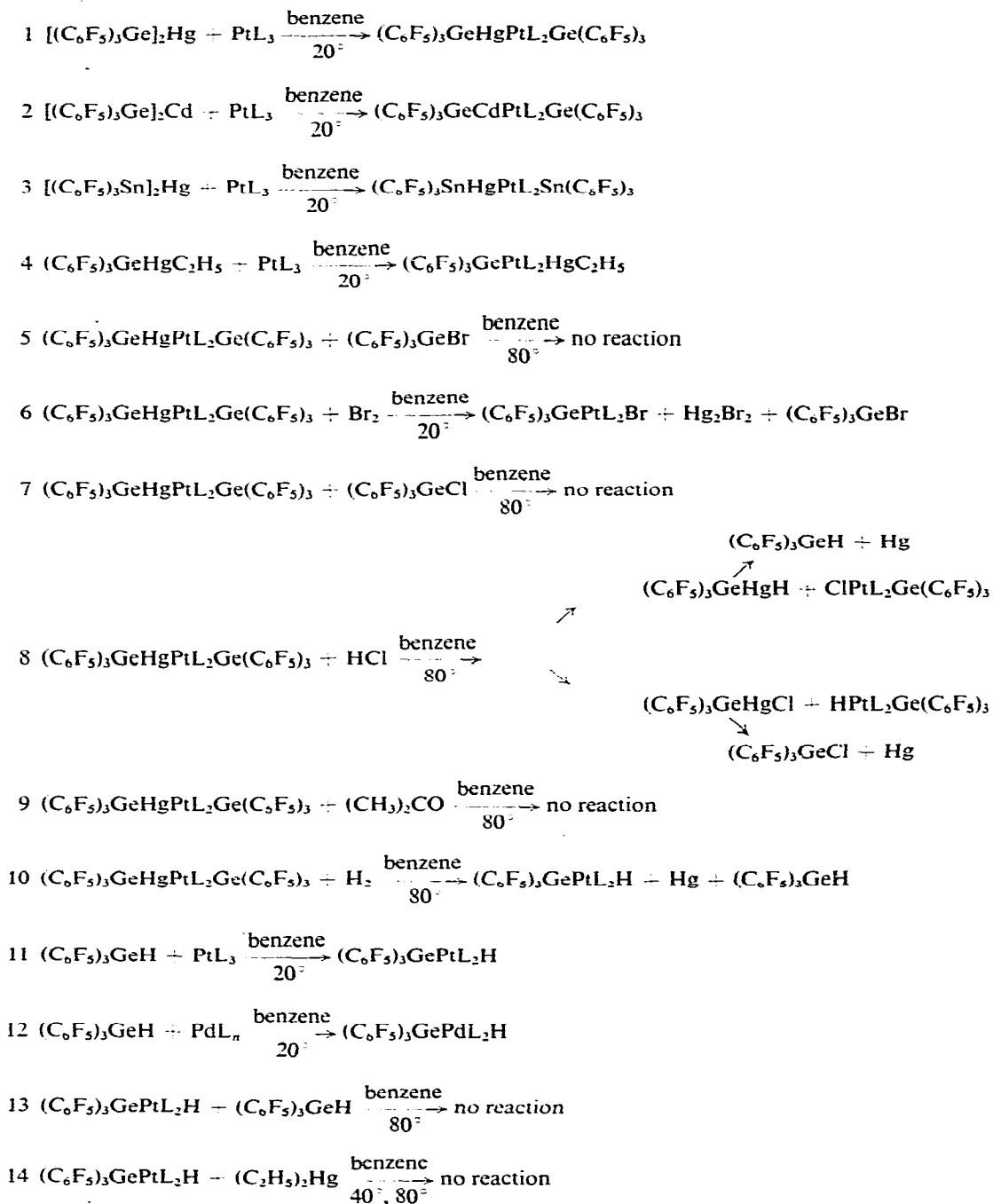
L = P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>; THF = tetrahydrofuran.

TABLE I (continued)

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15	$(C_6F_5)_3GePtL_2H + HCl \xrightarrow[80^\circ, 17\ h]{benzene} (C_6F_5)_3GeH + Cl_2PtL_2$
16	$(C_6F_5)_3GePtL_2H + (C_6F_5)_3GeBr \xrightarrow[80^\circ]{benzene} \text{no reaction}$
17	$(C_6F_5)_3GePtL_2H + Br_2 \xrightarrow[20^\circ]{benzene} (C_6F_5)_3GeBr + Br_2PtL_2 + (C_6F_5)_3GePtL_2Br$
18	$(C_6F_5)_3GePtL_2H + S \xrightarrow[20^\circ]{benzene} \text{no reaction}$
19	$(C_6F_5)_3GePtL_2H + (C_6F_5)_3GeGe(C_6F_5)_3 \xrightarrow[100^\circ]{THF} \text{no reaction}$
20	$(C_6F_5)_3GeH_2 + PtL_3 \xrightarrow[20^\circ]{benzene} (C_6F_5)_2Ge(H)PtL_2H$
21	$(C_6F_5)_2Ge(H)PtL_2H + (C_2H_5)_2Hg \xrightarrow[100^\circ]{THF} \text{no reaction}$
22	$(C_6F_5)_2Ge(H)PtL_2H + PtL_3 \xrightarrow[80^\circ]{benzene} \text{destruction of products occurs}$
23	$(C_6F_5)_2Ge(H)Ge(H)(C_6F_5)_2 + PtL_3 \xrightarrow[20^\circ]{benzene} (C_6F_5)_2Ge(PtL_2H)Ge(PtL_2H)(C_6F_5)_2$
24	$(C_6F_5)_3GeSH + PtL_3 \xrightarrow[20^\circ]{benzene} (C_6F_5)_3GeSPtL_2H + [(C_6F_5)_3GeS]_2PtL_2$
25	$(C_6F_5)_3GeSeH + PtL_3 \xrightarrow[20^\circ]{benzene} (C_6F_5)_3GeSePtL_2H + [(C_6F_5)_3GeSe]_2PtL_2$

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## EXPERIMENTAL

The investigations were performed on a Tsvet 304 liquid chromatograph equipped with a UV detector (254 nm) and at an inlet pressure of 80–100 atm. As in a previous paper<sup>6</sup>, stainless-steel columns (25 or 30 cm long, 1 or 4 mm I.D.) packed with Silochrom C-80 (specific surface areas 80 m<sup>2</sup>/g; grain size, 5–8 μm and ~15 μm) were used. Mixtures of *n*-hexane with diethyl ether (32:1 and 24:1) served as the eluent. The analyses were performed at room temperature and at 45°. Samples were injected with a 10-μl syringe.

## RESULTS AND DISCUSSION

Liquid–solid chromatography was preferred over liquid–liquid chromatography for the separation and analysis of pentafluorophenyl organopolymetallic compounds since use of the latter method results in depletion of the stationary phase

by the eluents. Macroporous Silochrom C-80 was used in this study since pentafluorophenyl organopolymetallic compounds are strongly retained on microporous silica gels. The best separations were achieved when using *n*-hexane with different amounts of diethyl ether as eluent.

Table I gives oxidative-addition reactions of triphenylphosphine complexes of platinum and palladium investigated by LSC. The reaction mixtures were sampled at intervals and introduced into the chromatograph. A decrease in the peak area of the starting reagent and the appearance and growth of a new peak enabled the course of the reaction to be followed. Chromatographic investigations showed that reactions 1–4 (Table I) proceed readily at room temperature. The purity of the components isolated from the reaction mixture was also determined by LSC, while their structure was determined by elemental analysis and IR spectroscopy.

The retention times of the organopolymetallic products obtained differ greatly from those of the starting reagents (Fig. 1). Preliminary X-ray and  $^{31}\text{P}$  NMR investigations showed that most of the compounds have a square-planar *cis*-configuration. However, in some cases, *trans*-isomers<sup>2</sup> were expected to be present in the products but we could not confirm this by LSC.

It was found that compounds with Ge–Hg–Pt–Ge, Sn–Hg–Pt–Sn and Ge–Hg–Pt chains are stable in air while the Ge–Cd–Pt–Ge analogues underwent trans-

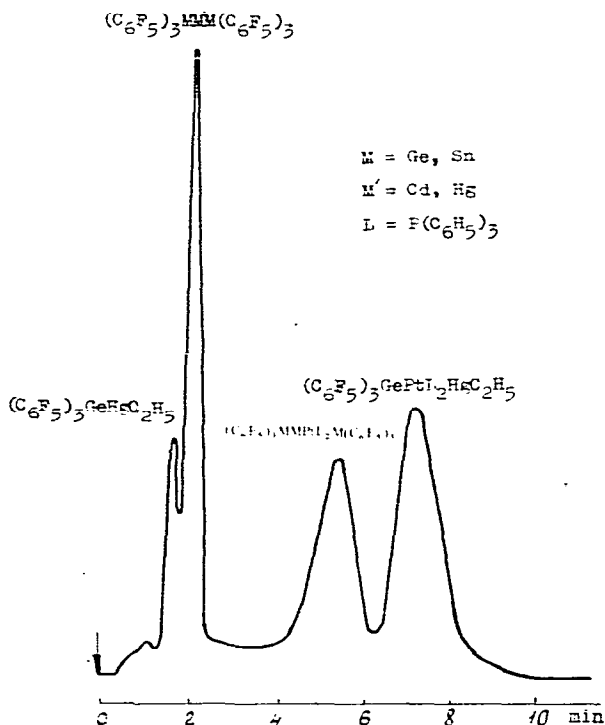


Fig. 1. Chromatogram of pentafluorophenyl organopolymetallic compounds (reactions 1–4 in Table I). Column, 35 cm  $\times$  4 mm I.D.; adsorbent, Silochrom C-80 (grain size 15  $\mu\text{m}$ ); eluent, *n*-hexane–diethyl ether (24:1) (flow-rate 1.85  $\text{cm}^3/\text{min}$ ); column inlet pressure, 55 atm; temperature, 45 $^\circ$ ; UV detector (254 nm).

formation on exposure to air (Fig. 2). Thus the peak area of the compound  $(C_6F_5)_3GeCdPtL_2Ge(C_6F_5)_3$  was greatly reduced and some unidentified peaks were present in the chromatogram.

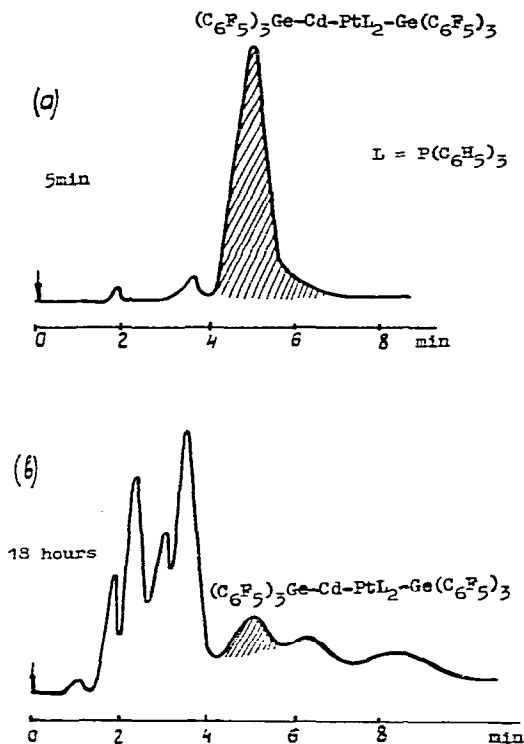


Fig. 2. Chromatogram of  $(C_6F_5)_3GeCdPtL_2Ge(C_6F_5)_3$  after exposure to air for (a) 5 min, (b) 18 h. Operating conditions as in Fig. 1.

The reactivity of pentafluorophenyl organopolymetallic compounds has been investigated by LSC using  $(C_6F_5)_3GeHgPtL_2Ge(C_6F_5)_3$  (I) as a test compound (reactions 5–10 in Table I). The chromatogram of the reaction of this compound with bromide showed the appearance of two peaks (Fig. 3). The retention time of the expected product tris(pentafluorophenyl)germanium bromide was shown to coincide with that of the starting complex (I). Therefore this compound was identified by gas-liquid chromatography (GLC) and IR spectroscopy after its isolation from the reaction mixture. The products identified by chromatography confirm the reaction scheme reported previously<sup>2</sup>.

Complex I reacts slowly with HCl in boiling benzene. Chromatograms (Fig. 4) recorded at intervals showed that the process is practically complete in 2 h. Tris(pentafluorophenyl)germane, tris(pentafluorophenyl)germanium chloride and platinum hydrides  $(C_6F_5)_3GePtL_2H$  were identified by chromatography. The reaction products also contain a small amount of an unidentified component, apparently,  $(C_6F_5)_3GePtL_2Cl$ . An attempt to isolate this compound failed. Tris(pentafluorophenyl)germanium chloride was isolated from the reaction mixture by recrystallization and identified by GLC; LSC was in this case unsuccessful.

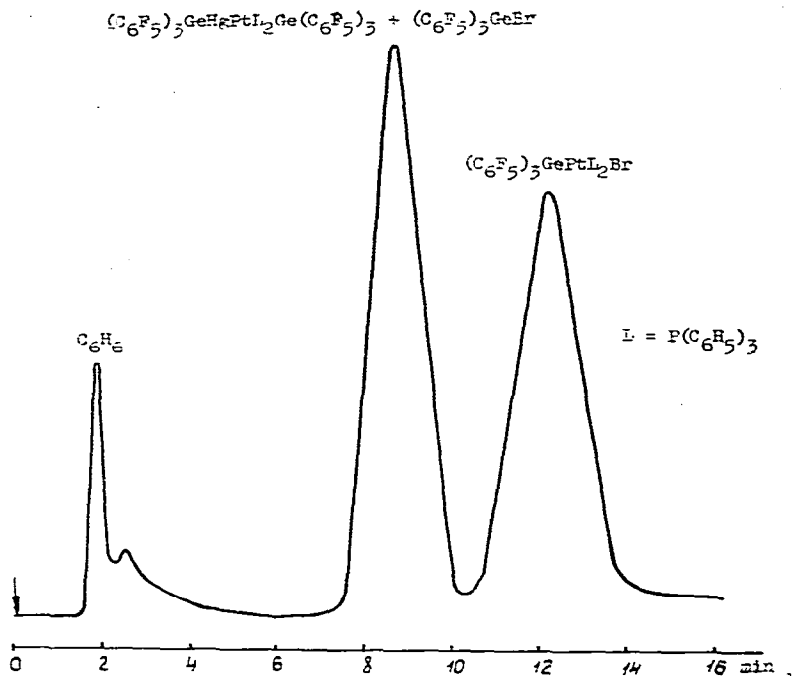


Fig. 3. Chromatogram of products of reaction between  $(\text{C}_6\text{F}_5)_3\text{GeHgPtL}_2\text{Ge}(\text{C}_6\text{F}_5)_3$  and  $\text{Br}_2$ . Operating conditions as in Fig. 1, but flow-rate  $1.0 \text{ cm}^3/\text{min}$ .

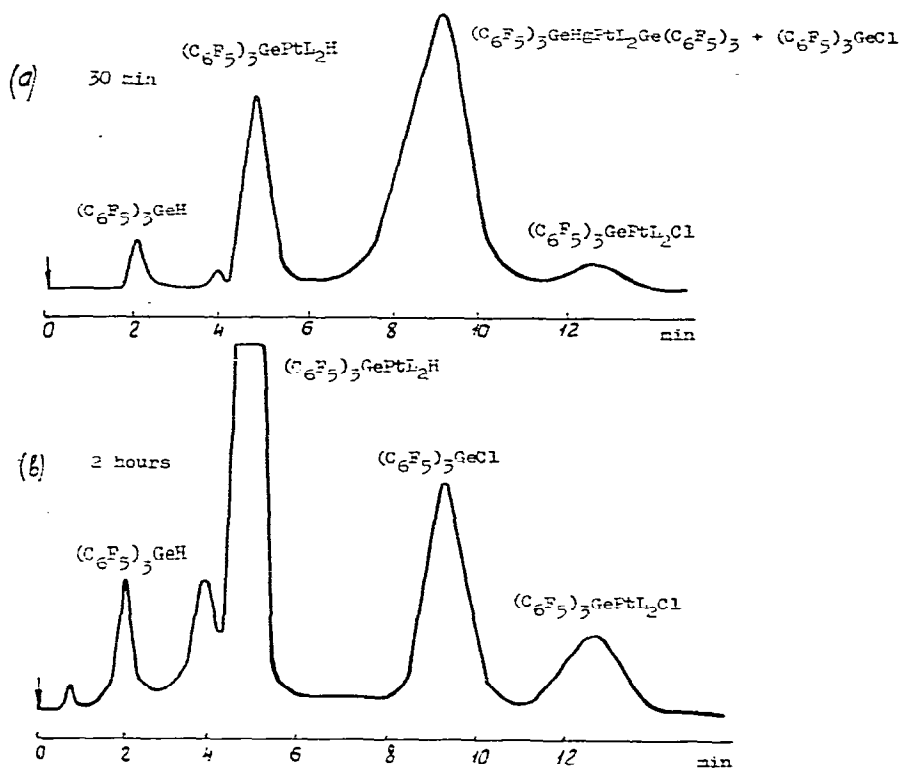


Fig. 4. Chromatogram of products of reaction between  $(\text{C}_6\text{F}_5)_3\text{GeHgPtL}_2\text{Ge}(\text{C}_6\text{F}_5)_3$  and  $\text{HCl}$ : (a) after 30 min; (b) after 2 h. Operating conditions as in Fig. 1.

LSC analysis of the mixture obtained after the reaction of complex I with hydrogen showed the presence of six components, four of which were identified (Fig. 5).

LSC investigations showed that the synthesis of the hydrides  $(C_6F_5)_3GePtL_2H$  and  $(C_6F_5)_3GePdL_2H$  (reactions 11 and 12 in Table I) proceeds readily at room temperature. The peak area of the initial compound  $(C_6F_5)_3GeH$  had greatly decreased (by a factor of *ca.* 10) 30 min after the start of the reaction.

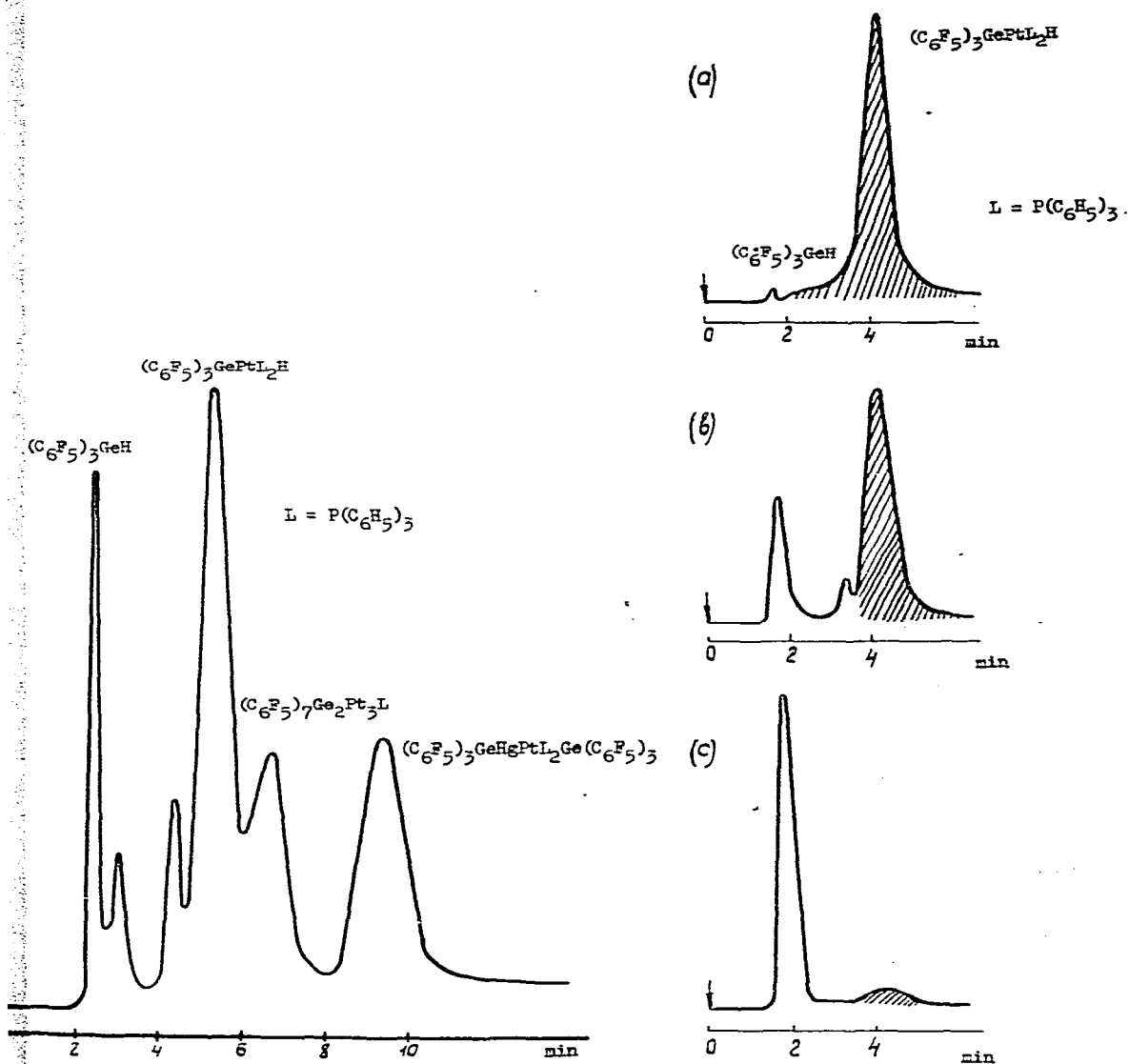


Fig. 5. Chromatogram of the products of reaction between  $(C_6F_5)_3GeHgPtL_2Ge(C_6F_5)_3$  and  $H_2$ . Operating conditions as in Fig. 1.

Fig. 6. Chromatogram of the products of reaction between  $(C_6F_5)_3GePtL_2H$  and  $HCl$ : (a) at  $23^\circ$  for 15 min; (b) at  $80^\circ$  for 9 h; (c) at  $80^\circ$  for 17 h. Eluent: *n*-hexane-diethyl ether (32:1); flow-rate,  $2.15\text{ cm}^3/\text{min}$ . Pressure on the column inlet, 75 atm. Other conditions as in Fig. 1.

Fig. 6 shows that the reaction of  $(C_6F_5)_3GePtL_2H$  (complex II) with HCl is nearly complete in 17 h. The product  $(C_6F_5)_3GeH$  was isolated by LSC and its structure was confirmed by IR spectroscopy, LSC and elemental analysis.

The analysis of the mixture obtained in the reaction of complex II with  $Br_2$  showed the presence of five components (Fig. 7). During the reaction the peak area of the initial hydride (II) decreases and the peaks of the components  $(C_6F_5)_3GeBr$  and  $(C_6H_5)_3GePtL_2Br$  simultaneously increase. Tris(pentafluorophenyl)germanium bromide was identified from the expected stoichiometry of the mixture.  $(C_6F_5)_3GePtL_2Br$  (Fig. 7b) was isolated from the reaction mixture by repeated recrystallization in benzene-hexane.

Some reactions (20–23, Table I) of zerovalent triphenylphosphineplatinum complexes with the series of hydrides  $(C_6F_5)_2GeH_2$ ,  $(C_6F_5)_2Ge(H)PtL_2H$  and  $(C_6F_5)_2Ge(H)-Ge(H)(C_6F_5)_2$  were studied by LSC. The interaction of  $(C_6F_5)_2GeH_2$  with  $PtL_3$  did not give a diplatinum derivative (Fig. 8). The chromatogram shows that the main product is  $(C_6F_5)_2Ge(H)PtL_2H$ . IR spectroscopic investigations showed that the compound obtained possesses Ge–H and Pt–H bonds, *i.e.*, a  $PtL_2$  fragment has been

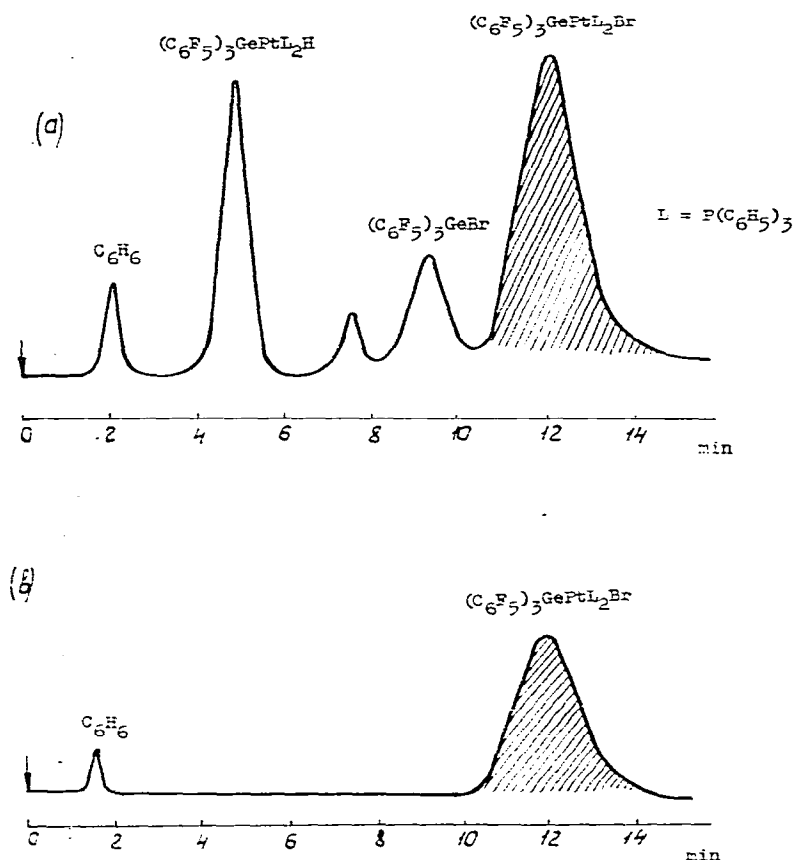


Fig. 7. Chromatogram of the products of reaction between  $(C_6F_5)_3GePtL_2H$  and  $Br_2$ : (a) the mixture; (b) the component  $(C_6F_5)_3GePtL_2Br$  after two recrystallizations. Operating conditions as in Fig. 1.



inserted into one of the Ge–H bonds. The chromatogram of this product when exposed to air for 2.5 h showed that the hydride is unstable and undergoes transformations.

The chromatogram of the mixture (Fig. 9) formed in the reaction of  $(C_6F_5)_2Ge(H)(C_6F_5)_2$  with  $PtL_3$  (reaction 23 in Table I) exhibited three peaks, due to the starting digermene, the product of insertion of  $PtL_2$  into one Ge–H bond and the diplatinum complex  $(C_6F_5)_2Ge(PtL_2H)-Ge(PtL_2H)(C_6F_5)_2$ . The yields of these products were dependent on the molar ratio of the starting compounds. Moreover, monitoring of the reaction by LSC showed that the addition of the first  $PtL_2$  fragment proceeds slightly more readily than the second one.

The chromatogram of the reaction of  $(C_6F_5)_3GeSH$  with  $PtL_3$  (reaction 24 in Table I) shows (Fig. 10) that the mixture contains four components. The presence of  $(C_6F_5)_3GePtL_2H$  is due to the existence of tris(pentafluorophenyl)germane in the starting germanethiol. The thio-derivatives were isolated by fractional crystallization from hexane–benzene, and their purity was controlled by LSC.

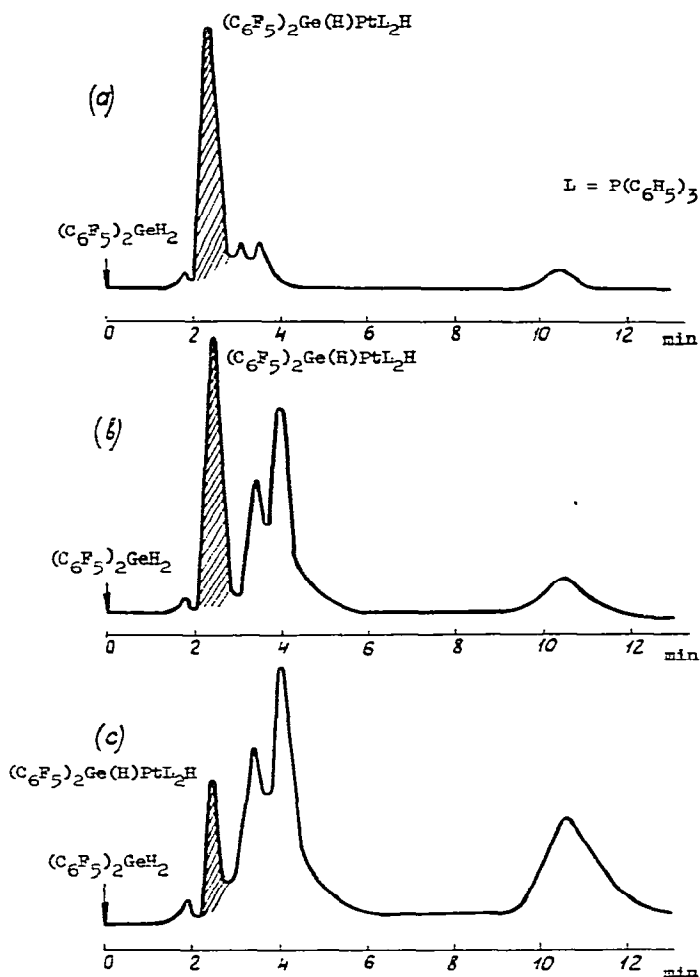


Fig. 8. Chromatogram of the products of reaction between  $(C_6F_5)_2GeH_2$  and  $PtL_3$ . Sampling performed: (a) in 5 min; (b) in 2.5 h; (c) in 3.5 h. Operating conditions as in Fig. 1.

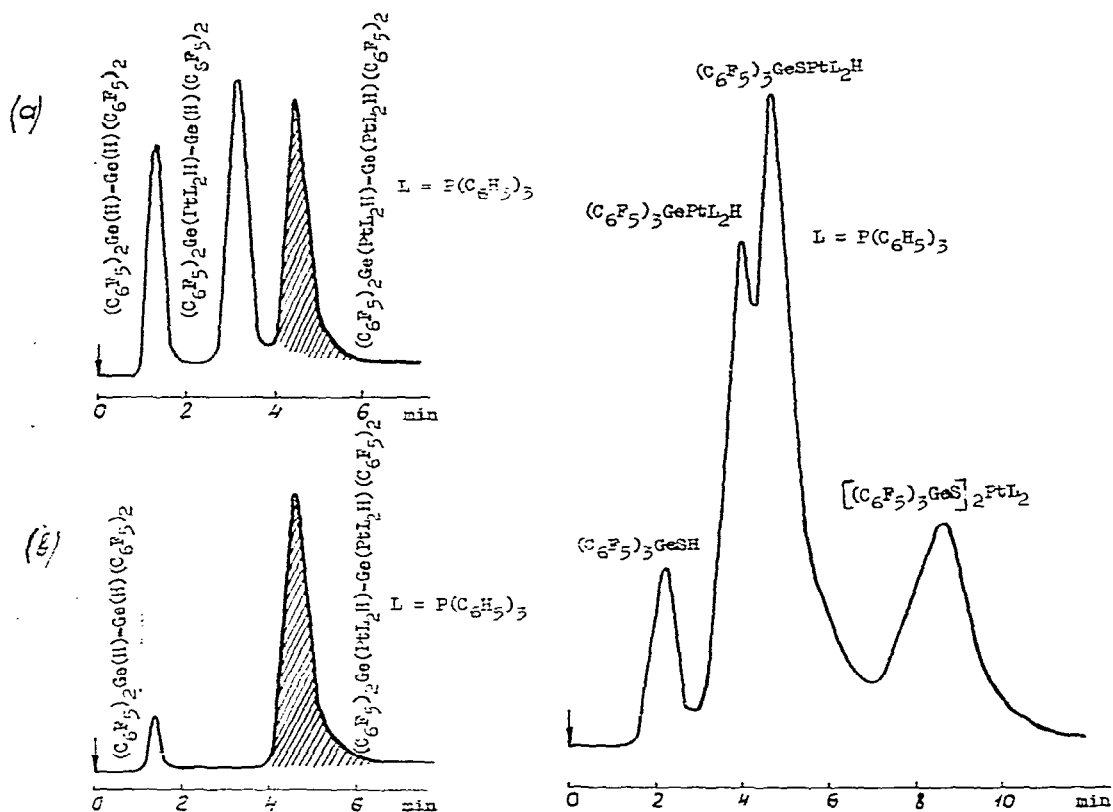


Fig. 9. Chromatogram of the products of reaction of  $(C_6F_5)_2Ge(H)Ge(H)(C_6F_5)_2$  with  $PtL_3$ : (a) untreated mixture; (b) after repeated recrystallization from *n*-hexane. Column, 15 cm  $\times$  4 mm I.D.; adsorbent, Silochrom C-80 (grain size 5–8  $\mu$ m); eluent, *n*-hexane–diethyl ether (32:1) (flow-rate 1.7  $cm^3/min$ ); column inlet pressure, 50 atm; temperature, 45°; UV detector (254 nm).

Fig. 10. Chromatogram of the products of reaction between  $(C_6F_5)_3GeSH$  and  $PtL_3$ . Eluent flow-rate, 0.4  $cm^3/min$ ; pressure on column inlet, 80 atm. Other operating conditions as in Fig. 9.

The interaction of  $(C_6F_5)_3GeSeH$  with  $PtL_3$  (reaction 25 in Table I) proceeds in a similar way (Fig. 11). In this case the starting selenol contained tris(pentafluorophenyl)germanium bromide. It was shown in a separate experiment that this compound does not react with  $PtL_3$  under the same conditions. Therefore a peak due to  $(C_6F_5)_3GeBr$  is present in the chromatogram of the reaction mixture. We could not identify the last peak in this chromatogram since this product was not isolated, but this compound is probably the diselenide  $[(C_6F_5)_3GeSe]_2PtL_2$ .

Thus, we have demonstrated the possibility of using LSC for the separation and analysis of pentafluorophenyl organopolymetallic compounds having low volatility and relatively low thermal stability. Good separations of the compounds has been achieved on unmodified commercial macroporous Silochrom C-80.

It should be noted that the retention times of the products containing Pt or Pd is appreciably longer than those of the starting compounds. This may be explained in terms of differences in the intermolecular interactions of organometallic compounds with the adsorbent surface. These differences may be due to changes in the configura-

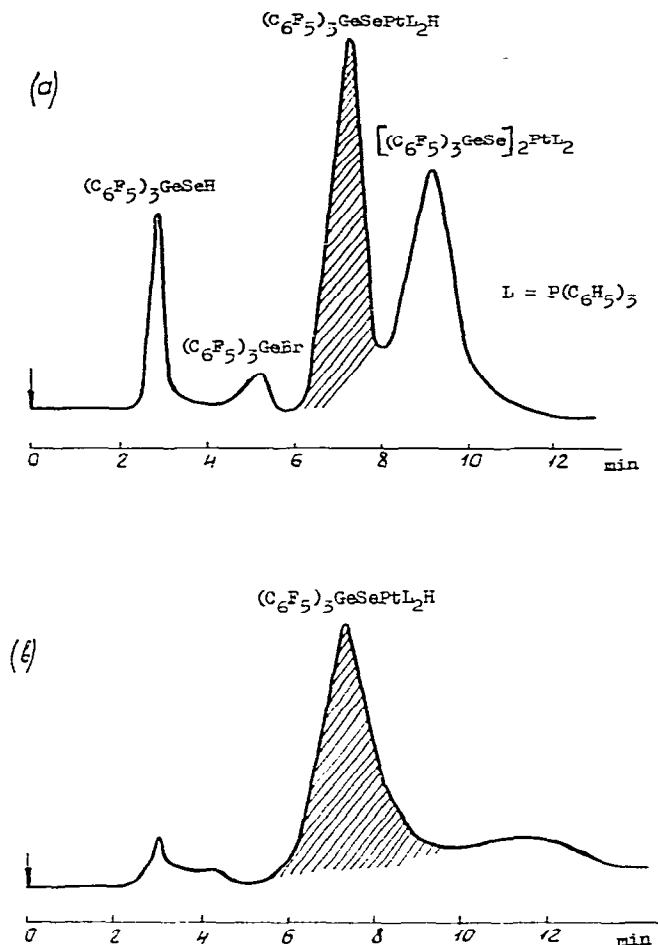


Fig. 11. Chromatogram of the products of reaction between  $(C_6F_5)_3GeSeH$  and  $PtL_3$ ; (a) untreated mixture; (b) after repeated recrystallization from *n*-hexane. Eluent: *n*-hexane-diethyl ether (32:1); flow-rate, 1.8  $cm^3/min$ , column inlet pressure, 50 atm. Other operating conditions as in Fig. 1.

tions of the organometallic compounds after addition of  $ML_2$  fragments and the appearance of new donor-acceptor properties.

LSC allows one to investigate and monitor the course of reactions of organopolymetallic compounds. The data obtained provide information concerning the mechanism of reaction, the relative rates of reaction and the stability of the reaction products.

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