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ADVANCES IN THE CHEMISTRY OF ORGANOMETALLIC POLYNUCLEAR COMPOUNDS CONTAINING σ-BONDED METALS

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One of the important aspects of the development of organometallic chemistry is the synthesis and investigation of compounds containing two or more atoms of heteroelements bonded to each other **. Such substances are often referred to as polynuclear organometallic compounds. Species containing chains, rings and other geometrical configurations formed by atoms of different heteroelements seem to be the most interesting compounds of this type. A distinctive feature of these compounds which distinguishes them from a wide range of clusters is the σ-character of the metal—metal bond. We summarize the below results of work carried out during the last years by Gorky chemists in the synthesis and reactions of such compounds.

Four main synthetic routes to the compounds are known:

1. The hydride method.
2. Insertion of free heteroelements and low-valent complexes of metals into metal—metal bonds.
3. Transmetallation reactions.
4. Condensation reactions involving derivatives of alkali metals of the type R_nMLi.

The last method has been little used in our work, and so is not considered in this review.

1. The hydride method

The most used method of forming metal—metal bonds involves the reaction of organometallic hydrides with metal alkyls and amido- and alkoxy-derivatives. The method was developed for preparation of binuclear and trinuclear derivatives of non-transition metals of the types $(R_3Si)_2Hg$ and R_3GeHgR' in our laboratory [1,2] and simultaneously by W.P. Neumann and his coworkers [2,3];

Detailed investigation has shown that the method has a considerable potential,

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* Written in association with M.N. Bochkarev.

** The terms "metal" and "heteroelement" are used interchangeably throughout, and imply that the element concerned is not C, H, O, N or halogen.

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and permits the preparation of longer chains of heteroelements having various combinations of heteroelements, including transition metals. Thus the chains $R_3SiSeMSeSiR_3$ (M = Zn, Cd) [4], $R_3SiXHgXSiR_3$, $R_3SiXHgGeR_3$ (X = S, Se, Te) [5], $R_3MXM'Et_2$, $R_3SiSAl(R)SSiR_3$ (M = Si, Ge; X = S, Se; M' = Al, Ga, In) [6,7] have been obtained by the reaction of organometallic hydrochalcogenides R_3MXH (M = Si, Ge; X = S, Se, Te) with Et_nM' (M' = Zn, Cd, Hg, $n = 2$; M' = Al, Ga, In, $n = 3$). Such a procedure also gave trinuclear vanadium-containing compounds [8]:

$$Cp_2VCH_2SiMe_3 + R_3GeXH \rightarrow Cp_2V{-}X{-}GeR_3 + Me_4Si$$

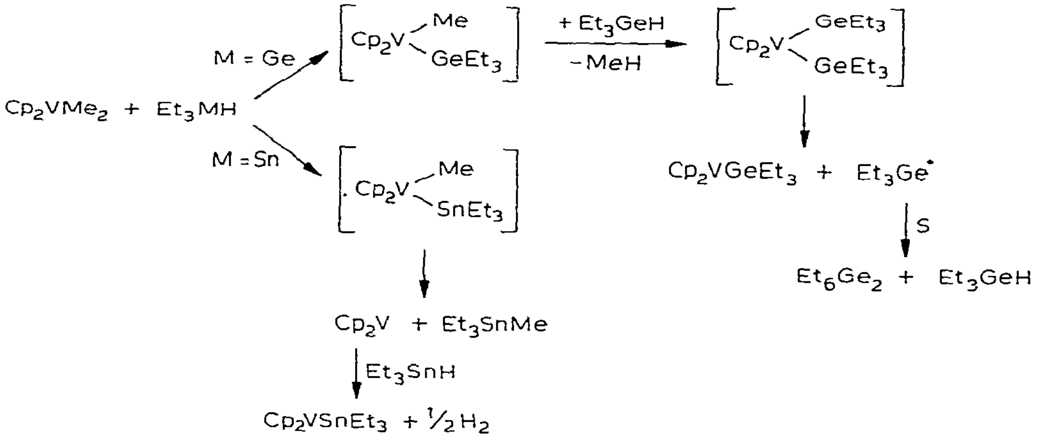
$$X = S, Se;\ R = Et,\ i\text{-}Pr$$

Cp_2VMe and $CpVGeEt_3$ react in a similar way. In the latter case a trinuclear product and triethylgermane were isolated. Organohydrides of Group IVB elements can also abstract an R-group from Cp_2VR. In these reactions binuclear germylvanadium and stannylvanadium compounds are formed [8]:

$$Cp_2VR + Et_3MH \rightarrow Cp_2V{-}MEt + RH$$

$$M = Ge, Sn$$

The reaction of vanadocene, containing two V—C σ-bonds, with triethylgermane and triethylstannane also gives Cp_2VMEt_3 along with Et_3MMe, methane and hydrogen [9]. The unstable intermediate $Cp_2V(GeEt_3)_2$ is evidently formed in the reaction with Et_3GeH, as confirmed by ESR studies.



The Sn—V bond is weaker then the Ge—V bond, and so the decomposition of the intermediate $Cp_2V(Me)SnEt_3$ proceeds more rapidly than its reaction with starting hydride. Ti—Ge and Zr—Ge linkages are much less stable, and so interaction of triethylgermane with Cp_2MMe_2 only leads to the reduction of the metal to the divalent (M = Ti) or trivalent (M = Zr) state [10].

It is well known that the groups bonded to the heteroatom greatly influence the stability and reactivity of organometallic compounds. Bulky substituents and substituents without hydrogen atoms on the β-carbon atom increase the stability. In the latter case the enhancement of the stability is due to the prevention of the so-called hydride decomposition. Perhalogenaryl substituents also usually have a considerable effect; this is evidently the consequence of several factors: intramolecular coordination, conjugation effects, the strong electron-withdrawing effect of C_6X_5 groups, etc. The use of $(Me_3SiCH_2)_3SnH$ and $(C_6F_5)_3SnH$ in the reaction with Et_2Hg made it possible to obtain stable trinuclear stannylmercury compounds [11,12]

$$2\,R_3SnH + Et_2Hg \rightarrow R_3SnHgSnR_3 + 2\,EtH$$

$$R = CH_2SiMe_3,\ C_6F_5$$

The first product ($R = CH_2SiMe_3$) melts without decomposition at [illegible] while the second ($R = C_6F_5$) melts at 170 °C. When these compounds were subjected to reactions (with acyl peroxides, 1,2-dibromoethane, mercury chloride etc.) developed previously for characterization of the reactions of M–M bonds [1,13–17], the results did not differ much from those obtained with other derivatives of the type $(R_3M)_2Hg$ (M = Si, Ge). In all cases the reactions led to the cleavage of Sn–Hg bonds with the formation of metallic mercury and the corresponding R_3SnX compounds, but they proceed more slowly. It is interesting that an asymmetrical stannylmercurial which contains both types of stabilizing substituents together, $(C_6F_5)_3SnHgSn(CH_2SiMe_3)_3$, is unstable like the other stannylmercurials. The compound loses its mercury entirely at room temperature at the moment of its formation in the reaction of $[(Me_3SiCH_2)_3Sn]_2Hg$ with $[(C_6F_5)_3Sn]_2Hg$ [12]

$$[(Me_3SiCH_2)_3Sn]_2Hg + [(C_6F_5)_3Sn]_2Hg \xrightarrow{20\,°C}$$

$$[2(Me_3SiCH_2)_3SnHgSn(C_6F_5)_3] \xrightarrow{20\,°C} 2\,Hg + 2(Me_3SiCH_2)_3SnSn(C_6F_5)_3$$

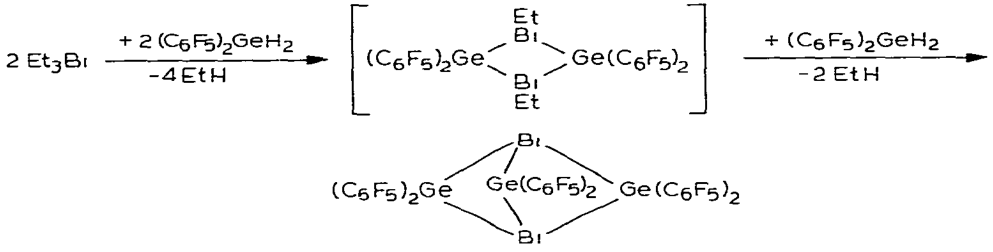
The synthesis of germylmercury compounds by reaction of [illegible] (pentafluorophenyl)germane proceeds at [illegible] of Et_3GeH and [illegible] binuclear and trinuclear [illegible] are formed [illegible]

$$n\,(C_6F_5)_3GeH + Et_2Hg \rightarrow [illegible]$$

$$n = 1,\ 2$$

[illegible]

SCHEME 1



such processes usually give polymers and oligomers with fairly long chains.

A comparison of the properties of $[(C_6F_5)_3Ge]_nBiEt_{3-n}$ with those of its non-fluorinated analogues showed that the presence of C_6F_5 substituents does not in this case increase the thermal stability or lower the chemical reactivity. They are easily oxidized in air, and react with bromine and hydrogen chloride to give $(C_6F_5)_3GeX$ (X = Br, H) and $Et_{3-n}BiX_n$ (X = Br, Cl). In contrast, the trigermyldibismuth derivative $[(C_6F_5)_2Ge]_3Bi_2$ is fairly stable towards these reagents. It is not changed in air, and the reaction with HCl in THF requires almost three days. The products of the reaction are $(C_6F_5)_2GeHCl$ and Bi.

The reaction of the dihydride $(C_6F_5)_2GeH_2$ with R_2Hg (R = Et, i-Pr, $N(SiMe_3)_2$) and the reaction of diphenylgermane with diethylmercury [3] both lead to unstable oligomers $[R_2GeHg]_n$. The ready demercuration of these compounds is apparently due to the location of the two mercury atoms on a

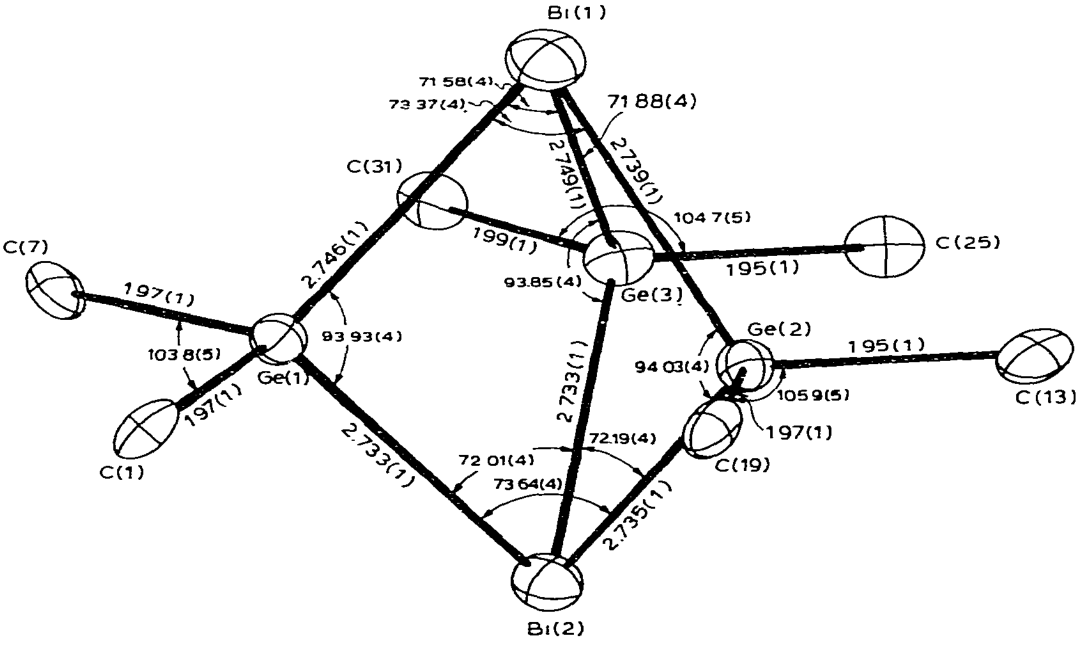
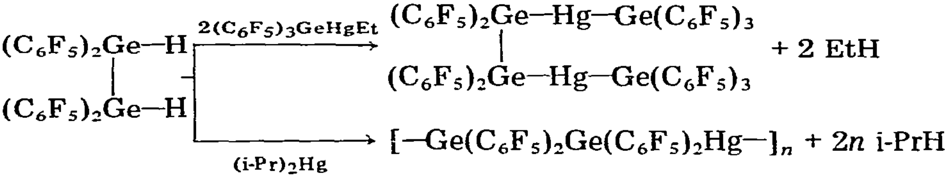


Fig. 1. Geometry of the polymetallic skeleton of $[(C_6F_5)_2Ge]_3Bi_2$.

single germanium atom. To examine this assumption, and also to prepare stable polynuclear germylmercury compounds we carried out the reaction of 1,2-dihydrodigermane $(C_6F_5)_2Ge(H)Ge(C_6F_5)_2H$ with the unsymmetrical ethyltris(pentafluorophenyl)germylmercury and diisopropylmercury. In both cases stable germylmercury compounds were isolated in high yield [21].



$$\begin{array}{l}(C_6F_5)_2Ge-H\\ \quad |\\ (C_6F_5)_2Ge-H\end{array} \xrightarrow{2(C_6F_5)_3GeHgEt} \begin{array}{l}(C_6F_5)_2Ge-Hg-Ge(C_6F_5)_3\\ \quad |\\ (C_6F_5)_2Ge-Hg-Ge(C_6F_5)_3\end{array} + 2\ EtH$$

$$\xrightarrow[(i\text{-}Pr)_2Hg]{} [-Ge(C_6F_5)_2Ge(C_6F_5)_2Hg-]_n + 2n\ i\text{-}PrH$$

The properties of the colourless hexanuclear product resemble those of bis[tris(pentafluorophenyl)germyl]mercury [22]. It is soluble in THF, DME, and aromatic solvents. It is not oxidized in air in the crystalline state. A special feature has been noted in the electron absorption spectra [23], viz. that the spectrum of the hexanuclear product shows long wave maxima (287 and 317 nm) which are apparently due to lengthening of the polymetallic chain.

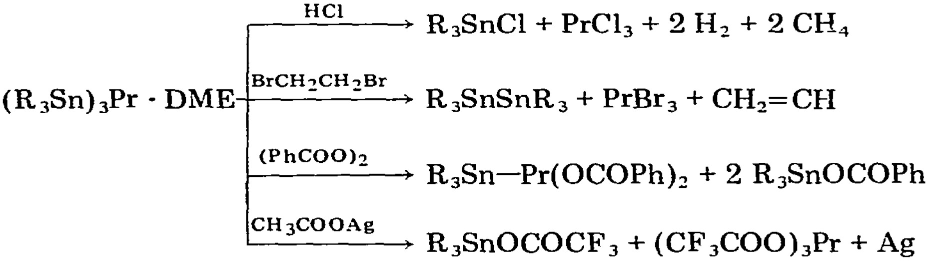
The oligomer $[-Ge(C_6F_5)_2-Ge(C_6F_5)_2-Hg-]_n$ is insoluble in common organic solvents and so investigation of its reactions and its possible use in syntheses are hampered.

The investigation of the chemical properties of the platinum hydride $(C_6F_5)_3$-$GePt(PPh)_2H$ has shown that the Pt—H bond is not active towards R_2Hg. Thus, only the Ge—H bond takes part in the reaction with Et_2Hg of the trinuclear compound $H-Pt(PPh_3)_2-Ge(C_6F_5)_2-Ge(C_6F_5)_2-H$, which contains both Pt—H and Ge—H bonds, and even when an excess of the hydride is used only one of the ethyl groups of the Et_2Hg is displaced [24]:

$$H-Pt(PPh_3)_2-Ge(C_6F_5)_2-Ge(C_6F_5)-H + Et_2Hg \xrightarrow[50-60°C]{} H-Pt(PPh_3)_2-Ge(C_6F_5)_2Ge(C_6F_5)_2-HgEt + EtH$$

Evolution of ethane also occurs in the reaction of the hydride $H-Pt(PPh_3)_2-Ge$-$(C_6F_5)_2-H$ with Et_2Hg, but in this case the outcome is complicated by the decomposition of the products.

The hydride method has been used for the synthesis of polynuclear derivatives of rare-earth metals [25,26]. It was shown that $(Me_3SiCH_2)_3SnH$ reacts with $[(Me_3Si)_2N]_3Ln$ (Ln = Pr, Nd) in DME solution at 80—100°C to afford hexamethyldisilazane and a product which has an elemental analysis consistent with the formula $[(Me_3SiCH_2)_3Sn]_3Ln \cdot DME$. The isolated compounds are slightly coloured, practically insoluble solids, with *T* decomp. = 270—290°C. The reactions of the complexes with hydrogen chloride, $BrCH_2CH_2Br$, benzoyl peroxide, or silver trifluoroacetate confirm the structure.



$$(R_3Sn)_3Pr \cdot DME \xrightarrow{HCl} R_3SnCl + PrCl_3 + 2\ H_2 + 2\ CH_4$$

$$(R_3Sn)_3Pr \cdot DME \xrightarrow{BrCH_2CH_2Br} R_3SnSnR_3 + PrBr_3 + CH_2{=}CH$$

$$(R_3Sn)_3Pr \cdot DME \xrightarrow{(PhCOO)_2} R_3Sn-Pr(OCOPh)_2 + 2\ R_3SnOCOPh$$

$$(R_3Sn)_3Pr \cdot DME \xrightarrow{CH_3COOAg} R_3SnOCOCF_3 + (CF_3COO)_3Pr + Ag$$

$R = CH_2SiMe_3$

The reaction with dibromoethane apparently proceeds via the formation of the monobromide $(R_3Sn)_2PrBr$ and the dibromide $R_3SnPrBr_2$ as intermediates, and these compounds react with the simultaneously forming bromostannane R_3SnBr to give the distannane and $PrBr_3$.

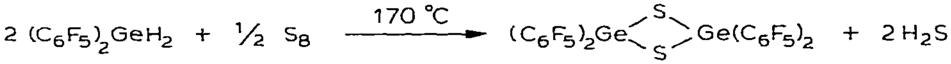
Hydrolysis of $(R_3Sn)_3Pr \cdot DME$ at 20°C leads to $(R_3Sn)_2O$, $Pr(OH)_3$, and the unexpected product R_3SnMe (85%), which arises from cleavage of an Me—O bond of dimethoxyethane. This indicates that dimethoxyethane plays an important role in the complex formation and that the product has a more complex structure than that shown above.

When triphenylgermane is used as a starting hydride, cleavage of the solvent occurs even during the synthesis of the polynuclear compound. In this case the elemental composition and the IR spectrum of the product are consistent with the formula $(Ph_3Ge)_2Pr(OCH_2CH_2OMe)$ [27].

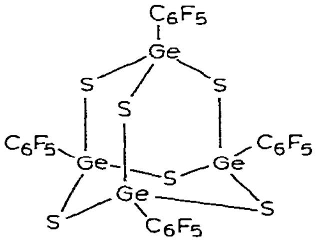
2. Insertion of free heteroelement and low-valent complexes of metals into metal—metal bonds

A convenient method of enlarging heteroelemental chains involves an insertion reaction of elemental chalcogens into metal—hydrogen and metal—metal bonds. This method was first used by Gilman and his coworkers and independently by Schumann, Schmidt and their co-workers for the preparation of organoelement chalcogenides of lithium, R_3MXLi (M = Si, Ge, Sn, Pb; X = S, Se, Te) [28—30]. We later demonstrated that chalcogens also insert readily into Si—H, Ge—H and Sn—H [31,32], Sn—Sn [31], Ge—Hg [22] and Ge—Cd [34] bonds, and give products with the corresponding groupings M—X—H (X = S, Se, Te), SnXSn, Ge—X—Hg—Ge, Ge—X—Cd—Ge (X = S, Se).

The dihydride $(C_6F_5)_2GeH_2$ reacts with sulphur to give a cyclic disulphide and hydrogen sulphide, which are the products of disproportionation of an intermediate dithiol $(C_6F_5)_2Ge(SH)_2$ [35].



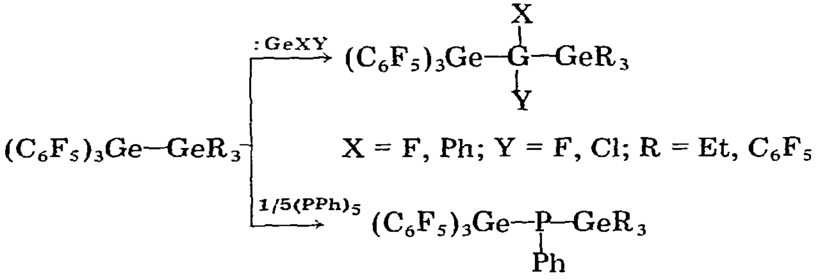
The trihydride $C_6F_5GeH_3$ under similar conditions forms a product with an adamantane structure:



The Ge—Ge bond in hexaorganodigermane is known to show a high chemical stability and in particular it is not cleaved by sulphur. However this bond is more active in pentafluorophenyldigermanes, $(C_6F_5)_3GeGeR_3$ [36,37], and reactions of such digermanes with sulphur or selenium in THF solution take place at 20—100°C to give trinuclear chalcogenides $(C_6F_5)_3GeXGeR_3$.

Sulphur and selenium can also insert into binuclear groupings containing transition metals. For example, interaction of Cp_2VMR_3 (M = Ge, Sn) with chalcogens in hexane solution at 20°C gives $Cp_2V{-}X{-}MR_3$ (X = S, Se) [8]. However, the germanium—platinum bond is stable towards sulphur [38]. From a comparison of the available data it can be concluded that these reactions, which can be regarded as reductive addition reactions, proceed readily in the case of easily oxidizable substances having low ionization potentials and slowly in the case of difficultly oxidizable substances with high ionization potentials.

In collaboration with J. Satgé and his coworkers we found that phenylphosphylene and compounds of divalent germanium (difluorogermylene and phenylchlorogermylene) can, like chalcogens, insert into the Ge—Ge bond in pentafluorophenyldigermanes [39]:



$$(C_6F_5)_3Ge{-}GeR_3 \xrightarrow{:GeXY} (C_6F_5)_3Ge{-}\overset{X}{\underset{Y}{Ge}}{-}GeR_3$$

$$X = F, Ph;\ Y = F, Cl;\ R = Et, C_6F_5$$

$$(C_6F_5)_3Ge{-}GeR_3 \xrightarrow{1/5(PPh)_5} (C_6F_5)_3Ge{-}\underset{Ph}{P}{-}GeR_3$$

The trigermanes formed in the first reaction are fairly stable, and can be isolated in 50—70% yield. The thermal decomposition of the trigermanes produces germylgermylenes $(C_6F_5)_3Ge{-}\ddot{G}eX$, which were identified as their adducts with dimethylbutadiene.

The oxidative addition reactions of zero-valent or low-valent complexes of transition metals with C—X (X = halogen, metal), H—Hal and other bonds are well known, but M—H and M—M bonds are no less reactive in such processes. Insertion of the triphenylphosphine complexes of nickel, platinum, palladium into the Ge—H bond of tris(pentafluorophenyl)germane in benzene at room temperature is complete in 1 hour [24]

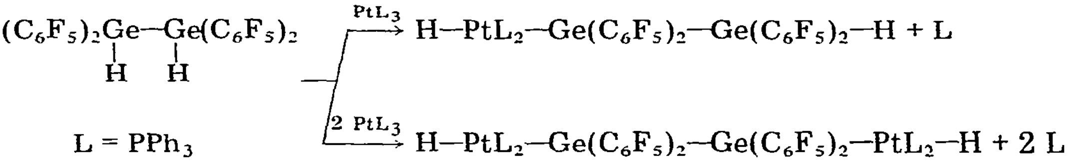
$$(C_6F_5)_3GeH + ML_n \xrightarrow[20^\circ C]{} (C_6F_5)_3Ge{-}ML_2{-}H + (n-2)L$$

$$M = Ni, Pd, Pt;\ L = PPh_3;\ n = 3, 4$$

After recrystallization from benzene the products are isolated as colourless or slightly-coloured microcrystalline powders. Their reactivities and, in particular, their sensitivity towards oxygen, increase in the order Pt < Pd < Ni. In comparison with its nonfluorinated analogues [40,41], the platinum complex $(C_6F_5)_3GePt(PPh_3)_2H$ is considerably less reactive. Its reaction with HCl in refluxing benzene gives tris(pentafluorophenyl)germane, Cl_2PtL_2 and hydrogen. Titration with bromide leads to Br_2PtL_2, $(C_6F_5)_3GeBr$, and a small amount of $(C_6F_5)_3GePtL_2Br$.

The course of the reaction of $Pt(PPh_3)_3$ with dihydrogermanes depends on the position of the Ge—H bonds in the germane molecule. Bis(pentafluorophenyl)germane adds only one equivalent of platinum, while 1,2-dihydro-1,1,2,2-tetrakis(pentafluorphenyl)digermane gives the monoplatinum product

$H{-}PtL_2{-}Ge(C_6F_5)_2{-}Ge(C_6F_5)_2{-}H$ or the diplatinum product $H{-}PtL_2{-}Ge(C_6F_5)_2{-}Ge(C_6F_5)_2{-}PtL_2{-}H$ depending on the reagent ratio. Monitoring the reaction by IR-spectroscopy and solid-liquid chromatography [42] shows that the insertion of the first PtL_2 moiety occurs a little faster than that of the second.



$$(C_6F_5)_2\underset{H}{Ge}{-}\underset{H}{Ge}(C_6F_5)_2 \xrightarrow{PtL_3} H{-}PtL_2{-}Ge(C_6F_5)_2{-}Ge(C_6F_5)_2{-}H + L$$

$$L = PPh_3 \qquad \xrightarrow{2\ PtL_3} H{-}PtL_2{-}Ge(C_6F_5)_2{-}Ge(C_6F_5)_2{-}PtL_2{-}H + 2\ L$$

In the reaction of tris(triphenylphosphine)platinum with $(C_6F_5)_3GeXH$ ($X =$ S, Se) the platinum complex inserts only into the X—H bond; the Ge—X linkage remaining unaffected [24].

$$(C_6F_5)_3GeXH + PtL_3 \rightarrow (C_6F_5)_3Ge{-}X{-}PtL_2{-}H + L \qquad X = S, Se$$

In addition to the platinum hydride these reactions give the 5-nuclear derivatives $(C_6F_5)_3Ge{-}X{-}PtL_2{-}X{-}Ge(C_6F_5)_3$ in 5—10% yield.

In contrast to organometallic chalcogenides trinuclear derivatives of zinc, cadmium, and mercury undergo insertion of ML_n ($M =$ Ni, Pd, Pt) complexes into the metal—metal bond to form the corresponding polymetallic chains [38,43—46]:

$$R_3Ge{-}M{-}GeR_3 + M'(PPh_3)_n \rightarrow R_3Ge{-}M{-}M'(PPh_3)_2{-}GeR_3 + (n-2)PPh_3$$

$M = Zn;\quad R = C_6F_5;\quad M' = Pt;\quad n = 3$
$M = Cd;\quad R = C_6F_5, Ph;\quad M' = Pt, Pd;\quad n = 3$
$M = Hg;\quad R = C_6F_5;\quad M' = Pt, Pd;\quad n = 3$
$M = Hg;\quad R = Ph;\quad M' = Ni;\quad n = 4$

$$(C_6F_5)_3Sn{-}Hg{-}M(C_6F_5)_3 + Pt(PPh_3)_3 \rightarrow (C_6F_5)_3Sn{-}Pt(PPh_3)_2{-}Hg{-}M(C_6F_5)_3 + PPh_3$$

$$M = Ge, Sn$$

The rates of the reactions and the stabilities of the polynuclear compounds formed are determined to a considerable extent by the nature of the organic group R. Pentafluorophenyl derivatives react more readily (at 20°C) in benzene solution and give chemically and thermally more stable products. Compounds containing ethyl radicals, $(Et_3Ge)_2Hg$ and $(Et_3Ge)_2Cd$, add platinum and palladium as readily as their C_6F_5-analogues but the polynuclear products are so unstable that they decompose completely during the reaction.

If the starting compound contains M—Hg and Hg—C bonds insertion of PtL_3 occurs only into the M—M bond [38].

$$(C_6F_5)_3GeHgEt + Pt(PPh_3)_3 \rightarrow (C_6F_5)_3Ge{-}Pt(PPh_3)_2{-}Hg{-}Et + PPh_3$$

An X-ray structural study of the insertion product from $(C_6F_5)_3SnHgGe(C_6F_5)_3$ and a platinum complex has shown that it has a planar-square structure (Fig. 2) [46], with the phosphine ligands *cis* to each other. Contamination by *trans*-isomer and by an isomer containing the linkage Ge—Pt—Hg—Sn is shown by the X-ray analysis and ^{31}P NMR spectroscopy to be not more than 10—20%.

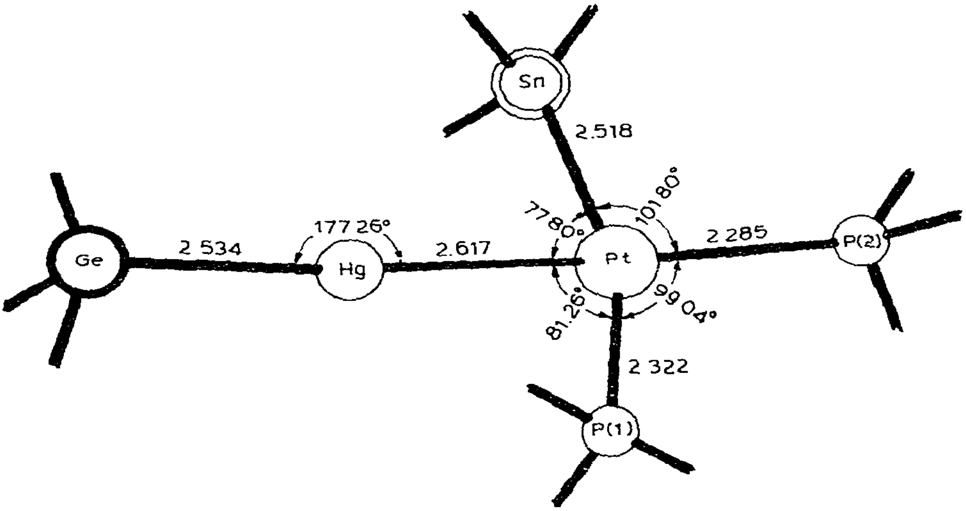


Fig. 2. Polymetallic backbone of $(C_6F_5)_3GeHgPt(PPh_3)_2Sn(C_6F_5)_3$.

All the tetranuclear products prepared have similar structures. The Hg—Pt (2.617 Å) and Sn—Pt (2.518 Å) bond lengths are a little shorter than the sums of the covalent radii of the relevant atoms (2.73 Å and 2.83 Å) while the Ge—Hg (2.53 Å) bond length is almost equal to the sum of the covalent radii of mercury and germanium. It is interesting that the Ge—Hg bond length in $[(C_6F_5)_3Ge]_2Hg$ is significantly shorter (2.483 Å) [47].

The reactivity of $(C_6F_5)_3GeHgPt(PPh_3)_2Ge(C_6F_5)_3$ is illustrated by the reactions shown below.

$$\mathrm{R_3GeHgPt(PPh_3)_2GeR_3} \begin{cases} \xrightarrow{h\nu} \mathrm{R_3GeH + R_3GeGeR_3 + Hg + [R_3GePt(PPh_3)_2]_{\mathit{n}}} \\ \xrightarrow[20^\circ C]{Br_2} \mathrm{HgBr_2 + R_3GeBr + R_3GePtL_2Br} \\ \xrightarrow[\text{benzene } 80^\circ C]{HCl} \mathrm{Hg + R_3GeCl + R_3GeH + R_3GePtL_2H} \end{cases}$$

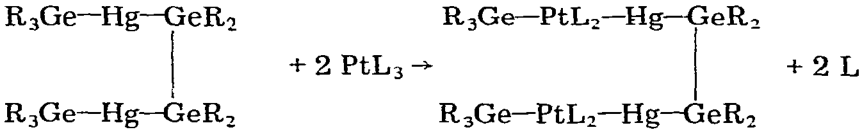
$R = C_6F_5$

The complex does not react at room temperature with oxygen, H_2, sulphur, Ph_3SiH, CF_3COOH, or methanolic KOH. Prolonged refluxing in benzene in a hydrogen atmosphere leads to partial decomposition of the complex and the formation of mercury, R_3GeH, R_3GePtL_2H, and some unidentified products [38].

The pentafluorophenyl derivatives of cadmium and especially of zinc are less stable; like all phenyl derivatives they are oxidized in air.

The reactions of the phenyl complexes $Ph_3GeHgPtL_2GePh_3$ and $Ph_3GeHgNiL_2GePh_3$ with hydrogen chloride occur in toluene at 20°C and give complete cleavage of the metal—metal bonds. The products are hydrogen, triphenylgermane, and $L_2MCl_2HgCl_2$ (M = Ni) [44,45]. In addition, dearylation of Ph_3Ge groups occurs, giving germanium tetrachloride in the products. The metal—metal bonds in $Ph_3GeCdML_2GePh_3$ (M = Ni, Pt) can also be cleaved at 60°C by acetic acid.

A distinctive feature of all the studied reactions of trinuclear compounds $R_3M—M'—MR_3$ with triphenylphosphine complexes of Ni, Pd, Pt is the formation of only tetranuclear products. The insertion of NiL_2, PdL_2 or PtL_2 moieties into one of the M—M′ bonds completely deactivates the second M—M′ bond in this compound towards the starting triphenylphosphine complexes. However, if the Ge—Hg bonds in the molecule of the polynuclear compound are separated by a Ge—Ge linkage, the insertion of the second equivalent of platinum occurs as readily as the first [21].

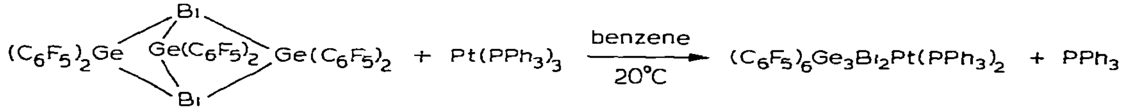


$$\begin{array}{l} R_3Ge—Hg—GeR_2 \\ \qquad\qquad\quad | \\ R_3Ge—Hg—GeR_2 \end{array} + 2\,PtL_3 \rightarrow \begin{array}{l} R_3Ge—PtL_2—Hg—GeR_2 \\ \qquad\qquad\qquad\qquad\quad | \\ R_3Ge—PtL_2—Hg—GeR_2 \end{array} + 2\,L$$

$R = C_6F_5 \quad L = PPh_3$

The octanuclear product of this reaction was isolated from benzene as a light-yellow micro-crystalline solid, stable in the air; *T* decomp. 206—211°C. To our knowledge, this compound possesses the longest known chain formed by atoms of three different heteroelements. In the equation is shown one of the three possible structural isomers. (Insertion of PtL_2 into the Ge—Ge bond under our conditions was ruled out by control experiments).

Interaction of $Pt(PPh_3)_3$ with pentafluorophenyl germylbismuth compounds depends on the structures of the latter [20]. The binuclear derivative $(C_6F_5)_3$-$GeBiEt_2$ does not oxidize tris(triphenylphosphine)platinum. Digermylbismuth $[(C_6F_5)_3Ge]_2BiEt$ adds platinum slowly at 20°C but the product is apparently unstable, and the expected Ge—Pr—Bi compound has not been isolated from the complex mixture of products. In contrast, the dibismuth compound $[(C_6F_5)_2Ge]_3$-Bi_2 readily reacts with $Pt(PPh_3)_3$ to give an unusual 6-nuclear derivative of the composition $(C_6F_5)_6Ge_3Bi_2Pt(PPh_3)_2$.



X-ray structural analysis of the product showed that the heavy-atom skeleton consists of a non-planar platinum-bismuth-germanium 5-membered ring with a bridging $(C_6F_5)_2Ge$ group (Fig. 3) [20]. The platinum-containing fragment of the molecule has the square planar configuration usual for tetracoordinated platinum. The angles GePtBi, BiPtP, PPtP, PPtGe are respectively 90.3, 80.1, 94.4, and 95.4°. The angles at Ge atoms differ significantly from the tetrahedral angle. One of them (PtGeBi) exceeds the tetrahedral angle by ~16°, and two others have values of 98.5 and 98.3°. These deviations and also a large GeBiPt angle (100.8, 100.6°) are associated with some strain in the skeleton of the molecule which apparently influences the chemical properties.

Deep-cherry crystals of this product are very soluble in THF, benzene and other solvents. In the crystalline state $(C_6F_5)_6Ge_3Bi_2Pt(PPh_3)_2$ is stable in air

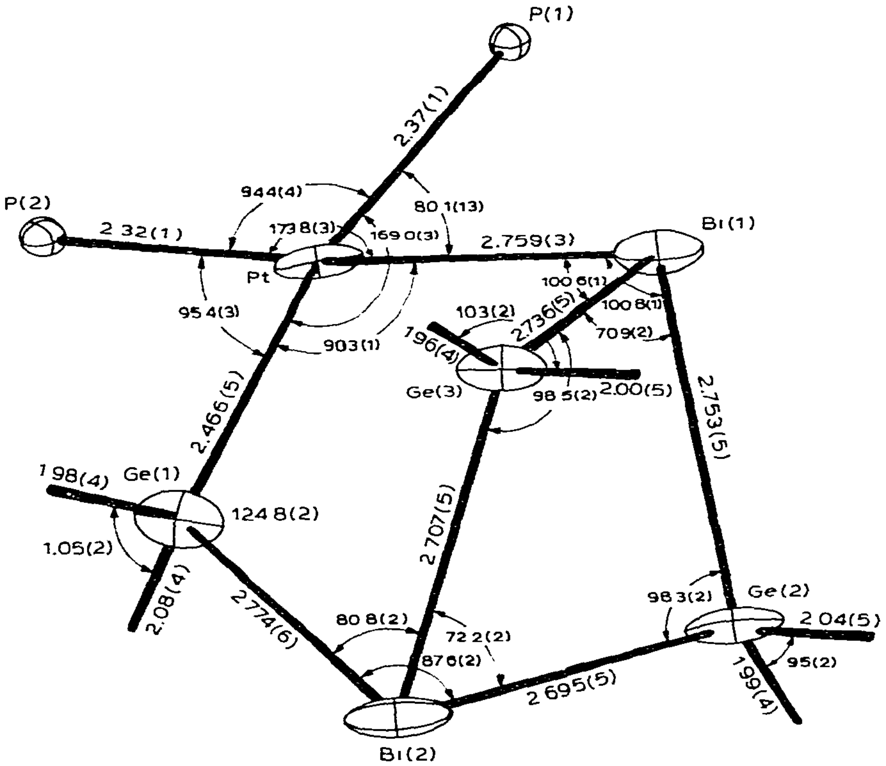
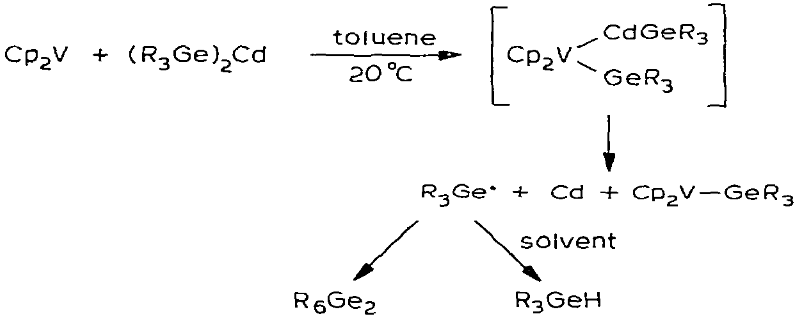


Fig. 3. Molecular geometry and labelling of heavy atoms in the $(C_6F_5)_6Ge_3Bi_2Pt(PPh_3)_2$ molecule.

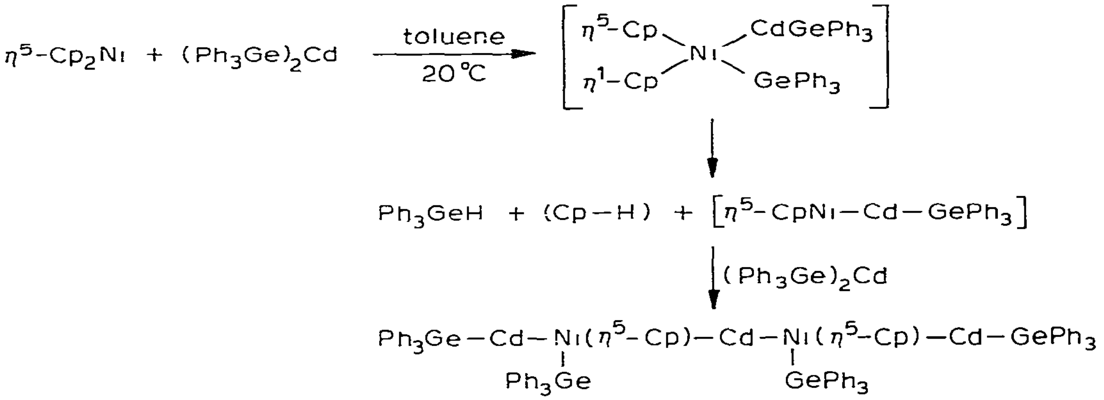
at room temperature for a few days. Our attempts to introduce a second $Pt(PPh_3)_2$ moiety into one of remaining Ge—Bi bonds in the complex have given only intractable mixtures containing more than ten products.

Ready reaction with compounds containing metal—metal bonds is not confined to zero-valent triphenylphosphine complexes of nickel, palladium and platinum. Cyclopentadienyl derivatives of transition metals in low-valent states show similar behaviour. Thus, the interaction of η^5-Cp_2V with bis(triethylgermyl)cadmium and its phenyl analogue is accompanied by an increase in the valency of vanadium [48]. It is assumed that the first step of the reaction is the insertion of vanadocene into the Ge—Cd bond with formation of a 4-nuclear intermediate. Decomposition of the intermediate is accompanied by the reduction of vanadium to the 3-valent state and formation of $R_3Ge\cdot$ radicals.



The yield of germylvanadium products reaches 90%. However, we cannot exclude an alternative mechanism for the reaction which involves ionic intermediates and we are studying this problem further.

The reaction of η^5-Cp_2Ni is much more complex and leads to the destruction of the "cene" - structure [49]. A 9-nuclear compound, containing a branched chain of atoms of germanium. cadmium and nickel, has been isolated as a final product of the reaction of bis(triphenylgermyl)cadmium with Cp_2Ni. The route seems to be the following:



The red crystals of the product are oxidized rapidly in air, and decompose at 190—194°C. The compound is very soluble in aromatic solvents and insoluble in hexane. In Fig. 4 is shown the heteroatomic backbone of this complex as determined by X-ray analysis [49].

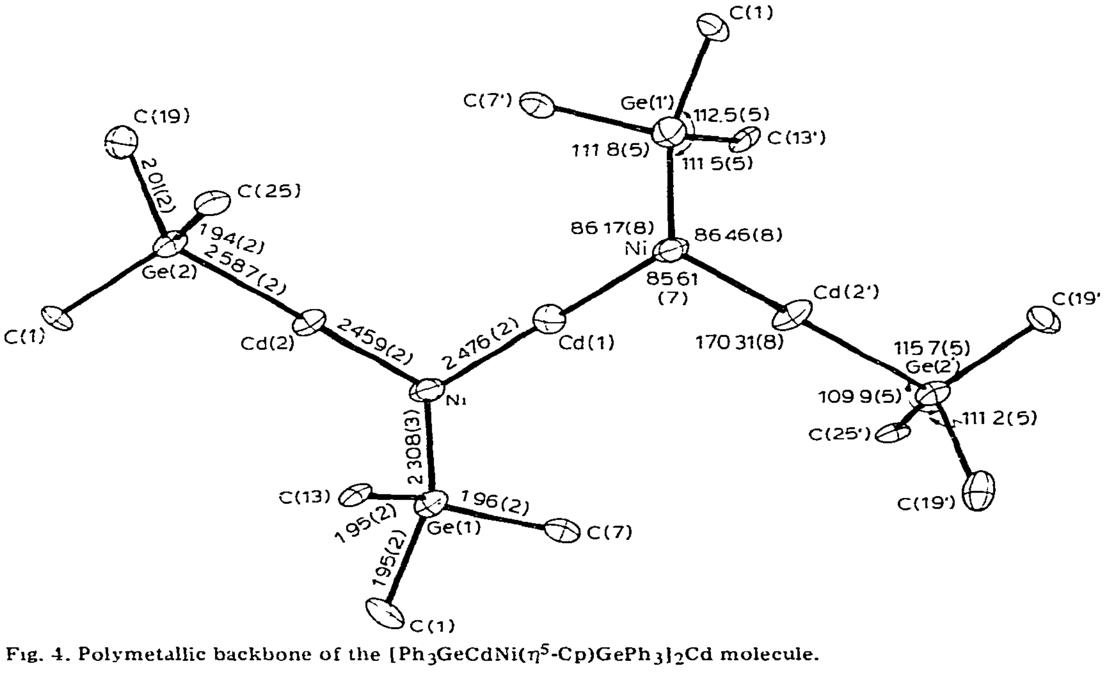


Fig. 4. Polymetallic backbone of the $[Ph_3GeCdNi(\eta^5\text{-}Cp)GePh_3]_2Cd$ molecule.

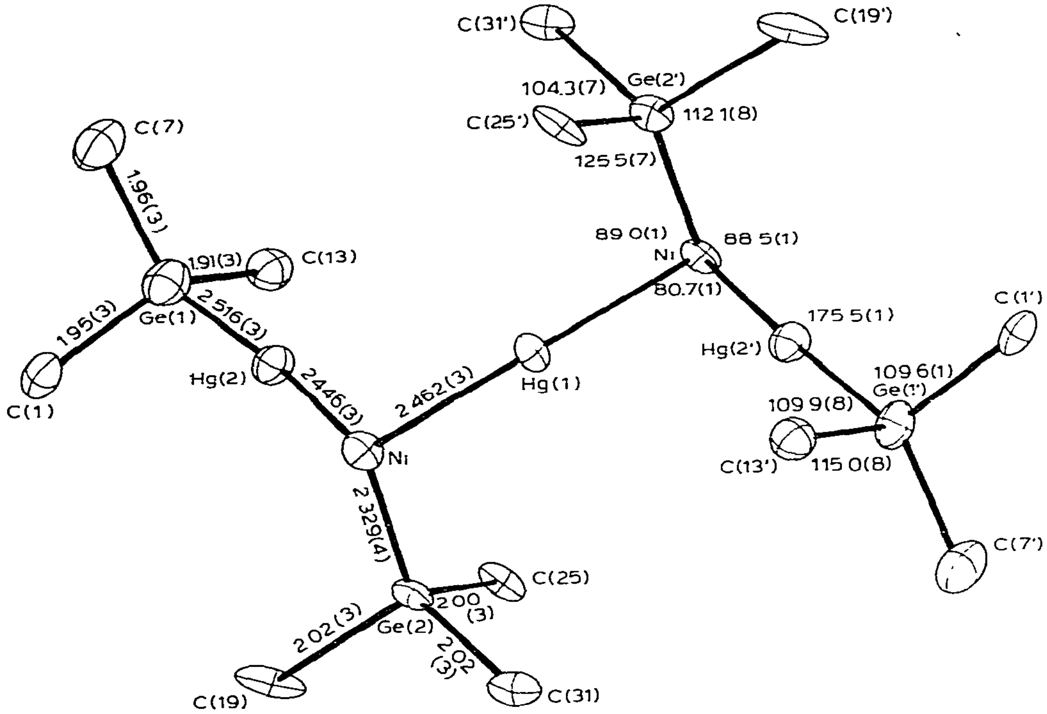


Fig. 5. Polymetallic backbone of the [Ph$_3$GeHgNi(η^5-Cp)GePh$_3$]$_2$Cd molecule.

The mercury analogue was obtained in 30% yield from the reaction of nickelocene with (Ph$_3$Ge)$_2$Hg; it has similar physical and chemical properties and an identical structure (Fig. 5) [50].

Determination of the structures of some of the polynuclear compounds we prepared permits comparison of the values of the atomic radii of the metals in the compounds with the covalent radii of the same metals given by Pauling (Table 1).

It can be seen from Table 1 that the derived values of r for all the atoms, except Bi and Ge are less than the corresponding Pauling covalent radii; that is, the M—M′ bond lengths in the compounds obtained are in almost all cases less

TABLE 1

VALUES OF SINGLE-BONDED COVALENT RADII (r) DERIVED FROM THE STRUCTURES SHOWN ABOVE AND THE CORRESPONDING RADII GIVEN BY PAULING [51]

	Found r (Å)	Pauling r (Å)
Cd	1.37	1.38
Hg	1.29	1.39
Ge	1.22	1.22
Bi	1.51	1.51
Ni	1.11	1.15
Pt	1.25	1.30

than the sums of the covalent radii of M and M′. This gives information about the strength of the bonds and also points to participation of additional factors besides electrons of σ-bonds in the formation of molecules of polynuclear compounds.

3. Transmetallation reactions

Transmetallation reactions provide a convenient synthetic pathway to polynuclear derivatives of many non-transition metals [2,22,52—54]. Organomercurials of the type $(R_3M)_2Hg$ are widely used as starting materials. These reactions usually lead to the formation of metallic mercury and a new polynuclear compound $(R_3M)_nM'$.

Interaction of $[(C_6F_5)_3Ge]_2Hg$ with thallium proceeds in a different way. When a mixture of the reagents is shaken at 95°C in dimethoxyethane, along with mercury a compound is formed which has an elemental analysis and an IR spectrum consistent with the formulation $\{[(C_6F_5)_3Ge]_3Hg\}Tl \cdot 1.5\ DME$ [55]. The structure is apparently similar to that of the lithium intermediate $(R_3M)_3HgLi$ formed in the reactions of $(R_3Si)_2Hg$ and $(R_3Ge)_2Hg$ with lithium [56,57].

$$3[(C_6F_5)_3Ge]_2Hg + 2\ Tl \xrightarrow[95^\circ C]{DME} 2\{[(C_6F_5)_3Ge]_3Hg\}Tl \cdot 1.5\ DME + Hg$$

The product is very soluble in DME and THF, and in hot toluene and benzene. In the crystalline state it is stable in air for a few days. Its structure has been confirmed by its reactions with hydrogen chloride, $(C_6F_5)_3GeBr$, and benzoyl peroxide. In all cases the reaction gives a thallium salt and an equivalent amount of bis[tris(pentafluorophenyl)germyl]mercury:

$$\begin{tikzcd}
 & (C_6F_5)_3GeH + [(C_6F_5)_3Ge]_2Hg + TlCl \\
\{[(C_6F_5)_3Ge]_3Hg\}Tl \arrow[ur, "HCl"] \arrow[r, "(C_6F_5)_3GeBr"] \arrow[dr, "(PhCOO)_2"'] & (C_6F_5)_3GeGe(C_6F_5)_3 + [(C_6F_5)_3Ge]_2Hg + TlBr \\
 & (C_6F_5)_3GeOCOPh + [(C_6F_5)_3Ge]_2Hg + TlOCOPh
\end{tikzcd}$$

The reaction with $HgCl_2$ gives, in addition to TlCl, the germylmercury product and $(C_6F_5)_3GeCl$, Hg_2Cl_2 and a small amount of metallic mercury.

Interaction of the thallium complex with dibenzenechromium iodide leads to the displacement of Tl^+ cation by the cation of dibenzenechromium, with an increase of the charge of the mercury anion to —2.

$$4\{[(C_6F_5)_3Ge]_3Hg\}Tl + 6(C_6H_6)_2CrI \xrightarrow[60^\circ C]{THF} 4\ TlI + Hg +$$
$$3\{[(C_6F_5)_3Ge]_4Hg\}^{2-}[Cr(C_6H_6)_2]_2^+ + [RI]$$

The chromium-mercury complex is stable in air like most $(C_6H_6)_2Cr^+$ salts, but in contrast to the latter it is very soluble in polar and aromatic solvents. The ESR spectrum (g_i 1.986, a_H 3.5 G, a_{Cr} 53.18 G) is characteristic of $(C_6H_6)_2Cr^+$.

Compounds containing similar germylmercury anions are formed in the reaction of $[(C_6F_5)_3Ge]_2Hg$ with rare-earth metals in DME [25,58—61]. The elemental composition of the polynuclear products of these reactions is consistent with the formulation $[(C_6F_5)_3Ge]_7Hg_2Ln \cdot 3\ DME$

$$7[(C_6F_5)_3Ge]_2Hg + 2\ Ln \rightarrow 2[(C_6F_5)_3Ge]_7Hg_2Ln \cdot 3\ DME + 3\ Hg$$

$$Ln = Pr, Nd, Ho$$

The products are slightly coloured, very soluble in DME and THF, and insoluble in non-polar solvents. They melt with decomposition above 200°C and are extremely sensitive to traces of moisture. Preliminary investigations indicated the formula $[(C_6F_5)_3Ge]_2Hg \cdot Ln[Ge(C_5F_5)_3]_3$ [58—60], but more detailed study of the elemental composition, infrared spectra and chemical properties of the complexes revealed that they contain no direct Ge—Ln bonds, and instead consist of the cation Ln^{3+} and two mercurate anions [25,61].

$$\{[(C_6F_5)_3Ge]_3Hg^- \qquad Pr^{3+} \qquad \overset{2-}{Hg}[Ge(C_6F_5)_3]_4\}$$

It is noteworthy that attempts to prepare derivatives with germanium—lanthanide bonds by the hydride method from $(C_6F_5)_3GeH$ and $(R_2N)_3Ln$ or $(RO)_3Ln$ were unsuccessful. In all cases formation of fluoride ion along with R_2NH (or ROH) was observed; the intermediates containing Ge—Ln bonds which are probably formed in the reactions dissociate immediately with the formation of the highly reactive anions $(C_6F_5)_3Ge^-$, which then attack C_6F_5 rings to displace fluoride ions.

Formation of $(C_6F_5)_3Ge^-$ anions can also be postulated in the reactions of $[(C_6F_5)_3Ge]_2Hg$ with lanthanides and thallium [25,55], but in these cases they are stabilized by addition to the initial germylmercury to give the less active R_3Hg^- and R_4Hg^{2-} anions.

Bis[tris(pentafluorophenyl)stannyl]mercury reacts with lanthanides more readily (20°C, 1 h) and gives products with similar physical and chemical properties [25,61], but the exact structures of these compounds are not fully established. The contents of $(C_6F_5)_3Sn$ groups, Hg atoms and lanthanide atoms suggest that there are Sn—Ln σ-bonds in these compounds but the other data do not confirm that. The reactions of the germylpraseodymium derivative, studied as representative of the polynuclear lanthanide complexes, confirm the ionic nature of the compounds. An equimolar amount of hydrogen chloride destroys one of mercurate anions. Reaction with three equivalents of HCl leads to destruction of both mercurate anions but the germylmercury linkages in the compound are not effected. Reaction with an excess of hydrogen chloride leads to cleavage of all the metal—metal bonds. In all the reactions the yields of the products reached 80—100%.

$$[(C_6F_5)_3Ge]_7Hg_2Pr \xrightarrow[20^\circ C]{THF} \begin{cases} \xrightarrow{HCl} (C_6F_5)_3GeH + [(C_6F_5)_3Ge]_2Hg + ClPrHg[Ge(C_6F_5)]_4 \\ \xrightarrow[3\ HCl]{} 3(C_6F_5)_3GeH + 2[(C_6F_5)_3Ge]_2Hg + PrCl_3 \\ \xrightarrow{HCl\ (excess)} 5(C_6F_5)_5GeH + 2(C_6F_5)_3GeCl + PrCl_3 + 2\ Hg \end{cases}$$

When the chloropraseodymium complex formed in the reaction with an equimolar amount of HCl is treated with two additional equivalents of hydrogen chloride it gives tris(pentafluorophenyl)germane, $[(C_6F_5)_3Ge]_2Hg$ and $PrCl_3$. A bromopraseodymium complex has been isolated from the reaction of $[(C_6F_5)_3Ge]_7Hg_2Pr$ with tris(pentafluorophenyl)germanium bromide.

$$[(C_6F_5)_3Ge]_7Hg_2Pr + (C_6F_5)_3GeBr \xrightarrow[20^\circ C]{DME}$$

$$BrPrHg[Ge(C_6F_5)_3]_4 \cdot 3\ DME + (C_6F_5)_3GeGe(C_6F_5)_3 + [(C_6F_5)_3Ge]_2Hg$$

The observed stabilization of $(C_6F_5)_3Ge^-$ anions by the addition to $[(C_6F_5)_3Ge]_2Hg$ enabled us to use the hydride method for the preparation of a polynuclear pentafluorophenylpraseodymium derivative [25,61].

$$Cl_2PrO\text{-}t\text{-}Bu + (C_6F_5)_3GeH + [(C_6F_5)_3Ge]_2Hg \rightarrow t\text{-}BuOH + Cl_2PrHg[Ge(C_6F_5)_3]_2$$

Carrying out this reaction in the presence of germylmercury led to complete suppression of the side reactions involving nucleophilic substitution of fluorine atoms in pentafluorophenyl rings, and the yield of the complex reached 80%.

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