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# SYNTHESIS OF STANNYL- AND GERMYL-MERCURIC DERIVATIVES OF PLATINUM AND PALLADIUM

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## Summary

$(Ph_3P)_2Pt$ or $(Ph_3P)_2Pd$ insertion into the mercury—germanium or —tin bond was achieved to afford new chains of four metal atoms. The starting compounds were $(C_6F_5)_3M$—Hg—R, M = Ge, Sn; R = $C_2H_5$, $Ge(C_6F_5)_3$, $Sn(C_6F_5)_3$. The pentafluorophenyl derivatives prepared are very stable in air and acids. Photolysis of these compounds in benzene or boiling in trifluoroacetic acid results in demercuration.

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There has recently been considerable interest in organopolymetallic compounds with chains of transition and non-transition metals. It is considered a reasonable direction for the search for the high-temperature superconductors [1,2]. In this paper we report the novel preparation of compounds with three- or four-atom chains of different metals.

Previously, we have shown that zerovalent platinum metal complexes may insert into the mercury—carbon and mercury—halogen bonds in various organomercurials [3—5]. The intermediates involved with a Hg—Pt or Hg—Pd bond are often of low stability and undergo demercuration in the course of the reaction. Pentafluorophenyl groups, however, can strongly stabilize the different kinds of organometallics which incorporate the metal—metal bonds [5—8]. It was reasonable to suppose an enhanced stability for the products of the reaction between the platinum(0) or palladium(0) complexes and organomercurials of the type $[(C_6F_5)_3M]_2Hg$. We have now found that these reactions proceed easily in benzene solution at room temperature and may be generalized as follows:

$$(C_6F_5)_3M'\text{—Hg—}M'(C_6F_5)_3 + M(PPh_3)_n \rightarrow$$

$$(C_6F_5)_3M'\text{—Hg—}M(PPh_3)_2\text{—}M'(C_6F_5)_3$$

(Ia—Ic)

a, M = Pt, M′ = Ge; b, M = Pd, M′ = Ge; c, M = Pt, M′ = Sn

TABLE 1

PROPERTIES AND ANALYTICAL DATA OF THE OLIGOMETALLIC COMPOUNDS PREPARED [a]

| Compound | | Yield (%) | M.p. (°C) | Colour | Analysis found (calcd.) (%) | | |
|---|---|---|---|---|---|---|---|
| | | | | | C | H | F |
| Ia | $(C_6F_5)_3GeHgPtL_2Ge(C_6F_5)_3 \cdot 2C_6H_6$ | 80 | 243—244 | white | 45.59<br>(45.37) | 1.89<br>(1.90) | *b* |
| Ib | $(C_6F_5)_3GeHgPdL_2Ge(C_6F_5)_3$ | 92 | 134 (dec.) | green-yellow | 43.82<br>(43.70) | 1.66<br>(1.53) | 29.02<br>(28.80) |
| Ic | $(C_6F_5)_3SnHgPtL_2Sn(C_6F_5)_3 \cdot C_6H_6$ | 84 | 170—171 | light yellow | 42.32<br>(41.89) | 1.71<br>(1.62) | 25.15<br>(25.47) |
| II | $(C_6F_5)_3GeHgPtL_2Sn(C_6F_5)_3 \cdot 2C_6H_6$ | 100 | 216—218 | white | 44.61<br>(44.45) | 1.86<br>(1.86) | 25.74<br>(25.11) |
| III | $(C_6F_5)_3GePtL_2HgC_2H_5 \cdot C_6H_6$ | 76 | 153—155 | light yellow | 46.42<br>(46.51) | 2.65<br>(2.58) | 17.83<br>(17.80) |

[a] All preparations were performed under argon. Starting germyl- and stannyl-mercurials were obtained as described previously [7,8]. L = $PPh_3$. [b] Found: P 2.90 %, calcd.: P 2.81 %.

The reaction of $(Ph_3P)_3Pt$ with the unsymmetrical compounds $(C_6F_5)_3$-Ge—Hg—Sn$(C_6F_5)_3$ and $(C_6F_5)_3$Ge—Hg—$C_2H_5$ follows the same pattern. The structure of the products is under investigation, and should give information concerning the regioselectivity of insertion. Attempts to introduce the second $L_2Pt$ moiety to prepare $(C_6F_5)_3$Ge—$PtL_2$—Hg—$PtL_2$—Ge$(C_6F_5)_3$ have so far failed. The interaction between $(Ph_3P)_3Pt$ and bis(triethylgermanium)mercury, as expected, resulted in the immediate demercuration of the unstable organoplatinummercurial.

Ia—Ic, II and III are crystalline solids which are quite stable in air and acids. They can be purified by chromatography on silica gel or crystallization. Benzene, tetrahydrofurane or ethyl acetate are the best solvents for them, solubility in hexane is very low. These oligometallic chains resist heating in $CF_3COOH$ for a short period of time. However, a longer boiling in this acid (4 h) or UV irradiation in benzene (30 min) broke up the substances and separated the metallic mercury completely. See Table 1 for properties and analytical data of compounds I—III.

All organooligometallics described here are likely to have a planar square arrangement of four groups around the platinum metal with a *cis* configuration of the phosphine ligands, like $CF_3$Hg—$PtL_2$—$CF_3$ [9]. To the best of our knowledge, Ib appears to be the first stable compound with a Hg—Pd bond.

IR spectra of Ia—Ic, II and III exhibit the absorption bands characteristic of $C_6F_5$ groups [10] as well as those near 700, 540, 525 and 500 nm due to triphenylphosphine ligands. The electronic spectra* show the following UV maxima (in dichloromethane), $\lambda_{max}$ ($\epsilon$): Ia: 218($1.5 \times 10^5$), 239($6.2 \times 10^4$), 266($5.3 \times 10^4$), 321($4.3 \times 10^4$); Ib: 220($1.6 \times 10^5$), 254($9.9 \times 10^4$), 354($2.1 \times 10^4$); Ic: 219($1.4 \times 10^5$), 236($8.7 \times 10^4$), 268($6.1 \times 10^4$), 330($4.2 \times 10^4$).

The absorption bands were not shifted when hexane was used as solvent. The presence of aromatic systems explains the bands below 280 nm [11]. The red-shifted maxima above 300 nm, however, may be connected with the oligometallic chains, as bis(trispentafluorophenyl)stannylmercury which contains a shorter three-atom chain does not have any maximum in this region [8]. Meanwhile, it is known that the absorption in polysilanes is red-shifted as the chain length is increased [12].

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*As studied by Dr. V.A. Kuznetsov.