Journal of Organometallic Chemistry, 111 (1976) C13—C16

Preliminary communication

FURTHER STUDY OF THE REACTION BETWEEN ZEROVALENT PLATINUM COMPLEXES AND ORGANOMERCURIALS: THE SYNTHESIS OF STABLE COMPOUNDS WITH A PLATINUM—MERCURY σ-BOND

V.I. SOKOLOV*, V.V. BASHILOV and O.A. REUTOV
Institute of Organo-Element Compounds, Moscow (U.S.S.R.)
(Received February 10th, 1976)

Summary

Compounds having platinum—mercury σ-bonds are shown to be the first stage product in the reaction between zerovalent platinum complexes and organomercury compounds. These organoplatinummercury compounds were prepared as quite stable substances when perfluorinated groups or steric hindrance near the bimetallic bond were present. The typical reaction for this type of compound is CF_3COOH acidolysis with demercuration.

It was discovered recently [1—3] that zerovalent platinum and palladium complexes react easily with organomercury compounds RHgX or R_2Hg to give σ-derivatives of the divalent metals as final products.

$$L_nM + RHgX \rightarrow L_2MRX + Hg$$

From the very beginning, the bimetallic intermediates were supposed to take part in this reaction [1]. More recently we have described in detail [2] the preparation of one stable compound of this kind starting with $(CF_3)_2Hg$ as the organomercury compound. In the meantime, it was found that organoplatinummercury compounds having a metal-to-metal bond can be isolated in many cases [3], their stability depends dramatically on both electronic and steric factors. In particular, all perfluorinated organomercury compounds used reacted with $(Ph_3P)_3Pt$ to afford quite stable bimetallic compounds.

$$R_fHgX + (Ph_3P)_3Pt \rightarrow R_fHgPt(PPh_3)_2X \quad (X = Hal, R_f)$$

It is likely that a powerful electron-withdrawing group removes the excessive electron density from the metal—metal bond, the stability being increased. The pentafluorophenyl derivative is more stable than the trifluoromethyl one. Unlike the latter it does not liberate metallic mercury on UV irradiation*. The first com-

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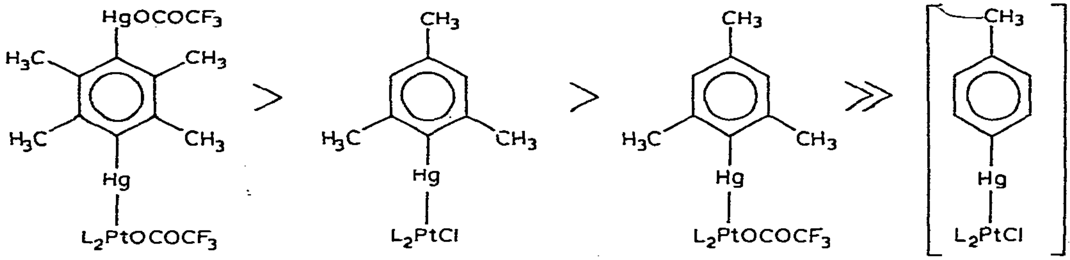
*Study of the photolytic behaviour of these organoplatinummercury compounds will be published in one of the forthcoming communications.

pound with a platinum—mercury σ-bond was apparently obtained by Nyholm and coworkers in 1967 [4]. This was an inorganic complex without any carbon—metal bond. It is less stable than the related fluorinated organometallics.

On the other hand, the stability of these bimetallic compounds can be easily increased by steric crowding near the intermetallic bond as can be seen from comparison of the methyl-substituted aryl series. *p*-Tolylmercuric chloride reacts completely with $(Ph_3P)_3Pt$ giving mercury in several minutes while mesitylmercuric chloride and 1,4-bis(trifluoroacetoxymercuri)durene (II) result in the highly stable platinum—mercury compounds. In the second case, only one bimetallic moiety is formed, perhaps due to the low solubility of a product. The anionic nature has a pronounced effect: mesitylmercuric trifluoroacetate gives metallic mercury, at least, in part. The stability order for bimetallics is as follows:

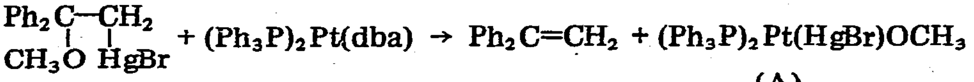


Until now, we did not make a choice between two isomeric structures which differ in the order of the bonding atoms: aryl—Hg—Pt-anion or aryl—Pt—Hg-anion. In general, both can be formed.

All organoplatinummercury compounds thus far prepared undergo the acidolysis with mercury elimination when treated with CF_3COOH. This is a sensitive probe for this type of intermetallic bond.

$$(C_6F_5Hg)C_6F_5Pt(PPh_3)_2 + CF_3COOH \rightarrow C_6F_5(CF_3COO)Pt(PPh_3)_2 + Hg + [C_6F_5H]$$

The products of conjugate mercuration, β-oxymercury compounds behave in a different way. The common reagent $(Ph_3P)_3Pt$ seems to be inappropriate as free triphenylphosphine will promote elimination. To avoid this, we used a mixed zerovalent complex $L_2Pt(dba)$ prepared by the slightly modified procedure [5]. However, the elimination appeared to be the single reaction path. Products were 1,1-diphenylethylene and an inorganic complex with a Pt—Hg bond which we assign structure A or B.



$$\underset{CH_3O\ \ HgBr}{Ph_2C{-}CH_2} + (Ph_3P)_2Pt(dba) \rightarrow Ph_2C{=}CH_2 + (Ph_3P)_2Pt(HgBr)OCH_3$$

(A)

or

$$(Ph_3P)_2Pt(HgOCH_3)Br$$

(B)

This compound is closely related to Nyholm's complex [4]. . imilar elimination was also observed with *trans*-methoxycyclohexylmercuric chloride.

No stable compounds with Pd—Hg bonds have so far been obtained by this method. However, the formation of this type of intermediate even without phosphine ligands, is possible in the course of the reaction of C_6F_5HgCl and $Pd(dba)_2$: after filtration under argon from insoluble solids a clear red-brown solution was treated with excess Ph_3P in benzene. The colour faded immediately and metallic mercury was formed as a grey precipitate at the same time. This means that some labile compound was present in the solution which did not resist Ph_3P addition. The product isolated appeared to be $(Ph_3P)_2PdCl_2$. The following reaction sequence seems to be probable.

$$C_6F_5HgCl + Pd(dba)_2 \rightarrow [C_6F_5HgPdCl,dba] \rightarrow \xrightarrow{Ph_3P} (Ph_3P)_2PdCl_2 + Hg + dba + ?$$

To summarize, the zerovalent complex or the respective species L_2Pt has the properties of a nucleophilic carbenoid as we have mentioned before [2, 3]*. In agreement with this formulation, insertion into the mercury—element bond proceeds more readily with the strongly electrophilic perfluoromercury compounds. The nucleophilic carbenoid nature of these zerovalent reagents is also in accordance with *cis*-configuration for $(CF_3Hg)(CF_3)Pt(PPh_3)_2$** if the transition state is planar, not tetrahedral.

Further aspects of this reaction are now under investigation. A point of special interest is its application in the synthesis of polymetallic chains and rings.

Experimental

All experiments with zerovalent complexes were performed under argon. Bis(pentafluorophenyl)mercury (I) was prepared by the Deacon procedure [8], m.p. 140°C, R_F 0.82, silufol, eluent benzene. 1,4-Bis(trifluoroacetoxymercuri)-durene (II) was obtained as described before [6], m.p. 239°C.

2,2-Diphenyl-2-methoxyethylmercuric bromide (III). 3.6 g (0.02 mol) of 1,1-diphenylethylene and 4.27 g (0.01 mol) of $Hg(OCOCF_3)_2$ were dissolved in 20 ml of absolute CH_3OH. After 1 h 50 ml of an aqueous 2 *M* solution of LiBr was added. The oily precipitate crystallized rapidly, in 84% yield of white crystals of III, m.p. 158.5°C (toluene/hexane 3:1). ^1H-NMR (benzene): δ (CH_3O) 2.96 ppm, δ (CH_2HgBr) 2.44 ppm, $J(^1H—^{199}Hg)$ 198.0 Hz.

Tris(triphenylphosphine)platinum (IV). IV was prepared as described in ref. 9 in 85% yield after precipitation from benzene with an equal volume of ethanol, m.p. 125-130°C (dec.).

Dibenzylideneacetonebis(triphenylphosphine)platinum (V). IV and dba (1:5 in moles) were dissolved in the mixture hexane/benzene (2:1). On cooling, the greenish-yellow crystals separated, m.p. 187°C, lit. [5] 188—190°C. Found: C, 66.54; H, 4.68; P,6.52; Pt, 20.55. $C_{53}H_{44}OP_2Pt$ calcd.: C, 66.73; H, 4.65; P, 6.49; Pt, 20.45%.

Pentafluorophenylmercuribis(triphenylphosphine)pentafluorophenylplatinum (VI). 0.27 g (0.0005 mol) of I and 0.49 g (0.0005 mol) of IV were jointly dis-

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*The carbenoid character of $(Ph_3P)_2Pt$ reactivity was recognised by Nefedov and Manakov in 1966 [7].

**As determined by Prof. Yu.T. Struchkov in an X-ray study of the acetone solvate.

solved in 20 ml of benzene. In several minutes the orange colour of the solution faded. The solvent was evaporated in vacuo and the residue was thoroughly washed with hexane to give 0.55 g (95%) of light yellow product VI, m.p. 261°C (benzene/hexane 1:1). Found: C, 45.35; H, 2.48; P, 4.93. $C_{48}H_{30}F_{10}HgP_2Pt$ calcd.: C, 45.96; H, 2.41; P, 4.94%.

Pentafluorophenylbis(triphenylphosphine)platinum trifluoroacetate (VII). 1.0 g (ca. 0.01 mol) of CF_3COOH was added to a solution of 0.62 g (0.001 mol) of VI in benzene (15 ml). Metallic mercury separated immediately. The filtrate was concentrated in vacuo and run through a short column (15 g of SiO_2) with benzene as eluent. 0.31 g (62%) of the colourless crystalline solid was obtained, m.p. 216-218°C (benzene/hexane), R_F 0.26, silufol, benzene/ethyl acetate (10:1). Found: C, 53.06; H, 3.24; P, 6.00. $C_{44}H_{30}F_8O_2P_2Pt$ calcd.: C, 52.86; H, 3.03; P, 6.20%.

1-Trifluoroacetoxymercuri-4-mercuribis(triphenylphosphine)platinumtrifluoroacetate-2,3,5,6-tetramethylbenzene (VIII). To 2.00 g (0.002 mol) of IV dissolved in 50 ml of benzene was added, on stirring, 0.76 g (0.001 mol) of II. After 12 h yellow-green crystals were separated, washed with hexane and dried in vacuo. The weight of VIII was 1.42 g (96%), dec. 226°C. Found: C, 41.43; H, 2.99. $C_{50}H_{42}F_6Hg_2O_4P_2Pt$, 0.5 C_6H_6 calcd.: C, 41.94; H, 2.98%.

Reaction between III and V. Equimolar quantities (0.001 mol) of III and V were allowed to react in benzene. In a slower reaction than usual, a greyish precipitate was separated. It was insoluble in organic solvents and contained mercury, platinum and halogen. The yield of dried product IX was 0.46 g (45%). IX decomposed slowly to give metallic mercury. Found: C, 43.47; H, 3.04; Br, 10.10; Hg, 17.00. $C_{37}H_{33}BrHgOP_2Pt$ calcd.: C, 43.11; H, 3.23; Br, 7.75; Hg, 19.45%. In benzene solution 1,1-diphenylethylene was found using thin-layer chromatography on silufol as compared with known substance: R_F 0.65 (benzene), 0.28 (pentane).

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