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REACTION OF THE LOW-VALENT TRANSITION METAL COMPLEXES WITH NON-TRANSITION ORGANOMETALLIC COMPOUNDS*

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Summary

The zero-valent triphenylphosphine complexes of palladium and platinum were found to react readily under mild conditions with organomercurials RHgX and R_2Hg. Final products appear to be σ-bonded organic derivatives of Pd and Pt. In several cases, the relatively stable intermediates with platinum to mercury bond were isolated. Dibenzylideneacetone-palladium(0) and -platinum(0) complexes exhibit similar reactivity towards organomercurials.

The platinum group metals produce several series of derivatives with the metal atom in different oxidation states. Thus platinum in the oxidation state 0, +2, +4 gives three series. The low-valent complexes are strong electron donors and they are thus capable of oxidative addition of organic halides [1]. The activities of complexes in reactions involving an electron transfer depend considerably upon the nature of ligands at the metal atom. The oxidative addition of alkyl and aryl halides is well known for triphenylphosphine-platinum(0) and -palladium(0) complexes [2,3].

We found that such complexes react readily with organomercuric salts and symmetrical organomercurials R_2Hg which are good electron acceptors. Our preliminary communication has been reported [4] and we now describe the scope and synthetic possibilities of the reaction and the character of intermediate compounds in more detail.

The reaction occurs readily in benzene or in some other inert hydrocarbon at room temperature. The initial zero-valent complex disappears rapidly giving the intermediates. These decompose into metallic mercury and afford σ-bonded platinum or palladium organic compounds. The overall reaction is shown (eqn. 1).

$$L_nM^0 + R-Hg-R' \rightarrow L_2M^{II}RR' + Hg^0 + (n-2)\,L \qquad (1)$$

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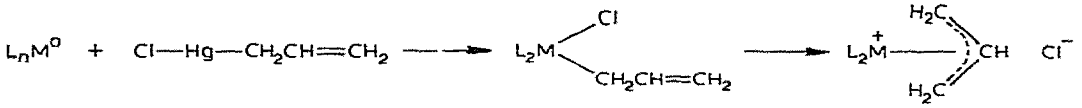
* Translated by N. Maryashkin.

In most of this work tris(triphenylphosphine)platinum(0) was used, though several experiments were conducted with tetrakis(triphenylphosphine)palladium(0).

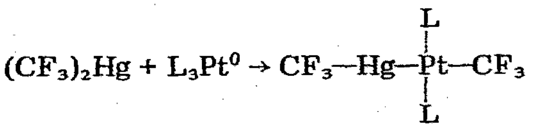
This method may be used for the synthesis of alkyl, vinyl and aryl derivatives and also for those containing some active functional groups (e.g. carbonyl). The new reaction is a convenient route to the synthesis of Pt^{II} and Pd^{II} derivatives under milder conditions than in the previous method [5], via organo-magnesium or -lithium compounds. In principle, the applicability of our method is limited only by availability of the respective organomercuric compounds, the chemistry of which is well developed. It is also possible to introduce simultaneously two different organic radicals when $R \neq R' \neq Hal$. It should be noted that in some cases by-processes may take place as well, for example RHgX compounds symmetrizing rapidly in the presence of free triphenylphosphine. If the resulting phosphine hinders the reaction then one may use other zero-valent complexes, and we consider an example in this paper.

The reaction may also be used for the synthesis of σ- and π-derivatives. Thus, in the fast reaction with allylmercuric chloride the σ-allyl product, if it ever forms, transforms rapidly into the π-allyl compound which can be isolated* (eqn. 2). A similar reaction may be expected also for cyclopentadienylmercuric halides which should afford the ionic π-cyclopentadienylbis(triphenylphosphine)-platinum halide.



(2)

Probably the primary reaction products are the compounds with a metal—mercury bond the stabilities of which depend on the nature of the radicals. This has been proposed in our earlier work [4] on the basis of observation that in some cases L_3Pt^0 disappears before the complete formation of metallic mercury. Now we have some evidence for this mechanism. From bis(trifluoromethyl)-mercury we obtained the first stable organic compound with a platinum—mercury σ-bond (eqn. 3). This compound crystallized rapidly upon mixing the reagents in benzene or xylene and it also crystallized from acetone in the form of analytically pure solvate with a solvent molecule. The presence of acetone was



$$(CF_3)_2Hg + L_3Pt^0 \rightarrow CF_3\text{—}Hg\text{—}\overset{\displaystyle L}{\underset{\displaystyle L}{Pt}}\text{—}CF_3 \qquad (3)$$

confirmed by the synthesis of its dinitrophenylhydrazone identified by thin layer chromatography and by the presence of carbonyl absorption at 1710 cm^{-1} in the IR spectrum of the crystalline product. The stability of such a bimetallic molecule may be explained by the strong electron-withdrawing effect of the CF_3 group. In our opinion this is also the reason for acetone being strongly coordinated at the mercury atom producing its trigonal configuration.

We still face the problem of elucidating the structural factors responsible for stability of such compounds with the transition metal—mercury bond. It

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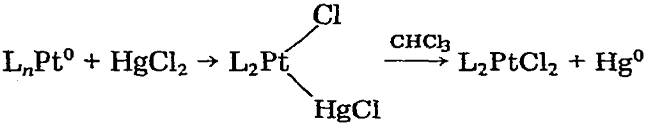
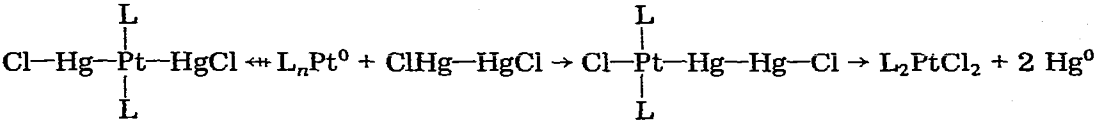
* Prepared by Dr. A.Z. Rubezhov.

should be pointed out that the first purely inorganic complex with a platinum—mercury bond has been prepared by Nyholm et al. [6] in 1967. This was an inorganic prototype of the here described reaction. We confirmed the result of this paper [6]. The Nyholm chloride complex, however, is essentially less stable than the bis(trifluoromethyl) derivative. Even when treated with chloroform it converts into the dichloride and metallic mercury (eqn. 4). Rather unexpectedly



$$\mathrm{L_nPt^0 + HgCl_2 \rightarrow L_2Pt}\begin{smallmatrix}\diagup \mathrm{Cl} \\ \diagdown \mathrm{HgCl}\end{smallmatrix} \xrightarrow{\mathrm{CHCl_3}} \mathrm{L_2PtCl_2 + Hg^0} \qquad (4)$$

Hg_2Cl_2 gave no Nyholm mercuric chloride but platinum dichloride and mercury. Since it is known already that the Pt—Hg—Cl grouping is sufficiently stable, it seems to us that this may serve as evidence of one (or possibly two) ways of splitting the mercurous chloride molecule (eqn. 5). Obviously an intermediate



$$\mathrm{Cl{-}Hg{-}}\underset{\mathrm{L}}{\overset{\mathrm{L}}{\mathrm{Pt}}}\mathrm{{-}HgCl} \nleftarrow \mathrm{L_nPt^0 + ClHg{-}HgCl} \rightarrow \mathrm{Cl{-}}\underset{\mathrm{L}}{\overset{\mathrm{L}}{\mathrm{Pt}}}\mathrm{{-}Hg{-}Hg{-}Cl} \rightarrow \mathrm{L_2PtCl_2 + 2\ Hg^0} \qquad (5)$$

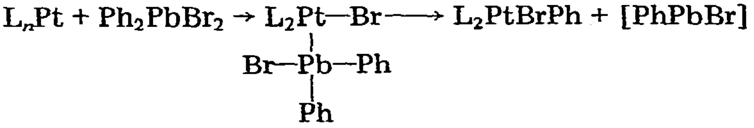
with an asymmetric polymetallic Pt—Hg—Hg chain is a strong electron acceptor, moreover it is unable to decompose with a loss of only one mercury atom. It may thus be concluded that an electron transfer to the Hg_2Cl_2 molecule results in cleavage of the Hg—Cl instead of Hg—Hg bond.

Unlike mercuric chloride the more polar mercuric trifluoroacetate affords no stable bimetallic intermediate but reacts instantly giving mercury and $L_2Pt(OCOCF_3)_2$ which has a melting point and some characteristics different from the known *cis*-di-trifluoroacetate [7] and is probably the *trans* isomer.

Thus an overall reaction may be described by eqn. 6.

$$\mathrm{L_nM^0 + R{-}Hg{-}R' \rightarrow L_2M^{II}(HgR')R + L_2M^{II}(HgR)R' + (\mathit{n} - 2)\ L}$$
$$\rightarrow \mathrm{L_2M^{II}R'R + Hg^0 + (\mathit{n} - 2)\ L} \qquad (6)$$

When $R \neq R'$ two reaction routes may generally be realized and which of them is preferable depends on the nature of R and R'. It may be assumed that the rapidly formed isomeric bimetallic intermediates then undergo decomposition at different rates. If one of them is relatively stable then some metallic mercury is produced, the remaining metal forming gradually in the course of further reaction.



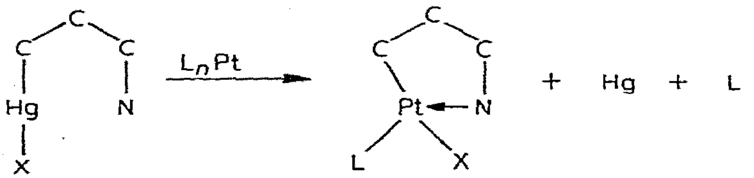
$$\mathrm{L_nPt + Ph_2PbBr_2 \rightarrow L_2}\underset{\mathrm{Br{-}\underset{Ph}{Pb}{-}Ph}}{\mathrm{Pt}}\mathrm{{-}Br} \longrightarrow \mathrm{L_2PtBrPh + [PhPbBr]} \qquad (7)$$

$$\mathrm{2[PhPbBr] \rightarrow Ph_2PbBr_2 + Pb}$$

This reaction can be extended to organic compounds of other non-transition metals. To date, we have extended it to the tin and lead derivatives. Thus diphenyllead dibromide gave exclusively phenylbis(triphenylphosphine)platinum bromide in high yield along with formation of metallic lead (eqn. 7). The formation of lead powder is explained by fast disproportionation of the divalent lead derivative eliminating from the bimetallic intermediate. The reason why selective transfer of two different radicals to the platinum occurs is unknown. The reaction with triphenylchlorostannane [6] gave a stable adduct with platinum—tin bond.

Formally the described reaction could be discussed as an insertion of the $(Ph_3P)_2Pt$ moiety into the R—Hg σ-bond, which is one of the features of carbenoid type reactivity specific for zero-valent bis(triphenylphosphine)platinum. Another example of the carbenoid reactivity may be found in the recently reported addition to the *ortho* quinone system [8].

It is known that a possibility of formation of the intramolecules cycles may essentially stimulate the generation of new carbon—non-transition metal bonds. Here we outline the usefulness of new reaction for the synthesis of chelate metallocycles described in detail earlier (eqn. 8) [9].

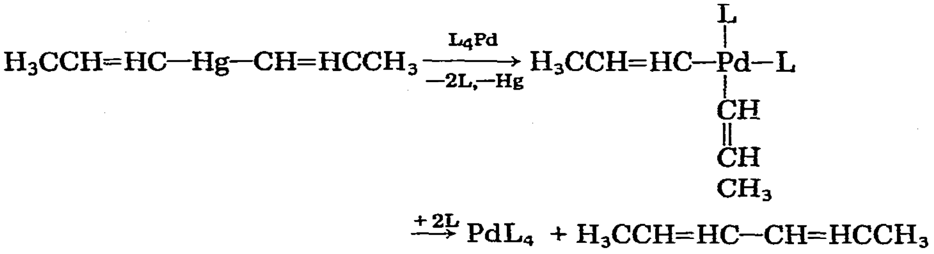


(8)

The electron transfer to the organomercurials is also observed in the case of zero-valent palladium and platinum dibenzylideneacetone complexes. However it is difficult to obtain the stable products. Dibenzylideneacetone is a loosely bonded ligand, its dissociation results in the coordinatively unsaturated product, which decomposes. Thus, the reaction of $Pd(DBA)_2$ and diphenylmercury in benzene at room temperature gave instantly the mixture of metallic mercury and palladium and diphenyl. It can be assumed that phenylmercuripalladium(II)phenyl is an unstable intermediate undergoing intramolecular homolytic decay. An alternative mechanism may be the formation of unstable tetraphenylpalladium(IV). In the same manner bis(trifluoromethyl)mercury gave more slowly the mixture of two metals (eqn. 9). Addition of some ligand before the reaction, e.g. phenanthroline, enables preparation of the L_2PdRR' compounds. Probably there is formed initially a mixed complex DBA·Pd(phen) described recently [10]. It is not necessary to add a foreign ligand if the structure provides saturation of a coordination site, for example, allylmercuric chloride should give the dimeric π-allylpalladium chloride. It should be noted that for the same reason an oxidative coupling of alkyl halides and $Pd(DBA)_2$ has been attained only for allyl halides [11].

$$(DBA)_2Pd + R_2Hg \xrightarrow{-2DBA} [R\text{—}Hg\text{—}Pd\text{—}R] \rightarrow R\text{—}R + Hg + Pd \qquad (9)$$

In our opinion this reaction is closely related to the recently reported stereoselective transformation of bis(propenyl)mercury into 2,4-hexadiene in the presence of catalytic amounts of $Pd(PPh_3)_4$ [12]. The following scheme involving an intramolecular elimination of a dimeric hydrocarbon from an unstable σ-organopalladium compound seems to be quite probable.



$$H_3CCH{=}HC{-}Hg{-}CH{=}HCCH_3 \xrightarrow[-2L,-Hg]{L_4Pd} H_3CCH{=}HC{-}\underset{\substack{|\\ CH\\ \|\\ CH\\ CH_3}}{\overset{\substack{L\\ |}}{Pd}}{-}L \xrightarrow{+2L} PdL_4 + H_3CCH{=}HC{-}CH{=}HCCH_3$$

Experimental

All the experiments were performed under argon.

Bis(triphenylphosphine)-p-tolylplatinum(II) bromide

0.36 g (0.001 mol) of *p*-tolylmercuric bromide was added to a solution of 0.98 g (0.001 mol) of tris(triphenylphosphine)platinum(0) in 50 ml of dry benzene. The suspension was stirred vigorously for 15 min, the orange colour disappeared and grey metallic mercury precipitated. The mixture was passed through a silica gel (L 40/100 μ) layer (2 cm). The filtrate was evaporated, the dry solid was treated with 150 ml of pentane from which 0.75 g (84%) of a white substance was isolated. This was reprecipitated with pentane from chloroform solution, m.p. 270.5-271°C. (Found: C, 58.10; H, 5.44; Br, 9.21; P, 6.99. $C_{43}H_{37}BrP_2Pt$ calcd.: C, 57.97; H, 4.19; Br, 8.97; P, 6.95%.)

Bis(triphenylphosphine)diphenylplatinum(II)

0.98 g (0.001 mol) of $(Ph_3P)_3Pt^0$ and 0.38 g (0.001 mol) of diphenylmercury were dissolved in 40 ml of dry benzene. The solution became deep red after several minutes with noticeable formation of metallic mercury. After a day the metallic mercury was separated (0.18 g, 54%) and the mixture was placed on a 7 cm silica gel column, the product was eluted with 150 ml of benzene. The benzene was evaporated and the residue washed with pentane to remove triphenylphosphine. 0.39 g (45%) of the complex was obtained, which decomposed above 140°C. Crystallization from benzene/hexane (50/30 ml) gave a sample with m.p. 140-160°C (dec.) (lit. 144-160°C [5]). (Found: C, 65.58; H, 4.57; P, 7.12. $C_{48}H_{40}P_2Pt$ calcd.: C, 65.97; H, 4.61; P, 7.09%.)

Bis(triphenylphosphine)di(isobutylcarboxymethyl)platinum(II)

0.43 g (0.001 mol) of mercurybis(isobutylacetate) was added to a solution of 0.98 g (0.001 mol) of $(Ph_3P)_3Pt$ in 20 ml of dry benzene. In 15 min mercury started to precipitate from the solution. The mixture was allowed to stand a day and then passed through silica gel layer. The eluate was evaporated to dryness and the residue washed with hexane and dried. The residue contained 47% of product and 53% of the initial organomercurial according to the PMR spectrum data (a comparison of methylene group intensities). Reprecipitation (twice) with pentane from CCl_4 afforded pure complex in the form of needle-like crystals, (m.p. 159-160°C). (Found: C, 60.58; H, 5.61; P, 6.48; Pt, 20.40. $C_{48}H_{52}O_4P_2Pt$ calcd.: C, 60.68; H, 5.52; P, 6.52; Pt, 20.53%.) IR spectrum: 1680 cm^{-1}; PMR spectrum: CH_2—P δ 2.89, J(H—Pt) 89.2 Hz.

trans-Bis(triphenylphosphine)methylcarboxymethylplatinum(II) chloride

1.24 g (0.0013 mol) of $(Ph_3P)_3Pt^0$ and 0.31 g (0.001 mol) of methyl chloromercury acetate were dissolved in 45 ml of benzene. The colour of $(Ph_3P)_3Pt$ disappeared in 10 min but the quantity of mercury generated was rather small. The mixture was diluted with 40 ml of acetone and refluxed for 1 h. The mercury was filtered off and the solution evaporated to dryness. The dry residue was washed with hexane from triphenylphosphine and the product reprecipitated with hexane from 20 ml of benzene. 0.6 g (72%) of the crystalline complex was obtained. The product was chromatographed on SiO_2 and eluted with acetone, additional reprecipitation with hexane from benzene gave m.p. 193-194°C. (Found: C, 56.91; H, 4.37; Cl, 4.46. $C_{35}H_{35}ClO_2P_2Pt$ calcd.: C, 56.56; H, 4.26; Cl, 4.28%.) IR spectrum: C=O 1710 cm^{-1}, PMR spectrum: CH_2—P δ 2.28, $J(H—^{195}Pt)$ 96.1 Hz, $J(H—^{31}P)$ 8.3 Hz, ^{31}P NMR spectrum: s + 25.1 ppm from H_3PO_4, $J(^{31}P—^{195}Pt)$ 3037 Hz.

Bis(triphenylphosphine)methylplatinum(II) iodide

1.24 g (0.001 mol) of tetrakis(triphenylphosphine)platinum(0) and 0.34 g (0.001 mol) of methylmercuric iodide were dissolved in 15 ml of benzene. The mercury (0.2 g, 100%) was separated after 2 h and the reaction mixture poured on a thin layer and the silica gel washed with benzene/acetone (2/1). The filtrate was evaporated and the residue washed with hexane and crystallized from toluene. 0.50 g (58%) of the complex was obtained (m.p. 264-267°C) which after two crystallizations from benzene gave sample with m.p. 256-259°C (lit. 270-274°C [5]). (Found: C, 51.64; H, 3.83; I, 14.80. $C_{37}H_{33}IP_2Pt$ calcd.: C, 51.58; H, 3.86; I, 14.73%.) PMR spectrum: CH_3 δ 0.95 (benzene).

Bis(triphenylphosphine)-2,2-di-p-anisylvinylplatinum(II) chloride (I)

1.0 g (0.001 mol) of $(Ph_3P)_3Pt$ and 0.38 g (0.001 mol) of 2,2-di-*p*-anisylvinylmercuric chloride were dissolved in 50 ml of dry benzene. After 3 h the benzene solution was passed through a thin layer of SiO_2 and the latter washed with 50 ml of acetone. The filtrate was evaporated and the residue washed with hexane. 0.53 g (66%) of the complex was obtained (m.p. 234-236°C). For analysis the substance was purified by chromatography in thick layer on a plate (silica gel L 40/100, eluent - acetone, R_f 0.87) to give yellow crystals (m.p. 239-242 °C). (Found: C, 62.50; H, 4.66; Cl, 3.75; P, 6.28; Pt, 19.70. $C_{52}H_{45}ClO_2P_2Pt$ calcd.: C, 62.81; H, 4.56; Cl, 3.47; P, 6.23; Pt, 19.62%.)

2,2-Di-p-anisylvinylmercuric chloride by direct mercuration [13]

4.00 g (0.017 mol) of 1,1-di-*p*-anisylethylene, 7.10 g (0.017 mol) of mercuric trifluoroacetate and 2 g of $BF_3 \cdot Me_2O$ were dissolved in 200 ml of absolute ether. The red mixture was treated with 200 ml of 7% aqueous NaCl. Without separating the layers the ether was evaporated under vacuo, the residue filtered off, washed with water and dried under vacuo. 7.93 g (94%) of the crude product was obtained (m.p. 90-105°C). Chromatography on thick layer (silica gel L40-100μ eluent - benzene, R_f 0.38) on a plate and crystallization from ethanol afforded 3.8 g of the yellow crystals (m.p. 146.5°C). (Found: C, 40.54; H, 3.18; Cl, 7.41; Hg, 41.63. Calcd.: C, 40.42; H, 3.18; Cl, 7.46; Hg, 42.20%.) PMR spectrum: =CH—Hg δ 6.17, $J(^1H—^{199}Hg)$ 198.0 Hz.

trans-Bis(triphenylphosphine)bis-trifluoroacetateplatinum(II)

0.98 g of I and 0.43 g (0.001 mol) of mercuric trifluoroacetate were dissolved in 25 ml of dry benzene. Instantly a bright red colour appeared and rapidly disappeared with quantitative precipitation of mercury. After ordinary purification on silica gel the substance was crystallized from benzene/hexane. 0.67 g of colourless crystals were obtained, m.p. 242-243°C (lit. for *cis*-isomer 230-235°C [7].) (Found: C, 50.74; H, 3.27; F, 12.27. $C_{40}H_{30}F_6O_4P_2Pt$ calcd.: C, 50.81; H, 3.20; F, 12.06%.)

Bis(triphenylphosphine)-π-allylplatinum(II) chloride

0.11 g (0.0004 mol) of allylmercuric chloride in 20 ml of benzene was added to a solution of 0.5 g (0.0004 mol) of $(Ph_3P)_4Pt$ in 50 ml of dry benzene. After 5 min the mixture lost its colour with precipitation of metallic mercury. The mixture was stirred for 1 h, filtered and the filtrate diluted with ether. The product precipitated was filtered off, carefully washed with ether from triphenylphosphine and crystallized from benzene. 0.28 g (70%) of bis(triphenylphosphine)-π-allylplatinum chloride was obtained, dec. p. 194-196°C (lit. m.p. 195°C (dec.) [14]). (Found: C, 58.51; H, 4.36; Cl, 4.90. $C_{39}H_{35}ClP_2Pt$ calcd.: C, 58.83; H, 4.43; Cl, 4.45%.)

Trifluoromethylmercury-bis(triphenylphosphine)trifluoromethylplatinum

0.34 g (0.001 mol) of bis(trifluoromethyl)mercury and 1.24 g (0.001 mol) of $(Ph_3P)_4Pt$ were dissolved in 25 ml of dry benzene and the mixture was allowed to stand for a day. The white crystalline solid precipitated was filtered off, washed with hexane and dried. 0.91 g (86%) of the complex was obtained. It was soluble in acetone, chloroform and benzene. The action of CF_3COOH immediately resulted in precipitation of metallic mercury. Crystallization from acetone/pentane gave product of m.p. 187-201°C (dec.). The product contains a molecule of crystallization of acetone. (Found: C, 44.39; H, 3.58; P, 5.54. $C_{38}H_{30}FHgP_2Pt·CH_3COCH_3$ calcd.: C, 44.11; H, 3.25; P, 5.55%.) IR spectrum: C=O 1715 cm^{-1}. Acetone was identified from its 2,4-dinitrophenylhydrazone, using an authentic sample and thin layer chromatography (silufol, eluent - benzene, $R_f = 0.33$).

The reaction of diphenyllead(IV) dibromide with tris(triphenylphosphine)platinum(0)

0.26 g (0.0005 mol) of diphenyllead dibromide was added to the solution of 0.49 g (0.0005 mol) of I in 35 ml of dry benzene. The orange colour of the initial platinum complex disappeared with precipitation of finely dispersed metallic lead. The solution was passed through a SiO_2 layer and washed with 200 ml of benzene. The benzene was evaporated, the dry residue washed with pentane and dried to give product of m.p. 252-259°C. Reprecipitation from 15 ml of benzene with 20 ml of pentane gave 0.34 g (77%) of the white crystalline solid (m.p. 258-259°C (dec.)). (Found: C, 57.87; H, 4.13; Br, 9.12. $C_{42}H_{35}BrP_2Pt$ calcd.: C, 57.54; H, 4.03; Br, 9.11%.)

(o-Phenanthroline)-p-tolylpalladium(II) chloride

0.40 g (0.002 mol) of *o*-phenanthroline monohydrate was added to the suspension of 0.99 g (0.001 mol) of $Pd_2(DBA)_3 \cdot C_6H_6$ complex in 50 ml of dry benzene. The violet colour turned yellow-brown. The solution was shaken for 15 min with 0.65 g (0.002 mol) of *p*-tolylmercuric chloride, and separated from metallic mercury after 3 h by passing through a thin layer of SiO_2. The filtrate was evaporated to dryness, the residue crystallized from benzene. 0.77 g (93%) of the yellow crystalline product was obtained which decomposed above 220°C. (Found: C, 54.53; H, 3.68; Cl, 9.21; Pd, 25.92. $C_{19}H_{15}ClN_2Pd$ calcd.: C, 55.23; H, 3.66; Cl, 8.58; Pd, 25.75%.)

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