385. *Triphenylphosphine Derivatives of Platinum*(0).

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Chopoorian *et al.*[1] recently reported that the triphenylphosphineplatinum compounds first prepared by Malatesta and Cariello [2] and considered to be the platinum(0) derivatives (I) and (II) must be regarded as dihydridoplatinum(II) derivatives (IA) and (IIA).

PtL_4	PtL_3	PtH_2L_4	PtH_2L_3	PtH_2L_2	$L = PPh_3$
I	II	IA	IIA	III	

Chopoorian *et al.* also proposed that all the other platinum compounds analogous to, or prepared from, those triphenylphosphine derivatives and originally considered as platinum(0) derivatives, should be formulated as hydrides of bivalent platinum. However, Chatt [3] has since shown that his di-(1,2-bisdiphenylphosphinoethane)platinum is a derivative of platinum(0), and Allen and Cook [4] reported that the compound obtained from platinum(II) chloride and tri-*p*-fluorophenylphosphine, in the way described by Malatesta *et al.*, is in fact a true platinum(0) complex similar to the tris(tri-*p*-chlorophenylphosphine)platinum(0) of Malatesta *et al.*

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[1] Chopoorian, Lewis, and Nyholm, *Nature*, 1961, **190**, 528.
[2] Malatesta and Cariello, *J.*, 1958, 2323.
[3] Chatt and Rowe, *Nature*, 1961, **191**, 1191.
[4] Allen and Cook, *Proc. Chem. Soc.*, 1962, 218.

We have now re-examined our compounds and we confirm our original structures for reasons that can be summarized as follows:

(1) If benzene solutions of compounds (I) and (II) are kept under nitrogen for not less than a week, the compound $\mathrm{PtH_2(PPh_3)_2}$ (III) separates, and on the formulation of this as the dihydride we completely agree. This reaction, interpreted as a dissociation of the compounds (IA) and (IIA), prompted Chopoorian *et al.* to consider the original phosphine compound as a dihydride. We have proved, on the contrary, that the formation of compound (III) cannot be due to dissociation of a pre-existing hydrido-compound, since we could obtain it in a much shorter time by the action of hydrogen, at high pressure, on benzene solutions of compounds (I) and (II). We think that the hydrogen required to transform these complexes into the hydrido-complex (III), in benzene solution and in absence of molecular hydrogen, comes from the solvent or, more probably, from traces of water according to the reaction: $\mathrm{Pt(PPh_3)_3} + \mathrm{H_2O} \longrightarrow \mathrm{PtH_2(PPh_3)_2} + \mathrm{OPPh_3}$.

(2) Titration of compounds (I) and (II) with bromine solution, which was the main chemical argument in favour of formulæ (IA) and (IIA), cannot take place as formulated by Chopoorian *et al.* because the triphenylphosphine set free in the reaction reacts with bromine (as with iodine) immediately and completely to form the complex $\mathrm{Br_2PPh_3}$, which by hydrolysis then gives two equivalents of acid. We performed an iodometric titration of compounds (I), (II), and (III) in benzene, and then added water; subsequent acidimetric titration yielded results corresponding to the following equations:

$$\mathrm{Pt(PPh_3)_4} + 3\mathrm{I_2} \longrightarrow \mathrm{I_2Pt(PPh_3)_2} + 2\mathrm{I_2,PPh_3}\text{: } \mathrm{I_2}\ 6\ \text{equiv., NaOH 4 equiv.}$$

$$\mathrm{Pt(PPh_3)_3} + 2\mathrm{I_2} \longrightarrow \mathrm{I_2Pt(PPh_3)_2} + \mathrm{I_2PPh_3}\text{: } \mathrm{I_2}\ 4\ \text{,, NaOH 2 ,,}$$

$$\mathrm{PtH_2(PPh_3)_2} + \mathrm{I_2} \longrightarrow \mathrm{I_2Pt(PPh_3)_2} + \mathrm{H_2}\text{: } \mathrm{I_2}\ 2\ \text{,, NaOH 0 ,,}$$

It is noteworthy that, according to the second equation, compound (II) gives the same results as the hydride (IIA) would if it reacted as indicated by Chopoorian *et al.*

(3) The hydride (III), unlike compounds (I) and (II), has infrared absorption characteristic of hydride-hydrogen. This was not considered by Chopoorian *et al.* an important argument against the formulation of complexes (I) and (II) as hydrides, but in our opinion it is highly significant because, of the very many hydrido-compounds already studied, only one, namely, $\mathrm{OsHCl[(CH_2{\cdot}PPh_2)_2],C_6H_6}$ (ref. 5), has been reported as not showing the typical Me–H stretching vibration.

(4) Complexes (I) and (II) are rapidly decomposed by carbon tetrachloride, but the hydride (III) can be recovered unaltered after having been suspended in this solvent for 24 hours.

(5) Compounds (I) and (II) evolve no trace of gas when treated with iodine in pyridine, but the hydride (III) gives immediately almost 1 mol. of hydrogen in this reaction. This seems to confirm the number of hydride-hydrogen atoms as two in this compound, as had been postulated, but not determined, previously.

We conclude, therefore, that the original formulation of these phosphine complexes by Malatesta and Cariello as derivatives of platinum(0) was correct and that these and analogous derivatives are well-defined and well-characterised compounds. In benzene solution the triphenylphosphine compounds (I) and (II) slowly change to the more stable and less soluble dihydridobis(triphenylphosphine)platinum(II) which, however, is obtained more conveniently by the action of hydrogen under pressure.

Experimental.—Preparations. The complexes (I) and (II) were prepared as already described.[2] *Dihydridobistriphenylplatinum*(II) (III) was obtained in the following ways: (*a*) A solution of complex (I) (1 g.) in benzene (30 ml.) was kept under nitrogen for 8 days at room temperature. The white crystalline precipitate of the hydride was washed with benzene and dried (0·1 g.). (*b*) A solution of the complex (I) (1 g.) in benzene (15 ml.) was kept for 5 hr. under hydrogen at 200 atm. at room temperature. The very fine crystalline precipitate,

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[5] Chatt and Hayter, *J.*, 1961, 2605.

separated by centrifugation (0·27 g.), had the same analysis, infrared spectrum, and m. p. 177° (decomp.), as that obtained as in (*a*). The hydride (in Nujol) had $\nu_{\max.}$ 1670 and 816 cm.$^{-1}$ and was insoluble in alcohol or acetone and not very soluble in benzene, but soluble in methylene chloride. It is much more stable in air and in solution than are the compounds (I) and (II).

Iodometric and acidimetric titration. The compounds were dissolved in benzene (I and II) or methylene dichloride (III), and an excess of a 0·1N-solution of iodine in benzene was added. After addition of aqueous potassium iodide, the mixtures were titrated first with sodium thiosulphate and then with sodium hydroxide. The results are summarized in the Table.

	(I) $C_{72}H_{60}P_4Pt$		(II) $C_{54}H_{55}P_3Pt$		(III) $C_{36}H_{32}P_2Pt$		PPh_3	
	Found	Required	Found	Required	Found	Required	Found	Required
(%)	69·1	69·6	65·7	66	59·8	59·7		
H (%)	4·8	4·8	4·4	4·6	4·3	4·4		
I_2 (equiv.)	5·90	6	4·10	4	1·8	2	2·02	2
NaOH (equiv.)	3·90	4	2·13	2	0	0	1·95	2
H_2 (mol.).........	0	0	0	0	0·84	1	0	0

The Table shows also titration results for triphenylphosphine, which reacted in the same way with bromine as with iodine.

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