

### 67. *Organic Compounds of Platinum. Part I. The Preparation and Constitution of Trimethylplatinum Compounds.*

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A convenient method of obtaining trimethylplatinum compounds is described which starts from the readily accessible and non-hygroscopic *cis*-dipyridinotetrachloroplatinum. This compound with methylmagnesium iodide gives a 70% yield of the dimer  $[\text{Me}_3\text{Pt pyI}]_2$ , a halogen-bridged compound converted by more pyridine into the known  $\text{Me}_3\text{Pt py}_2\text{I}$ . One molecule of pyridine is removed from the latter dipyridine complex by dilute acid, to regenerate the monopyridine complex, the second molecule is more firmly bound, but is displaced when the dimer reacts in chloroform with excess of ethylenediamine, the compound  $2\text{Me}_3\text{PtI}, 3\text{en}$  crystallising. The last reacts with hydriodic acid to give trimethylplatinum iodide.

In tetrameric  $[\text{Me}_3\text{PtCl}]_4$  each platinum atom has an octahedral configuration and the three methyl groups linked to it are *cis* to one another. It is suggested that the same arrangement persists in the above co-ordination compounds, which are formulated accordingly. The inability to prepare trimethylplatinum compounds from *trans*-dipyridinotetrachloroplatinum lends support to this view.

THE first organic compound of platinum, trimethylplatinum iodide, was prepared in 1909 by treatment of anhydrous platinum tetrachloride with methylmagnesium iodide (Pope and Peachey, *J.*, **95**, 571). Trimethylplatinum compounds have since been investigated by Menzies *et al.* (*J.*, 1928, 565; 1933, 21; 1933, 1250; 1949, 1168), Gilman and Lichtenwalter (*J. Amer. Chem. Soc.*, 1939, **61**, 957), Lichtenwalter (*Iowa State Coll. J. Sci.*, 1939, **14**, 57), and Rundle and Sturdivant (*J. Amer. Chem. Soc.*, 1947, **69**, 1561), some of whose results are referred to below.

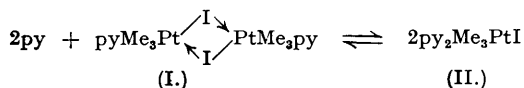
Although the trimethylplatinum derivatives are among the most stable of organometallic compounds, the study of organoplatinum compounds in general has received but scant attention. The preparation of anhydrous platinum tetrachloride, which has hitherto been used as a source of trimethylplatinum compounds, involves a somewhat laborious procedure for the thermal decomposition of chloroplatinic acid (*Inorg. Synth.*, Vol. II, p. 253), and our first problem was to find a more convenient starting material. The success experienced with pyridinotri-

chlorogold as a source of dialkylgold compounds (Gibson *et al.*, *J.*, 1935, 219 *et seq.*) prompted us to investigate the use of *cis*- or *trans*-dipyridinotetrachloroplatinum. The former separates almost quantitatively when sodium chloroplatinate is refluxed with the requisite quantity of pyridine in aqueous solution (Jørgensen, *Z. anorg. Chem.*, 1900, **25**, 369). The latter is obtained by oxidation of tetrapyridinoplatinous chloride  $[\text{py}_4\text{Pt}]\text{Cl}_2$ , which is itself readily prepared from potassium chloroplatinite (Jørgensen, *J. pr. Chem.*, 1886, [ii], **33**, 504).

It may be said at once that with the *trans*-isomer and methylmagnesium iodide very little, if any, alkylation occurred, the main product being dipyridinodi-iodoplatinum, presumably in the *trans*-modification. Certainly there was no indication of any trimethylplatinum compound.

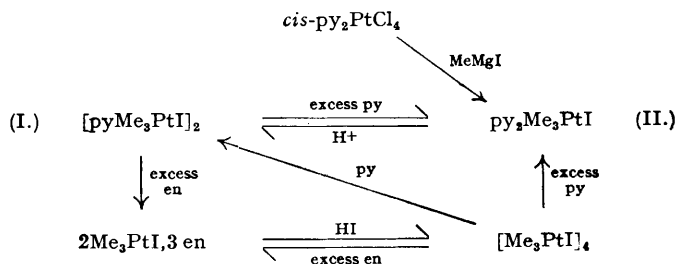
The *cis*-isomer, suspended in an anhydrous mixture of benzene and ether reacted completely with the Grignard reagent in 2 hours at 0—15°, giving, in 70% yield, a compound having an empirical formula  $\text{pyMe}_3\text{PtI}$ . The molecular weight, determined cryoscopically in benzene, showed clearly that the compound is binuclear and, without for the moment any attempt being made to elaborate the stereochemical configuration, may thus be represented by (I). The preservation of the characteristic 6-covalency of quadrivalent platinum (Lile and Menzies, *J.*, 1949, 1168; 1950, 617) by the halogen bridge is fully in keeping with the known structure of tetrameric trimethylplatinum chloride (Rundle and Sturdivant, *loc. cit.*) in which the same type of bridging occurs.

Dipyridinohexamethyl- $\mu\mu'$ -di-iododiplatinum (I) is sparingly soluble in water, alcohol, ether, or acetone but soluble in chloroform or benzene. It is stable in dilute acid or alkaline solution, but decomposes in hot alkali, liberating pyridine. With further pyridine it is converted into dipyridinotrimethyliodoplatinum  $\text{Me}_3\text{Pt py}_2\text{I}$  (II), identical with the complex prepared directly from trimethylplatinum iodide and excess of pyridine (Lile and Menzies, *loc. cit.*). The variation of freezing point depression of (II) in benzene, with concentration, indicated a dissociation in dilute solution: the apparent molecular weight (340) at infinite dilution is almost exactly two-thirds of the formula weight (525); at high concentrations the value approaches 525 (*cf.* p. 302). These observations may be interpreted in terms of the equilibrium :



Shaking a benzene solution of (II) with dilute hydrochloric acid removes one molecule of co-ordinated pyridine, with regeneration of the dimer (I).

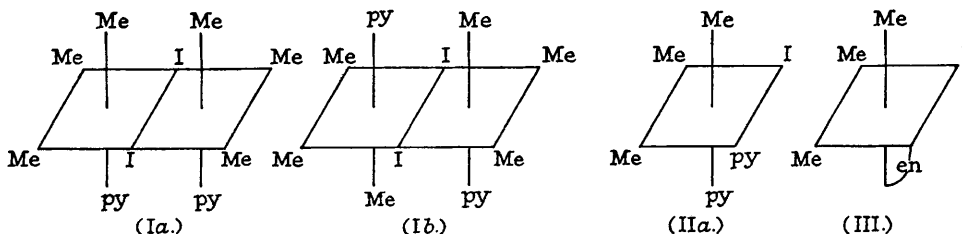
The stability of the dimer in dilute acid indicates that the second molecule of pyridine is held very much more firmly, but it may be displaced by addition of ethylenediamine to a chloroform solution of (I). The compound  $2\text{Me}_3\text{PtI}\cdot 3\text{en}$ , named by Lile and Menzies (*loc. cit.*) sesquiethylenediaminotrimethylplatinic iodide, separates as colourless crystals almost quantitatively. It has now been shown that by addition of hydriodic acid to a hot aqueous solution of this ethylenediamine complex, trimethylplatinum iodide  $(\text{Me}_3\text{PtI})_4$  may be obtained in good yield. The latter has in turn been converted into the dimer (I) by reaction with one equivalent of pyridine. These reactions are summarised in the scheme.



The constitutions of the various co-ordination complexes cannot be settled finally, but it is possible to make certain predictions.

In the tetramer trimethylplatinum chloride the three methyl groups attached to each platinum are *cis* to one another, *i.e.*, the three Pt—C bonds are mutually perpendicular. Assuming that trimethylplatinum iodide has a similar structure—and the molecular weight evidence of

Menzies and Overton (*J.*, 1933, 1291) would seem to confirm this—it is clear that formation of a co-ordination complex must involve a progressive splitting of the Pt–halogen links in the tetramer. That being so, co-ordination by one molecule of a monoamine, such as pyridine or ammonia, to each platinum will result in a dimer such as (Ia), in which the four-membered ring is one face of the original cubic tetramer.



Co-ordination of two molecules of a monoamine or one molecule of a diamine will give rise to a monomeric complex, as in (IIa) or (III). The former is thus the most probable constitution of dipyridineiodotrimethylplatinum, and the latter that of Lile and Menzies's compound  $\text{Me}_3\text{Pt enI}$ .

In the sesquiethylenediamine compound, the process has been continued still further with the rupture of the sole remaining Pt–I bond, so that a salt is formed, of which the cation contains two platinum atoms bridged by at least one molecule of ethylenediamine, as for instance in (IV). The formula (V) suggested by Lile and Menzies cannot be ruled out on the evidence available, although our experience in the dialkylgold series (Foss and Gibson, *J.*, 1949, 3063) suggests that wherever possible ethylenediamine will chelate.



In *cis*-dipyridinotetrachloroplatinum, three methyl groups replacing three chlorine atoms may assume a mutually *cis*-position; this is not possible with the *trans*-isomer unless replacement is accompanied by reorientation of the groups attached to the platinum. The inability to isolate any trimethylplatinum compound from the *trans*-isomer, combined with the exceptionally high yield of pure compound prepared from the *cis*-isomer, seems to rule out the possibility of reorientation, and supports a mutually *cis*-arrangement of the methyl groups in these trimethylplatinum compounds.

*cis*-Dipyridinotetrachloroplatinum thus reacts with methylmagnesium iodide to give first *cis*-dipyridineiodotrimethylplatinum (IIa), which in the presence of acid loses one molecule of pyridine and dimerises, to give dipyridinohexamethyl- $\mu\mu'$ -di-iododiplatinum. Either (Ia) or (Ib) may result from the dimerisation, but only one compound has been isolated in practice. That this compound proves to be identical with that obtained from trimethylplatinum iodide and one equivalent of pyridine favours the structure (Ia).

Finally, it is interesting to compare the stability of the halogen bridge in the dimer (I), and in the parent trimethylplatinum halides too, with the weakness of the bridge in the recently described binuclear platinum complex, hexachlorobis(tri-*n*-propylphosphine)- $\mu\mu'$ -dichlorodiplatinum (Chatt, *J.*, 1950, 2301).

#### EXPERIMENTAL.

*cis*-Dipyridinotetrachloroplatinum.—A mixture of sodium chloroplatinate (28.4 g.) and pyridine (8 g.) was refluxed in water (1.5 l.) for 16 hours. The yellow compound which separated was collected, washed with water, and dried *in vacuo*, first over calcium chloride and then over phosphoric oxide (yield 24 g., 95%) (Found: Pt, 39.5. Calc. for  $\text{C}_{10}\text{H}_{10}\text{N}_2\text{Cl}_4\text{Pt}$ : Pt, 39.4%).

*cis*-Dipyridinodichloroplatinum.—Pyridine (9.5 g.) was added to a solution of potassium chloroplatinate (25 g.) in water (300 c.c.), and the mixture was kept for 24 hours. The pale yellow solid which separated, was collected, washed with water and dried (yield 24 g., 94%).

*Tetrapyridinoplatinous Chloride* ( $\text{py}_4\text{PtCl}_2 \cdot 3\text{H}_2\text{O}$ ).—The preceding compound (24 g.) was dissolved in 50% aqueous pyridine (50 c.c.) on a water-bath. On the addition of ethanol (600 c.c.) and ether (3 l.) to the cold aqueous solution, the hydrated tetrapyridine salt separated as a white crystalline powder, which was collected, washed with ether, and air-dried. The yield was 34.5 g. (97%).

*trans-Dipyridinotetrachloroplatinum*.—Finely powdered potassium permanganate (12.4 g.) was added to a solution of the previous compound (30 g.) in concentrated hydrochloric acid (180 c.c.). The oxidation was allowed to proceed overnight, a further quantity of hydrochloric acid (300 c.c.) and then water (300 c.c.) were added, and the mixture was heated with stirring for 5 hours. The yellow amorphous solid which separated was collected, washed with water, and dried (yield 23 g., 93%) (Found : Pt, 39.0%).

*Dipyridinohexamethyl- $\mu\mu'$ -di-iododiplatinum* (I).—A solution of methylmagnesium iodide (6 mols.; from 3.7 g. of magnesium, 21.6 g. of methyl iodide, and 50 c.c. of ether) was run into a well stirred suspension of *cis*-dipyridinotetrachloroplatinum (12.4 g.) in dry benzene (200 c.c.) and ether (60 c.c.) at 0°. Stirring was continued for 2 hours, and the temperature was allowed to rise to 15°. A further 50 c.c. of benzene were added, followed by water (200 c.c.) and concentrated hydrochloric acid (50 c.c.). The mixture was then filtered, and the benzene layer separated; the aqueous layer was extracted thoroughly with benzene (2  $\times$  100 c.c.), and the combined benzene solutions were washed with water and dried (Na<sub>2</sub>SO<sub>4</sub>). After removal of the benzene at reduced pressure, an orange-coloured solid (9.6 g.) remained. This was recrystallised from warm benzene, to which a little ligroin had been added to aid crystallisation.

*Dipyridinohexamethyl- $\mu\mu'$ -di-iododiplatinum* was thus obtained as pale yellow prisms (7.7 g., 70%), which decomposed slowly above 150° and completely at 217°. The platinum content was determined by carefully igniting the solid, in the presence of a few drops of chloroform and a few crystals of iodine. The molecular weight, determined cryoscopically in benzene, showed the complex to be binuclear (Found : C, 21.5; H, 2.9; N, 3.6; Pt, 43.7%; *M*, 891, 894. C<sub>18</sub>H<sub>28</sub>N<sub>2</sub>I<sub>2</sub>Pt<sub>2</sub> requires C, 21.5; H, 3.1; N, 3.1; Pt, 43.7%; *M*, 892). The compound is sparingly soluble in water, alcohol, and ether, soluble in chloroform and benzene, and very soluble in pyridine.

*Dipyridinotrimethyliodoplatinum* (II).—A solution of the preceding compound (3 g.) in pyridine (10 c.c.) was evaporated to dryness *in vacuo* over phosphoric oxide. The residue, when recrystallised from methanol, gave pale yellow crystals of dipyridinotrimethyliodoplatinum (2.4 g.) which melted at 168° (without decomp.), not depressed when mixed with Lile and Menzies's compound (personal communication) (Found : C, 29.9; H, 3.7; Pt, 37.1. Calc. for C<sub>13</sub>H<sub>19</sub>N<sub>2</sub>IPt : C, 29.7; H, 3.6; Pt, 37.1%). The compound is sparingly soluble in water and cold alcohol, but dissolves readily in benzene, chloroform, acetone, and hot alcohol.

The table below shows the values of the observed freezing point depressions ( $\Delta t$ ) and of the apparent molecular weight (*M*) at a series of concentrations (*C*; g. of solute/1000 g. of solvent):

<i>C</i> .....	3.85	8.92	13.68	18.07	24.2	29.03
$\Delta t$ .....	0.050°	0.113°	0.160°	0.195°	0.250°	0.258°
<i>M</i> .....	369	413	447	485	507	527

By extrapolation of a derived graph, the apparent molecular weight at infinite dilution is found to be 340.

A benzene solution of dipyridinotrimethyliodoplatinum (0.5 g.) was shaken with dilute hydrochloric acid (25 ml. : 0.4*N*.). The benzene layer was then separated, dried (Na<sub>2</sub>SO<sub>4</sub>), and evaporated, to give pure dipyridinohexamethyl- $\mu\mu'$ -di-iododiplatinum (0.39 g., 92%), m. p. 216° (decomp.).

*Sesquiethylenediaminotrimethylplatinic Iodide*.—When ethylenediamine (0.1 g.) was added to a solution of dipyridinohexamethyl- $\mu\mu'$ -di-iododiplatinum (0.5 g.) in chloroform (20 c.c.), and the mixture warmed for a few minutes on a water-bath, colourless crystals of sesquiethylenediaminotrimethylplatinic iodide (0.50 g.) separated. The compound was water-soluble, darkened above 240° and melted with decomposition at 269° (cf. Lile and Menzies) (Found : Pt, 42.2. Calc. for C<sub>12</sub>H<sub>42</sub>N<sub>6</sub>I<sub>2</sub>Pt<sub>2</sub> : Pt, 42.7%). The aqueous solution with silver nitrate gave an immediate precipitate of silver iodide.

*Trimethylplatinum Iodide*.—A hot aqueous solution of sesquiethylenediaminotrimethylplatinic iodide (0.62 g.) was treated with hydriodic acid (0.6 ml.; 7.3*N*.). The pale yellow solid which separated (0.46 g.) was collected, dried, and recrystallised from chloroform (Found : Pt, 52.5. Calc. for C<sub>12</sub>H<sub>36</sub>Pt<sub>4</sub>I<sub>4</sub> : Pt, 53.1%). When a chloroform solution (5 ml.) of trimethylplatinum iodide (0.1 g.), to which one equivalent (0.02 ml.) of pyridine had been added, was evaporated to a small bulk (approx. 1 ml.), crystals of dipyridinohexamethyl- $\mu\mu'$ -di-iododiplatinum (0.07 g.) separated; they had m. p. 215° (decomp.), undepressed when mixed with an authentic specimen.

*Reaction of trans-Dipyridinotetrachloroplatinum with Methylmagnesium Iodide*.—A solution of methylmagnesium iodide (Mg, 1.85 g.; MeI, 10.8 g.; Et<sub>2</sub>O, 25 c.c.) was run into a well-stirred suspension of *trans*-dipyridinotetrachloroplatinum (6.2 g.) in dry benzene (100 c.c.) and dry ether (30 c.c.) at 0°. Stirring was continued for 2 hours, and the temperature was allowed to rise to 15°. As the reaction proceeded, the suspended solid became chocolate-brown. A further 50 c.c. of benzene were added, followed by water (100 c.c.) and concentrated hydrochloric acid (20 c.c.). The mixture was then filtered, and the solid collected was washed thoroughly with water and benzene. The dry substance (7.6 g.) was a dark brown amorphous powder, very sparingly soluble in all solvents except hot nitrobenzene from which separated on cooling, golden-yellow needles (3.7 g.) of dipyridinodi-iodoplatinum (Found : Pt, 32.4. Calc. for C<sub>10</sub>H<sub>10</sub>N<sub>2</sub>I<sub>2</sub>Pt : Pt, 32.1%). From the benzene layer of the filtrate was isolated only a small quantity (0.5 g.) of orange-coloured solid which has not been characterised.

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