LXXIII.—*The Alkyl Compounds of Platinum.*

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SOME years ago we observed that many inorganic chlorides, bromides, and iodides react vigorously with the Grignard reagent, and showed that the alkyl compounds of tin may be conveniently prepared by the action of the magnesium alkyl chlorides, bromides, or iodides on stannic chloride (Proc., 1903, **19**, 290). Since that time Pfeiffer and his co-workers have applied the reaction to the preparation of a number of other organo-metallic compounds, and Kipping has shown that the alkyl silicon compounds can in many cases be readily prepared by its aid. The Grignard reagent not only furnishes a convenient means for preparing organo-metallic compounds of the types which had been previously discovered, principally by E. Frankland, with the aid of the zinc alkyl compounds, but Pope and Gibson have shown (Trans., 1907, **91**, 2061) that the gold alkyl compounds, which were previously unknown, can be prepared by the action of magnesium alkyl iodides on auric bromide. Frankland has noted (*Quart. Journ. Chem. Soc.*, 1861, **13**, 188) that, although the zinc alkyl compounds act violently on halogen compounds of platinum, the organic group does not unite with the metal. In the present paper we describe the preparation and properties of a new series of organo-metallic compounds, namely, those of platinum, which are obtained by the action of magnesium methyl iodide on platinic chloride.

By aid of the reaction just mentioned, we have succeeded in obtaining *trimethylplatinic iodide*, $(CH_3)_3PtI$, which proves to be a salt-like substance derived from a very feebly basic hydroxide, *trimethylplatinic hydroxide*, $(CH_3)_3Pt \cdot OH$. The examination of the latter substance and its salts indicates that the quadrivalent platinum atom resembles the quinquevalent nitrogen atom, in that it appears impossible to attach four alkyl groups to the former just as it is impossible to obtain compounds in which five basic groups are attached to the same nitrogen atom. The new substances now described are further of importance in that they are the first representatives to be prepared of the alkyl derivatives of the nine metals composing group VIII of the periodic classification.

Trimethylplatinic Iodide, $(CH_3)_3PtI$.

The successful preparation of trimethylplatinic iodide requires attention to a number of details, and it is consequently desirable to describe the necessary precautions at some length. Chloroplatinic acid, contained in a distilling flask, is heated at $200°$ in a metal-

bath under a low atmospheric pressure, the water and hydrogen chloride evolved being absorbed by suction through a Woulff's bottle containing solid potassium hydroxide ; after some hours' heating, decomposition comes to an end, and nearly pure platinic chloride remains in the distilling flask.   This material is treated with anhydrous ether in sufficient quantity to dissolve part of it and to convert the remainder into a dark red syrup; the solution and syrup are then slowly run into a solution of magnesium methyl iodide, the mixture being constantly cooled and shaken.   The magnesium methyl iodide solution used is prepared with the aid of the minimum quantity of ether, and is afterwards diluted with five volumes of anhydrous benzene ; a considerable excess of the magnesium methyl iodide is used, about twice as much as is indicated by the following equation :

$$PtCl_4 + 3CH_3 \cdot MgI = (CH_3)_3PtI + 2MgCl_2 + MgI_2.$$

The addition of the platinic chloride solution to the Grignard reagent leads to a vigorous reaction accompanied by considerable evolution of heat.   After standing for an hour, the mixture is poured into ice-water and the benzene solution separated, the aqueous solution being subsequently extracted several times with benzene.   After washing with water, the benzene extracts are distilled from the water-bath under diminished pressure, when a heavy sandy powder of a brownish-yellow colour remains behind.   This dissolves readily in boiling benzene, and, after filtration, the solution on rapid cooling deposits trimethylplatinic iodide as a bright yellow, crystalline powder.

The analysis of the substance presents some difficulties, owing to a tendency to explosive decomposition on heating.   The platinum may be determined by treating a weighed quantity with solid iodine and a few drops of chloroform in a porcelain crucible and very slowly heating to redness.   The iodine is determined by slowly heating with lime and titrating in the usual way with silver nitrate and thiocyanate solutions :

0·1500 gave 0·0795 Pt.   Pt = 53·00.
0·2308   ,,   0·0791 I.   I = 34·27.
          C_3H_9IPt requires Pt = 53·10 ; I = 34·61 per cent.

Trimethylplatinic iodide dissolves freely in hot benzene or chloroform and crystallises well from either solvent.   On slow evaporation of its solution in benzene it separates in square, doubly refracting plates of an amber-yellow colour, which rapidly become opaque owing to loss of solvent of crystallisation.   It is readily soluble in cold ethyl bromide or methyl iodide, and from solutions in the former is deposited in hexagonal plates which apparently belong to the cubic

system. It is insoluble in water and very sparingly soluble in ether, alcohol, acetone, or light petroleum. The substance is not attacked in the cold by bromine or iodine, nor by concentrated acids or alkalis; alkali sulphides cause no darkening in colour. When heated with concentrated nitric acid it slowly dissolves, with elimination of iodine, and on evaporating the solution a white residue remains which explodes on further heating, giving a mixture of carbon and platinum.

On heating with concentrated sulphuric acid, the substance slowly dissolves, leaving a black residue which probably consists of platinum; part of the iodine is expelled by this treatment and the remainder is given off on evaporating and heating, a residue of platinum remaining. When heated alone, the compound decomposes with a slight explosion, leaving a sooty residue of carbon and platinum; when slowly heated in a melting-point tube a gradual decomposition occurs and appears to be complete below $250°$. On heating in a flame, the substance catches fire and burns with a smoky, lurid flame, leaving a residue of platinum.

Diamminotrimethylplatinic Iodide, $(CH_3)_3PtI(NH_3)_2$.

The difficulty with which ammonia acts on trimethylplatinic iodide led at first to the view that no combination could be induced between these two substances; more careful investigation showed, however, that the iodide combines with two molecular equivalents of ammonia in accordance with Werner's classification. On heating trimethylplatinic iodide with a mixture of benzene, alcohol, and concentrated ammonia on the water-bath and evaporating to dryness, white, crystalline scales are deposited. The substance thus produced is but slightly soluble in water, moderately so in benzene or ether, and dissolves very readily in alcohol, ethyl acetate, or acetone; it is practically insoluble in chloroform or light petroleum, and yields free ammonia on heating with potassium hydroxide:

0·2291 gave 0·1106 Pt. Pt $= 48·27$.

$C_3H_{15}N_2IPt$ requires Pt $= 48·58$ per cent.

It is noteworthy that whilst the diauric halogen compound forms a monoammino-derivative, $(C_2H_5)_2AuBr(NH_3)$ (Trans., 1907, **91**, 2065), the corresponding trialkylplatinic compound yields a diammino-derivative, $(CH_3)_3PtI(NH_3)_2$, in accordance with Werner's theory.

Trimethylplatinic Hydroxide, $(CH_3)_3Pt·OH$.

This substance is prepared by boiling trimethylplatinic iodide in moist acetone solution with freshly precipitated silver hydroxide; the conversion occurs but slowly under these conditions, and is greatly

expedited by addition of benzene, which dissolves the iodide and hydroxide and forms a separate layer of liquid floating on the acetone solution. After filtration and washing with water, the benzene solution is evaporated, when the hydroxide separates in almost colourless, transparent crystal plates, which rapidly become opaque in the air. The crude trimethylplatinic hydroxide obtained in this way is purified by crystallisation from benzene ; it is deposited in massive square tablets, which are colourless and transparent, but become opaque on washing with light petroleum owing to loss of solvent. The crystals are doubly refracting, and show straight extinction and a perfect cleavage parallel to their longer edges ; they contain benzene of crystallisation, but the proportion of this could not be ascertained owing to the rapidity with which efflorescence occurs on exposure to the air. On heating, the substance burns explosively, leaving a sooty residue of carbon and platium ; it was analysed by gently incinerating with hydriodic acid, after heating at 100° until all the benzene had been driven off :

0·1666 gave 0·1261 Pt. Pt = 75·69.

$C_3H_{10}OPt$ requires Pt = 75·83 per cent.

Trimethylplatinic hydroxide is fairly soluble in ether, alcohol, acetone, ethyl acetate, chloroform, or benzene, and crystallises from the last three solvents named with solvent of crystallisation, which is quickly lost in the air. From alcohol or chloroform solutions it separates in solvent-free and nearly colourless crystals ; these are transparent, highly refractive, rhombic dodecahedra belonging to the .cubic system. The substance is insoluble in water, alkalis, or light petroleum ; it is not attacked in the cold by mineral acids, but dissolves on warming with nitric acid. Concentrated sulphuric acid partly decomposes the hydroxide.

Trimethylplatinic Sulphate, $(Me_3Pt)_2SO_4,2H_2O$.

Dilute sulphuric acid has little action on trimethylplatinic hydroxide, but the sulphate is conveniently prepared by boiling equivalent quantities of trimethylplatinic iodide and silver sulphate with a mixture of moist acetone and benzene under a reflux condenser for several hours. After action has ceased, the solution is filtered and evaporated, when *trimethylplatinic sulphate* separates in small, colourless, rectangular plates, which are transparent and show straight extinction.

The salt is readily soluble in water, alcohol, or acetone, but practically insoluble in benzene, light petroleum, ether, or chloroform. It is most conveniently crystallised from water, but is difficult to purify owing to its ready solubility ; the substance thus obtained contains water of

crystallisation, which it apparently retains at 100°. The platinum was determined in material dried at 100° by slowly incinerating after addition of iodine and chloroform ; the sulphur was estimated by precipitation with barium nitrate solution :

0·2560 gave 0·1626 Pt.   Pt = 63·51.

0·3612   ,,   0·1333 $BaSO_4$. SO_4 = 15·18.

$C_6H_{18}O_4SPt_2,2H_2O$ requires Pt = 63·67 ; SO_4 = 15·70 per cent.

It was not found possible to make a combustion of the substance owing to its explosive decomposition on heating alone, and as it decomposes when heated sufficiently to drive off the water of crystallisation, a direct determination of the latter was not attempted.

Trimethylplatinic Nitrate.

Trimethylplatinic hydroxide dissolves fairly readily when warmed with concentrated nitric acid, or when boiled for some time with the diluted acid, forming a nitrate which is very soluble and difficult to crystallise, especially from the acid solution. The crystalline salt is more easily prepared by treating an aqueous solution of trimethylplatinic sulphate with an equivalent amount of barium nitrate, filtering from barium sulphate, and evaporating. It separates from the pure aqueous solution in colourless, crystalline plates, which are so markedly deliquescent that their analysis was not attempted. The crystals are thin, flat plates with replaced ends ; the large face is perpendicular to the acute bisectrix of a fairly large optic axial angle, the extinction is straight, and the double refraction is negative in sign.

Owing to their ready solubility in water, trimethylplatinic sulphate and nitrate form convenient sources from which to derive a number of more sparingly soluble salts of the new base.

Trimethylplatinic Chloride, $(CH_3)_3PtCl$.

Trimethylplatinic chloride is easily prepared by precipitating an aqueous solution of the nitrate or sulphate with potassium chloride or by dissolving the hydroxide in alcohol and evaporating to dryness after addition of hydrochloric acid. It is practically insoluble in water, dissolves very sparingly in acetone, alcohol, or ethyl acetate, and is moderately soluble in benzene or chloroform, although distinctly less so than is the iodide. The substance crystallises from chloroform solutions in colourless, rhombic dodecahedra, which belong to the cubic system and contain no solvent of crystallisation. The following analysis was made by gently heating the substance in presence of iodine and chloroform and subsequently igniting strongly :

0·1840 gave 0·1300 Pt.   Pt = 70·65.

C_3H_9ClPt requires Pt = 70·75 per cent.

Trimethylplatinic Cyanide, $(CH_3)_3Pt\cdot CN$.

On adding potassium cyanide to a solution of trimethylplatinic nitrate or sulphate, a white, flocculent precipitate is thrown down which is partly soluble in excess of the precipitant; the substance is insoluble in water, and too sparingly soluble in organic solvents to allow of its ready purification. It was not obtained in crystalline form, and was consequently not analysed. When boiled with sodium hydroxide, ammonia is evolved, but no hydrolytic product of the nature of a carboxylic acid could be isolated from the small quantity available for investigation.

Potassium Trimethylplatinic Platinocyanide, $K(Me_3Pt)Pt(CN)_4$.

The addition of potassium platinocyanide to an aqueous solution of trimethylplatinic nitrate causes the deposition of a slimy, yellow precipitate, which is very difficult to filter and wash. It is insoluble in water and the usual organic solvents with the exception of acetone and alcohol, in which it dissolves freely; on evaporation of its solutions in the latter solvents, it remains as an amorphous, resinous film of a greenish-yellow colour. On igniting a known weight of this substance with iodine, white fumes of potassium cyanide were evolved at a red-heat; after prolonged ignition over the blow-pipe, the residue was weighed as platinum:

0·1730 gave 0·1168 Pt.   Pt = 67·51.

$C_7H_9N_4KPt_2$ requires Pt = 67·42 per cent.

It thus appears that the precipitate formed by potassium platinocyanide in a solution of trimethylplatinic nitrate consists of a *potassium trimethylplatinic platinocyanide* of the composition

$$K_2Pt(CN)_4,(Me_3Pt)_2Pt(CN)_4.$$
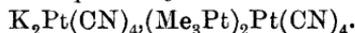
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