21. *Complexes of Octavalent Ruthenium and Osmium with Phosphorus Trifluoride.*

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The complexes $(MO_4)_2,PF_3$ and MO_4,PF_3 are formed by the tetroxides of ruthenium and osmium. Their preparations and properties are described and their relation with the few other compounds of the platinum metals with phosphorus halides is discussed.

Few complexes of phosphorus trifluoride are known, and they are restricted to Group VIII elements. They are the volatile $(PF_3)_2,PtCl_2$ and $(PF_3,PtCl_2)_2$ prepared by Chatt and Williams,[1] Moissan's PtF_2,PF_3,[2] and Wilkinson's $Ni(PF_3)_4$.[3] Of these only the first two were prepared by direct combination with phosphorus trifluoride. Moissan made PtF_2,PF_3 by passing phosphorus pentafluoride over platinum sponge at a dull red heat, and Wilkinson obtained the $Ni(PF_3)_4$ complex by treating the chlorine analogue either with antimony trifluoride or with phosphorus trifluoride under pressure. Chatt and Williams had no evidence of the formation of similar compounds by palladous chloride; indeed the only other phosphorus trihalide complexes reported are $IrCl_3,3PCl_3$,[4] $IrBr_3,3PBr_3$,[4] $PtCl_2,PCl_3$,[5] and $PtCl_2,2PCl_3$.[5]

Exploring the complexes of phosphorus trifluoride with Group VIII elements, we find that whereas neither metallic ruthenium and osmium nor their dioxides react with either phosphorus trifluoride or trichloride, both the trihalides combined with their tetroxides. Ruthenium tetroxide takes up phosphorus trifluoride at about −100° to give $(RuO_4)_2,PF_3$ and then, at 20°, combines with another molecule of the trifluoride to produce RuO_4,PF_3. Osmium tetroxide does the same, except that $(OsO_4)_2,PF_3$ must be heated to 70° before the further addition takes place. It is not possible to cause more phosphorus trifluoride to combine with the 1 : 1 complexes, nor could the reaction leading to their formation from the 2 : 1 complexes be reversed. All the compounds are black and extremely hygroscopic; they decompose without melting when heated at the ordinary pressure and, when kept under reduced pressure, give the metallic oxide and the trifluoride. These properties, and failure to find a liquid in which they dissolve without decomposition, prevented the determination of molecular weight.

By contrast, both phosphorus trichloride and tribromide reduce ruthenium tetroxide with vigour, sometimes explosively; but when the reactions are moderated by controlling the temperature, the black solids produced have compositions indicative of RuO_2,PCl_3 and RuO_2,PBr_3. Osmium tetroxide gives OsO_2,PCl_3. None of these MO_2 compounds can be made by direct addition to the dioxide.

Chatt and Williams advanced cogent reasons for believing that the bonding in their remarkably stable complexes is due to the acceptance of electrons from the filled *d* orbitals of the platinum into the empty *d* orbitals of the phosphorus. It is less certain that this back co-ordination happens with palladium, for palladous chloride cannot be attached to the trifluoride. Neither of the complexes described here has a stability approaching that of the platinum compounds, and it is reasonable to assume that another type of bonding operates. General expectation would be that phosphorus trifluoride should form complexes by direct donation of its lone pair. Both these tetroxides may be assumed to have a vacant *d* orbital and we suggest that this receives the lone pair from the phosphorus. Of the phosphorus tercovalent compounds, phosphorus trifluoride has the largest X–P–X angle, 104° (cf. PCl_3 101°, PBr_3 100°, PI_3 98°, PH_3 93°), which indicates that the lone-pair

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[1] Chatt and Williams, *J.*, 1951, 3061.
[2] Moissan, *Bull. Soc. chim. France*, 1891, 484.
[3] Wilkinson, *J. Amer. Chem. Soc.*, 1951, **73**, 5502.
[4] Strecker and Schurigen, *Ber.*, 1909, **42**, 1767.
[5] Schulzenberger, *Bull. Soc. chim. France*, 1872, **17**, 482.

orbital is narrower and reaches further out from the phosphorus atom in the trifluoride than in the other halides. This may contribute to the stability of these phosphorus trifluoride complexes; other factors must play a part, otherwise boron trifluoride would be expected to combine with phosphorus trifluoride. In the absence of structural data it is unprofitable to speculate on the arrangement of the units within the solids which have not been obtained sufficiently crystalline to give an *X*-ray pattern.

EXPERIMENTAL

Materials.—Ruthenium tetroxide was prepared by Martin's method:[6] ruthenium sponge was fused with potassium hydroxide and nitrate to give potassium ruthenate, which was dissolved in the minimum amount of water and treated with a mixture of equal parts of concentrated sulphuric acid and periodic acid from which the ruthenium tetroxide was distilled by heating on a water-bath. The oxide vapour thus obtained was dried by passage through " anhydrone " in a U-tube at 70°, followed by freezing on, and evaporation from, two separate lots of the same desiccant. This was done in a vacuum system from which the pure ruthenium tetroxide was distilled directly into the reaction apparatus, care being taken to prevent the vapour from coming into contact with tap grease or mercury, with both of which it readily reacts.

Osmium tetroxide was made by igniting the metal in a rapid stream of well dried oxygen. It also was transferred to the reaction apparatus in a vacuum, contact with tap grease being avoided.

Phosphorus trifluoride, prepared by the action of phosphorus trichloride on zinc fluoride,[1] was dried by slow passage through concentrated sulphuric acid followed by two traps at $-70°$.

Apparatus and Preparations.—The reactions were observed in a small vessel holding the solid tetroxide which formed part of a system of known volume, whose temperature could be controlled by a bath. Before the introduction of the reactants it was carefully dried by repeated changes of dry air and flaming out under a vacuum. The uptake of phosphorus trifluoride or other vapour was measured by means of a manometer.

Ruthenium compounds. A smooth reaction began at $-100°$ and a black solid was formed. The pressure decrease indicated a ratio $Ru : PF_3$ of 0·245 g. : 0·107 g., corresponding to $(RuO_4)_2,PF_3$. No further absorption of phosphorus trifluoride took place below 0°, but when the black material was warmed to about 20° the pressure again decreased without, however, observable change in the solid, indicating a ratio $Ru : PF_3$ of 0·245 g. : 0·213 g. for the *compound*, corresponding to RuO_4,PF_3 (Found: Ru, 40·80; F, 20·58. RuO_4,PF_3 requires Ru, 40·25; F, 22·56%). There was no trace of oxygen or phosphorus oxyfluoride after reaction was complete. The former, not being condensed by liquid oxygen, would have given a pressure observable on the manometer, and the latter would have condensed when the reaction bulb was subsequently cooled to $-70°$.

The 1 : 1 compound had an appreciable vapour pressure of phosphorus trifluoride at 20° and lost this gas when heated under a vacuum, reverting to ruthenium tetroxide. The change from the first to the second compound is irreversible. The second compound is extremely hygroscopic, being rapidly converted into a red liquid by atmospheric moisture. Hydrolysis then supervenes and black, hydrated ruthenium dioxide is precipitated. The typical odour of ruthenium tetroxide is evident, indicating the high valency of the compound.

Osmium compounds. Again a smooth reaction began at $-100°$ with the formation of a black solid. Pressure decrease indicated a ratio $Os : PF_3$ of 0·292 g. : 0·068 g. corresponding to $(OsO_4)_2,PF_3$. There was no further uptake of gas below 60°, at which temperature more phosphorus trifluoride was absorbed until the ratio $Os : PF_3$ of 0·292 g. : 0·13 g. was reached corresponding to OsO_4,PF_3. There was no observable change in the appearance of the solid *compound* (Found: Os, 53·5; F, 16·7. OsO_4,PF_3 requires Os, 55·6; F, 16·66%).

Attempts to make other complexes. Phosphorus trichloride condensed on ruthenium tetroxide and allowed to warm also gave a black solid which, as the temperature rose, was liable to change rapidly in colour and explode, possibly through the formation of an oxide of chlorine. When, however, the temperature was controlled or the reaction was carried out in carbon tetrachloride solution the solid was isolable. Both phosphorus and chlorine were present, and, though it varied a little, the average composition corresponded to RuO_2,PCl_3. Evidently phosphorus trichloride under suitable conditions reduces the tetroxide to the dioxide and forms complexes with the latter. Nevertheless it has not been possible to make such a compound directly from the dioxide. Osmium tetroxide, though not so strong an oxidising agent, was also reduced and appears to form the corresponding OsO_2,PCl_3 complex.

Phosphorus tribromide also reacted vigorously and exothermally with ruthenium tetroxide in carbon tetrachloride. The yellow phosphorus oxybromide produced was removed under a vacuum leaving a black residue containing ruthenium, phosphorus, and bromine and was probably a mixture of RuO_2 and RuO_2,PBr_3.

Rather surprisingly, phosphine did not react with osmium tetroxide below 70°, at which temperature there was a slight reduction but no evidence of the addition of phosphine. The effect on ruthenium tetroxide was not examined in view of its greater oxidising properties and a danger of explosion.

As expected of boron trifluoride, this acceptor molecule did not form a complex with RuO_4, OsO_4, or OsF_8 at any temperature between its b. p. ($-101°$) and 600°.

Analysis.—Fluorine. The analysis of these compounds for phosphorus and fluorine is difficult because they tend to lose phosphorus trifluoride on attack by fused or aqueous sodium carbonate or perchloric or nitric acids. The only satisfactory way of opening the complexes was fusion with metallic sodium. The resulting melt when dissolved in water and distilled with concentrated sulphuric acid gave a solution from which the fluorine could be precipitated as lead chlorofluoride. The phosphorus was always lost as phosphine.

Ruthenium and osmium. The first was generally determined by reducing the complex to the metal by heating in hydrogen, and sometimes by precipitating the dioxide by adding sodium carbonate to an aqueous solution of the compound. The gelatinous precipitate was separated, dried, and reduced in hydrogen to the metal. Each method gave consistent results which agreed with the other. Osmium was determined by reducing the preparation in hydrogen and allowing the metal to cool in a stream of carbon dioxide. In this way more than a trace of superficial oxidation was avoided.

Acknowledgment is made to Mesrs. Johnson Matthey for the loan of the precious metals and to the Department of Scientific and Industrial Research for a maintenance grant (M. L. H.).

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[*Received, July 26th,* 1957.]