

677. *The Nature of the Co-ordinate Link. Part IV.* Complex Formation by Phosphorus Trifluoride.*

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It is considered that the *trans* influence of certain ligands, notably ethylene, carbon monoxide, the nitro-group, and to a lesser extent trialkylphosphines, in platinous complexes, is due to a mechanism of co-ordination involving in some special manner electrons from *d*-orbitals of the metal, and consequently that phosphorus trifluoride, where the strongly electronegative fluorine should enhance this effect as compared with the trialkylphosphines, should show considerable resemblance to carbon monoxide in its complexes.

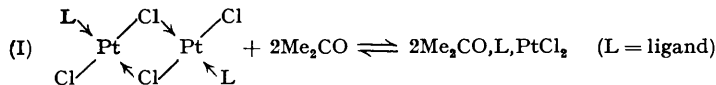
This was confirmed; with boron trifluoride and aluminium salts where *d*-electrons are not available, no complex formation takes place, but with platinous chloride were obtained two uniquely volatile stable compounds, $(PF_3)_2PtCl_2$ and $(PF_3)_2PtCl_2$, very similar to the corresponding carbonyl complexes. It was shown that either the mononuclear carbonyl and phosphorus trifluoride compounds have a *cis*-configuration or that their benzene solutions contain an exceptionally high proportion of the *cis*-isomer in equilibrium with the *trans*-compound, by dipole-moment measurement. With aurous and cuprous chlorides, phosphorus trifluoride behaves very much as does carbon monoxide, also it replaces carbon monoxide from nickel carbonyl without altering the character of the complex. It is suggested that there are two methods of co-ordination: (1) the classical co-ordinate link; and (2) a method of bonding also involving in some special manner *d*-electrons in the metal atom. The second method is essential for stable complex formation by carbon monoxide, ethylene, phosphorus trifluoride, and such ligands. Whether (2) is partial double bonding, the most obvious explanation, is still an open question. The bond (2) appears to be much less polar than (1), and to require for its formation the presence of vacant or potentially vacant orbitals in the donor atom as well as filled *d*-orbitals in the metal atom.

In a previous communication it was suggested that filled *d*-orbitals in a metal atom played a much more important part in general co-ordination than had hitherto been supposed, particularly that in the co-ordination of olefins to give covalent complex compounds, as in their co-ordination to platinous salts, the presence of filled *d*-orbitals on an energy level close to that of the outer shell *s*- and *p*-orbitals appears to be absolutely essential (Chatt, *J.*, 1949, 3340).

trans Influence and the Use of d-electrons in Co-ordination to Platinum(II).—Olefin complexes are not unique amongst platinous complexes; although their properties are somewhat different from those of the platinous amines, they resemble closely those of the analogous carbonyl compounds. This correspondence has been noted by most recent workers in this field (*e.g.*, Anderson, *J.*, 1934, 972), and in looking for a quantitative measure of this similarity it seemed that *trans* influence could be used. Chernyaev (*Ann. Inst. platine, U.R.S.S.*, 1926, 4, 261) established that certain groups [*e.g.*, $-NO_2$, $-CN$, $SC(NH_2)_2$] attached to platinum in platinous complexes produce considerable labilisation of the group in the *trans*-position to themselves, so that the *trans*-group is most easily eliminated during chemical reactions. The greater the *trans* influence the greater the labilising effect and the ease of elimination of the *trans*-substituent. The order of *trans* influence of various groups has been established only qualitatively, but ethylene and carbon monoxide show it to a marked degree (Hel'man, "Complex Compounds of Platinum with Unsaturated Molecules," *Soviet Acad. Sci.*, 1945; see also Chatt, *Ann. Reports*, 1946, 43, 120), whereas ammonia and water have no appreciable effect. The effect is also displayed by the tertiary phosphines and organic sulphides, but in our experience the *trans* influence of tri-*n*-propylphosphine is inferior to that of ethylene. Tri-*n*-propylphosphine has a greater *trans* influence than *p*-toluidine and ammonia because *trans*- $[C_2H_4, NH_3, PtCl_2]$ and *trans*- $[C_2H_4, p-C_7H_7, NH_2, PtCl_2]$ are stable compounds, whereas *trans*- $[C_2H_4, Pr^i_3P, PtCl_2]$ loses part of its ethylene at room temperature and has never been isolated (Chatt, *J.*, 1951, 652). This latter fact may suggest that tri-*n*-propylphosphine has a greater *trans* influence

* Part III, *J.*, 1951, 2532.

than ethylene because it is the ethylene which is eliminated, but it must be remembered that in any circumstances ethylene is only weakly bound to platinum, whereas the trialkylphosphines are amongst the more strongly bound ligands. Ethylene has in fact a much greater *trans* influence than tri-*n*-propylphosphine, a measure of which is provided by the stability of the halogen bridges in the bridged complexes, type (I). These complexes have normal molecular weights in boiling benzene but dissociate reversibly in boiling acetone, doubtless because the chlorine of the bridge is replaced by acetone in the same way, but to a much less extent than was shown to occur in the platinum series (Chatt, *J.*, 1950, 2301).



We find that when L is tripropylphosphine dissociation occurs to the extent of only *ca.* 45% as compared with *ca.* 70% when L is ethylene, both solutes at 0.03M. concentration. With sufficiently accurate molecular-weight determinations, this dissociation should provide a direct method for the assessment of bridge stability and of *trans* influence over the important range covered by the tertiary phosphines and similar molecules. We are attempting to make these measurements, but record this preliminary result because Syrkin (*Bull. Acad. Sci., U.R.S.S., Classe sci. chim.*, 1948, 69) considers alkylphosphines to show the greatest *trans* influence. He quotes no experimental evidence of this, but it is an important point in his hypothesis of *trans* influence.

Qualitatively, from numerous papers from Chernyaev's pupils, it appears that the best arrangement, in order of increasing *trans* influence, for a number of common ligands, is $\text{H}_2\text{O} < \text{OH} < \text{NH}_3 < \text{F} < \text{Cl} < \text{Br} < \text{I} \sim \text{R}_3\text{P} \sim \text{R}_2\text{S} < \text{SC}(\text{NH}_2)_2 < \text{NO}_2 < \text{CO} \sim \text{C}_2\text{H}_4 < \text{CN}$.

It appears significant that those groups showing greatest *trans* influence are those which combine only weakly with the salts of aluminium, magnesium, and other elements having no *d*-electrons. On the other hand, those near the beginning of the above series combine most strongly with the lighter group 2 and 3 elements but not markedly with the transition metals and others which have *d*-electrons. Also those groups showing highest *trans* influence are those which Pauling considered to co-ordinate by double bonds making use of filled *d*-orbitals of the metal atom for π -bond formation ("Nature of the Chemical Bond," pp. 231—238, Cornell, Univ. Press, 1939; see also Syrkin and Dyatkina, *Acta Physicochemica, U.R.S.S.*, 1945, 20, 137, 273; "Structure of Molecules," English Translation, p. 358—393, Butterworths).

Syrkin and Dyatkina also consider that double bonding, $\text{P}=\text{Pt}$, contributes to the strength of binding in the trialkylphosphine series of platinum complexes (*J. Gen. Chem. U.S.S.R.*, 1946, 16, 345; *Bull. Acad. Sci. U.R.S.S., Classe sci. chim.*, 1948, 75). Calvin and Melchior (*J. Amer. Chem. Soc.*, 1948, 70, 3270) in their study of chelate copper complexes also consider *d*-orbitals to contribute to the stability of suitably substituted chelate rings. We think that bonding which requires the use of the *d*-electrons in some special manner, perhaps in π -bonding, is the cause of *trans* influence; and the qualitative experiments with phosphorus trifluoride as ligand had the object of testing this idea.

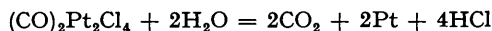
It should be noted that Grinberg (*Chem. Abs.*, 1945, 39, 252) has suggested an exactly opposite explanation of *trans* influence. He suggested that the weakening of the bond *trans* to the groups of high *trans* influence is due to the mobility (or polarizability) of electrons in these groups, and the ease with which they move towards the platinum atom. Our results are completely opposed to this idea.

It is obvious that if *trans* influence is due to the use of one or more filled *d*-orbitals in the platinum atom to bind by π -bonding the donor atom, then replacement of the alkyl groups in trialkylphosphines (R_3P) by more electronegative groups, thus increasing the drift of electrons in the *d*-orbitals towards the phosphorus atom, should cause the phosphines to be placed increasingly nearer to the right in the above *trans*-influence series as electronegativity of R is increased. We chose fluorine atoms as extremely electronegative groups, and hoped to find that phosphorus trifluoride would lie so far along the *trans*-influence series that its complexes would be very similar to those of carbon monoxide. This prediction was amply confirmed (see also Chatt, *Nature*, 1950, 165, 637).

The Co-ordination Chemistry of Phosphorus Trifluoride.—Phosphorus trifluoride complexes with metallic salts do not appear to be known, except that Moissan (*Bull. Soc. chim.*, 1891, [3], 5, 454) obtained a substance F_3PPt , by reaction of phosphorus pentafluoride with spongy platinum, considered to be analogous to Schützenberger's $\text{PCl}_3, \text{PtCl}_2$ (*ibid.*, 1872, 17, 482) which must be dimeric.

When phosphorus trifluoride was passed through a plug of powdered platinum chloride at 200–220°, two substances immediately started to sublime into the colder part of the tube. With phosphorus trifluoride in excess, there was obtained bis(trifluorophosphine)dichloro-platinum, $(PF_3)_2PtCl_2$, which we shall call the dichloride, in colourless crystals melting to a very pale yellow liquid at 102°. In a slow stream of the gas were obtained orange yellow crystals of composition PF_3PtCl_2 , doubtless dimeric dichlorobis(trifluorophosphine)- $\mu\mu'$ -dichlorodiplatinum with the structure (I; L = PF_3), which we shall call the tetrachloride, together with the dichloride which is considerably more volatile. The tetrachloride melts to a red liquid at 155–156°. These complexes closely resemble the corresponding carbonyl platinum halides which were hitherto the most volatile platinum complexes known. The phosphorus trifluoride complexes are, however, more stable and more volatile. The dichloride can be boiled under reflux at atmospheric pressure at about 240° but loses phosphorus trifluoride rapidly, passing into the tetrachloride with consequent rise in boiling point until at 285° decomposition with gradual separation of solid occurs. The tetrachloride can be distilled completely at 15–20 mm. pressure without any decomposition.

The P–F bond is unfortunately too easily hydrolysed to allow of a thorough study of the chemical properties of the chlorides. They dissolve in water to give clear solutions (colourless and orange-yellow, respectively) in which the platinum is so firmly bound that it cannot be precipitated from acid solution by metallic magnesium. These solutions probably contain the phosphorus acid derivatives described by Schützenberger (*ibid.*, 1872, 17, 482) and were not further examined. This hydrolysis has of course, no parallel in the carbonyl platinum halide series where another type of hydrolysis occurs with liberation of platinum (Schützenberger, *ibid.*, 1870, 14, 17) :



The white simple complex compounds, $(PF_3)_2PtCl_2$ and $(CO)_2PtCl_2$, are less soluble in benzene and carbon tetrachloride than the corresponding bridged compounds, $(PF_3PtCl_2)_2$ and $(COPtCl_2)_2$. These observations suggested that they have *cis*-configurations which were supported by the approximate values = 4.4 D and = 4.65 D, respectively, found for their dipole moments (1 D = 10^{-18} e.s.u.). When we consider that the Ni–Br bond appears to have a moment of about 2.5 D (Jensen and Nygaard, *Acta Chem. Scand.*, 1949, 3, 476), the greater part of these moments would be accounted for by the Pt–Cl bonds, and if they are the true moments of these molecules then the F_3P –Pt and OC –Pt groupings must be almost non polar.

The value 4.4 D is also to be contrasted with the values of the order 11 D found by Jensen for *cis*-bis(trialkylphosphine)dichloroplatinums (*Z. anorg. Chem.*, 1936, 229, 250). This great difference cannot be explained by the simple replacement of the alkyl groups by fluorine, which would lower the dipole moment by about 2–3 D so we would expect a moment of about 8–9 D for *cis*- $(PF_3)_2PtCl_2$ if the P–Pt link is the same as that in alkylphosphine-platinum complexes. Thus it appears that there is a large neutralisation of the Pt–P co-ordinate link by the opposing drift of *d*-electrons in the phosphorus trifluoride complexes. It is interesting too that the carbonyl and phosphorus trifluoride complexes have moments so closely similar.

However, the dipole moments could also be explained if we suppose that the solid *cis*-complexes isomerise spontaneously, and immediately in solution, to an equilibrium mixture of the *cis*- and the *trans*-isomers. We have no evidence of this occurring, but even if it does occur and the moment of pure *cis*- $(PF_3)_2PtCl_2$ is 8–9 D the equilibrium mixture must contain about 30% of *cis*-isomer. This is ten times the quantity of *cis*- $(PPr_3)_2PtCl_2$ observed for the same equilibrium in the tri-*n*-propylphosphine series and three times that in the triethylphosphine series (Chatt and Wilkins, Part V, unpublished).

Either of the above explanations shows that the stability of the *cis*-isomer relative to the *trans*-compound has been greatly increased by replacing alkyl groups by fluorine atoms. This fact is significant for the view that *d*-orbitals in the platinum atom take part in co-ordination, because *d*-orbitals are in planes at right angles to each other (see Coulson, *Quart. Reviews*, 1947, 1, 146). In whatever manner they are used in the binding, it is only in the *cis*-isomer that different *d*-orbitals are available to bind each molecule of the phosphine. In the *trans*-isomer the same *d*-orbitals would have to bind both phosphorus atoms to the platinum atom leading to weaker binding. The observed greater stability of the *cis*-isomer is thus good evidence that *d*-orbitals play a more significant part in binding phosphorus trifluoride than in the binding of alkyl phosphines to platinum.

With cuprous and aurous chloride, phosphorus trifluoride behaved qualitatively in a similar manner to carbon monoxide, but the complexes appeared slightly less stable; they were too

unstable for analysis. We obtained no complex with palladous chloride. The only carbonyl, $(\text{CO})_2\text{Pd}_2\text{Cl}_4$, is known to be very unstable (Manchot and König, *Ber.*, 1926, **59**, 883).

Attempt to prepare $\text{Ni}(\text{PF}_3)_4$.—It was expected that this compound would be volatile and similar to nickel carbonyl, but attempts to combine phosphorus trifluoride with freshly reduced nickel at atmospheric pressure and in sealed Carius tubes at pressures up to the bursting point at 100° for 6 hours gave no evidence of combination (cf. Mond, *J.*, 1890, **57**, 749). Nor would phosphorus trifluoride replace carbon monoxide from nickel carbonyl at room temperature. By recycling nickel carbonyl (b. p. 43° ; 100 c.c.) with phosphorus trifluoride through a heated tube for 100 hours, fractions boiling up to 68° were obtained. The high-boiling fractions from a number of experiments analysed in the range $(\text{CO})_2\text{Ni}(\text{PF}_3)_2$ — $(\text{CO})\text{Ni}(\text{PF}_3)_3$, and were liquids even at -78° . As considerable decomposition to metallic nickel occurred in the hot tube during the initial stages of the experiment, but not towards the end, the substituted nickel carbonyl is obviously more stable than nickel carbonyl itself. Nevertheless, because of its higher boiling point, considerable decomposition occurred during the fractionation of the product, and a pure fraction was not isolated. Although most donor substances, e.g. pyridine and triphenylphosphine, can replace two molecules of carbon monoxide from nickel carbonyl to yield solid derivatives, it was now obvious that phosphorus trifluoride can replace more than two, without producing a change in the character of the complex.

This partial replacement has an exact parallel in the replacement of carbon monoxide by cyanide ion. Although $\text{K}_4\text{Ni}(\text{CN})_4$ can be obtained by reduction of $\text{K}_2\text{Ni}(\text{CN})_4$ with potassium (Eastes and Burgess, *J. Amer. Chem. Soc.*, 1942, **64**, 1187) attempts at direct replacement lead to a mixture with maximum replacement of only three carbon monoxide molecules (Burg and Dayton, *J. Amer. Chem. Soc.*, 1949, **71**, 3233). Hieber (*Z. Naturforsch.*, 1950, **5b**, 129) also finds that only three molecules of carbon monoxide can be replaced directly by methyl isocyanide, but $\text{Ni}(\text{MeNC})_4$ was obtained indirectly. The increasing stability as carbon monoxide is replaced by phosphorus trifluoride indicated that $\text{Ni}(\text{PF}_3)_4$ would probably be obtained by a suitable indirect method. At this stage of the research, we learned that J. W. Irvine and G. Wilkinson of the Massachusetts Institute of Technology had prepared $\text{Ni}(\text{PCl}_3)_4$, a non-volatile solid (personal communication, to be published in *Science*, 1951), and later that Wilkinson had obtained $\text{Ni}(\text{PF}_3)_4$ from this chloride by reaction with antimony trifluoride and also by replacement of the phosphorus trichloride by phosphorus trifluoride under pressure (personal communication). It is a liquid, boiling without decomposition at 71° and melting at -54° . The analogy between phosphorus trifluoride and carbon monoxide in their behaviour with the transition metals and salts thus appears to be extremely close.

If co-ordination occurs only by the classical co-ordinate link we would not expect phosphorus trifluoride to form stable complexes because the tendency to donate the lone pair will be greatly reduced by the inductive effect of the fluorine atoms. We therefore attempted to prepare complexes with aluminium chloride and with aluminium bromide. Here there are no filled *d*-orbitals in the metal atom and no complex formation took place either when phosphorus trifluoride was passed over heated aluminium chloride or through a solution of aluminium bromide in cyclohexane. Boron trifluoride is one of the strongest acceptor molecules known, yet Booth and Walkup (*J. Amer. Chem. Soc.*, 1943, **65**, 2334) showed that no combination whatsoever took place between it and phosphorus trifluoride at temperatures down to the freezing points of mixtures of the gases. Here phosphorus trifluoride is behaving similarly to ethylene, which forms its most stable complexes with platinumous chloride, yet shows no association whatsoever with trimethylborine (Chatt, *J.*, 1949, 3343).

Phosphorus trichloride is closely similar in behaviour to phosphorus trifluoride, but, because of the more electropositive character of chlorine as compared with fluorine, the lone pair in phosphorus trichloride is not so inert, and an unstable complex $\text{BF}_3\cdot\text{PCl}_3$, decomposing at -6° , has been described (Baumgarten and Bruns, *Ber.*, 1947, **80**, 517). The well-known complexes with platinumous chloride, $(\text{PCl}_3)_2\text{PtCl}_2$ and $(\text{PCl}_3)_2\text{Pt}_2\text{Cl}_4$, are formed at 250° and, like the fluoro-complexes, have considerable thermal stability (Schützenberger, *Bull. Soc. chim.*, 1872, **17**, 482); also Jensen (*Z. anorg. Chem.*, 1937, **231**, 365) concludes from dipole-moment measurements that $(\text{PCl}_3)_2\text{PtCl}_2$ has a *cis*-configuration.

We are thus left with little doubt that the use of filled *d*-orbitals is essential for stable complex formation by ligands such as phosphorus trifluoride, carbon monoxide, ethylene, etc., which have a high *trans* influence, and that platinum probably owes its unique complex chemistry to a mechanism of co-ordination in which the use of filled *d*-orbitals is essential. There appear to be two distinct methods of co-ordination: (1) by the classical co-ordinate link, covalent or ion dipole, used in complex formation by compounds of boron, aluminium, magnesium,

etc., and (2) by a mechanism, essentially covalent, involving also filled d -orbitals of the acceptor atom. The second mechanism leads to a much less polar link than the first and is displayed particularly by platinous salts and complexes in which the metals display zero valency, but to a lesser extent by other metals having filled d -orbitals. It is also most marked when these metals are in a low valency state or in the last complete series of the Periodic Table, presumably because electrons from d -orbitals are then most readily available.

This second mechanism, which appears to be related to *trans* influence, is easiest visualised as double bonding, but its nature is still an open question. The original evidence for double bonding in the carbonyls and such complexes, based on short metal-ligand bond distances, has been severely criticised by Wells (*J.*, 1949, 55). In the carbonyl complexes, a double metal-carbon bond requires that the C-O bond should also be double, and in the metal carbonyls the C-O bond length (1.15 Å) which is only slightly altered from that in carbon monoxide (1.13 Å) (Sheline, *J. Amer. Chem. Soc.*, 1950, **72**, 5761), is very close to that in keten (1.17 Å) (Beach and Stevenson, *J. Chem. Phys.*, 1938, **6**, 75; see also, Long and Walsh, *Trans. Faraday Soc.*, 1947, **43**, 342); also those ligands which show greatest *trans* influence are those that have vacant orbitals, *e.g.*, the $3d$ in phosphorus trifluoride, or potentially vacant orbitals, *e.g.*, $2p$ in the nitro-group and carbon monoxide, and which could be used for π -bond formation with a filled d -orbital of the metal atom.* The chemistry of platinum complexes accords with this view, only if such π bonding also leads to a marked weakening of the σ bond in the *trans*-position, because all groups, even amines where no similar N-Pt double bond is possible, are subject to *trans* influence by the carbon monoxide type of ligand. The behaviour of phosphorus trifluoride as a ligand also rules out any suggestion that *trans* influence is a purely inductive effect, because the inductive effect of the fluorine atoms should lead to an increase in the strength of attachment of the other three ligands to the platinum, not to a decrease, in the attachment of the *trans*-ligand. Work is continuing to establish with more certainty whether or not the second method of co-ordination is in fact by double bonding.

EXPERIMENTAL.

Dissociation of Chlorine-bridged Platinous Complexes in boiling Acetone.—The apparent molecular weights of dichlorobis(tri-*n*-propylphosphine)- $\mu\mu'$ -dichlorodiplatinum and dichlorodiethylene- $\mu\mu'$ -dichlorodiplatinum (I; L = Pr₃P and I; L = C₂H₄) were determined by using a semimicro Swietoslowski apparatus (5 c.c.). The accuracy is only sufficient to give the order of the dissociation constant (K), but leaves no doubt that the ethylene complex is much more dissociated than the propylphosphine complex. Unchanged materials were recovered from the acetone solutions, thus proving that the dissociation does not occur at the metal-ligand bond. If this had occurred ethylene would have been lost rapidly from the boiling solution with deposition of insoluble platinous chloride and an apparently very large molecular weight would have been found.

(Pr ₃ PPtCl ₂) ₂ ; $M = 853$.				(C ₂ H ₄ PtCl ₂) ₂ ; $M = 588$.			
Molar concn.	Apparent M	% dissocn.	10 ² K	Molar concn.	Apparent M	% dissocn.	10 ² K
0.0157	555	53.8	3.9	0.0168	340	73.0	13.3
0.0268	571	49.4	5.2	0.0285	337	74.5	24.7
0.0306	591	44.3	4.35	0.0345	357	65.1	16.7
0.0316	591	44.3	4.5	0.0482	353	66.6	25.6
		Average	4.5			Average	20

Preparation of Phosphorus Trifluoride.—Zinc fluoride was dried at 140–150° for at least 12 hours, and phosphorus trichloride dropped (1 drop in 3 seconds) on to the dry powder (50–60 g.). There was an induction period of about 5 minutes, and care was necessary not to flood the zinc fluoride or the reaction may not start. When the reaction had started it was controlled by ice cooling, and the rate of flow of phosphorus trifluoride by the rate of addition of the trichloride. Finally it was necessary to warm the mixture to complete the reaction. About 40 c.c. of phosphorus trichloride were required and a brisk stream of the trifluoride was evolved for 1½ to 2 hours. We found it best to work on this scale, and if a faster stream of trifluoride is required, to run a number of preparations in parallel. Zinc fluoride was used rather than the more usual arsenic trifluoride because it is commercially available. The trifluoride was passed through two traps cooled in solid CO₂-acetone and a sulphuric acid bubbler before use.

Preparation of Bis(trifluorophosphine)dichloroplatinum, (PF₃)₂PtCl₂ (Dichloride).—Powdered platinous chloride (0.7 g.) was loosely packed between asbestos plugs in a Pyrex tube (*ca.* 6 mm. bore) and warmed in a stream of dry nitrogen to remove all moisture. The nitrogen was then replaced by phosphorus trifluoride and the temperature raised to 200–220°. Orange and white crystals sublimed into the

* [Added, Oct. 1st, 1951.] The necessity for vacant orbitals is well illustrated by Wilkinson's observation (*Nature*, 1951, **168**, 514) that PF₃, but not NF₃, combines with hæmoglobin in a manner similar to that in which CO combines. The inertness of NF₃ to hæmoglobin is attributed to the absence of $2d$ -orbitals.

cooler part of the tube, and, when all the platinous chloride had reacted leaving only a small black residue, the sublimate was resublimed in an excess of phosphorus trifluoride into a part of the tube between two constrictions where the *dichloride* condensed in pure white crystals. The tube was allowed to cool, the phosphorus trifluoride driven out by dry nitrogen, and the part of the tube containing the product (0.72 g.) sealed off at both ends to prevent ingress of moisture. This had m. p. 102°, melting to a faintly yellow liquid which reddened on further heating until it boiled at 240° in dry nitrogen at atmospheric pressure. There was rapid loss of phosphorus trifluoride. As boiling continued, the temperature gradually rose to 285° at which temperature decomposition with deposition of dark-coloured solids was also occurring (Found: Cl, 16.1; Pt, 43.9. Cl₂F₆P₂Pt requires Cl, 16.0; Pt, 44.15%). The dichloride is slightly soluble in dry benzene, and hydrolyses rapidly in air to give a deliquescent substance. Platinum could not be precipitated from the solution in water by magnesium metal, but chlorine was estimated gravimetrically. In the determination of platinum the solution was oxidised by boiling it with a few c.c. of aqua regia, taken to dryness twice with 20% hydrochloric acid, and platinum precipitated with magnesium.

Preparation of Dichlorobis(trifluorophosphine)-μ'-dichlorodiplatinum, (PF₃)₂Pt₂Cl₄ (Tetrachloride).—The mixed sublimate obtained as in the previous preparation was collected in a U-tube containing platinous chloride (0.8 g.), and the gaseous phosphorus trifluoride replaced by dry nitrogen. The solid was then melted on to the platinous chloride, and the liquid maintained at just above its freezing point for 3 hours; this necessitated a gradual rise in temperature. Any white solid subliming was melted and run back into contact with the platinous chloride. The tube was then sealed half-way down the limb from which the sublimate had entered, and the liquid gently refluxed with the platinous chloride at 100 mm. pressure until no further reddening of the liquid occurred (15–30 minutes). The red substance was now sublimed from the platinous chloride at 15 mm. pressure, and the orange-red *tetrachloride* separated from the residual more volatile dichloride by repeated fractional sublimation at 15–20 mm. pressure. It had m. p. 155–156°, b. p. ca. 290° (decomp.) (yield 1.1 g.) (Found: Cl, 19.4; Pt, 55.5. Cl₄F₆P₂Pt₂ requires Cl, 20.0; Pt, 55.1%). In air it deliquesced to a yellow solution.

Dipole Moments of (PF₃)₂PtCl₄ and (CO)₂PtCl₂ in Benzene.—These were determined by using a heterodyne beat apparatus based on that of Hill and Sutton (see *J.*, 1949, 2313) in a rhodium-plated cell identical with that described by Jenkins and Sutton (*J.*, 1935, 609). Owing to the low solubility and marked sensitivity to moisture of these materials only approximate moments, sufficiently accurate for our present purpose, were obtained from the dielectric-constant (ϵ) measurements. An allowance of 10% of the total molar polarisation (P_m) was made for the electron (P_e) and atom polarisations (P_a) (cf. Jensen, *Z. anorg. Chem.*, 1935, 225, 109). Moments were calculated by using the formulæ (cf. Jensen, *Acta. Chem. Scand.*, 1949, 3, 479):

$$P_m - P_a - P_e = 90\% P_m = \frac{900}{C} \left[\frac{\epsilon_{\text{soln.}} - 1}{\epsilon_{\text{soln.}} + 2} - \frac{\epsilon_B - 1}{\epsilon_B + 2} \right]$$

$$\mu = 0.01273 \sqrt{(P_m - P_a - P_e)T}$$

Measurements were made at 25°. The dielectric constant of pure benzene (ϵ_B) was assumed to be 2.273.

	Molar concn.	$\epsilon_{\text{soln.}}$	P_m	μ
(PF ₃) ₂ PtCl ₂	0.004697	2.285	426	4.4 ± 0.5
	0.004868	2.287	472.5	
	0.010743	2.3025	448	
(CO) ₂ PtCl ₂	0.004647	2.287	491	4.65 ± 0.5
	0.006097	2.292	508.5	

Reaction of Phosphorus Trifluoride with Cuprous Chloride.—Attempts to cause cuprous chloride to react with phosphorus trifluoride in the same way as platinous chloride at temperatures up to 340° were unsuccessful. Phosphorus trifluoride was passed through a suspension of cuprous chloride in dry chloroform; a slow reaction took place with formation of a brown solution, which was decanted from unreacted cuprous chloride, and warmed slightly; it became colourless with evolution of phosphorus trifluoride and separation of cuprous chloride. No complex was isolated (cf. Kharasch and Isbell, *J. Amer. Chem. Soc.*, 1930, 52, 2918, for the corresponding behaviour of carbon monoxide).

Reaction of Phosphorus Trifluoride with Aurous Chloride.—When phosphorus trifluoride was passed through a mixture of auric and aurous chloride at temperatures up to 150°, reduction to metallic gold was the main reaction, but at ca. 120° a small quantity of white volatile solid was obtained; it was too unstable for analysis. Pure aurous chloride behaved similarly, the volatile solid being obtained at 110°. Kharasch and Isbell (*loc. cit.*) also noted that carbon monoxide reacted only over a short temperature range about 110°.

When phosphorus trifluoride was passed through a benzene suspension of aurous chloride, a colourless solution was obtained which, on evaporation to dryness at 15 mm. pressure, deposited a white solid. This solid was sensitive to moisture and gradually deposited metallic gold, but is doubtless analogous to COAuCl similarly obtained by Kharasch and Isbell (*loc. cit.*).

Attempt to combine Phosphorus Trifluoride with Freshly-reduced Nickel.—Nickel monoxide (1 g.) in a Carius tube was reduced with hydrogen at 400° and the tube evacuated to 10⁻⁶ mm. pressure. Phosphorus trifluoride gas (2 l.) was condensed into the tube, which was then sealed and heated to 100° for 6 hours (pressure ca. 35 atmos.). When the tube was cold the gases were frozen (liquid nitrogen), the tube opened, and the gases escaping as it warmed were passed through a glass tube at 400°. These contained no volatile nickel compound as was evident from the absence of a nickel mirror or other stain on the hot glass. No liquid remained in the Carius tube and the nickel showed no sign of any reaction.

Reaction of Phosphorus Trifluoride with Nickel Carbonyl.—Phosphorus trifluoride was passed through nickel carbonyl (100 c.c.) at 40°, then through an Liebig condenser with an 18' steam-heated jacket.

The vapours were condensed (solid CO_2 -acetone trap), and the condensed product returned to the nickel carbonyl bubbler every 6 hours. The rate of flow was such that about half the carbonyl was carried through in that time. Some nickel was deposited as the vapours entered the hot condenser, but after *ca.* 70 hours this decomposition ceased. The product, which condensed to a solid during the early part of the experiment, now condensed as a liquid. After 100 hours, 65 c.c. of liquid (Ni, 17.7%) remained. This was fractionated, a modified Podbielniak still being used, but considerable decomposition occurred and no definite fractions were obtained. The highest-boiling fraction (3–4 c.c.), b. p. 66–67°, was analysed (Found: Ni, 16.3, 16.2. $\text{COF}_2\text{P}_3\text{Ni}$ requires 16.75%). The analysis thus corresponds to the replacement of three molecules of carbon monoxide, but we have no evidence from the boiling-point curve that this is a pure *substance*. Many similar experiments were tried without getting greater replacement.

Attempt to Combine Phosphorus Trifluoride with Aluminium Halides.—Phosphorus trifluoride was passed over freshly sublimed aluminium chloride at temperatures up to 250°. No evidence of combination was obtained and the sublimate, thus obtained in a stream of phosphorus trifluoride, contained no phosphorus. Aluminium bromide, obtained by cautious addition of bromine to aluminium turnings, was dissolved in dry *cyclohexane* and phosphorus trifluoride passed through. No precipitate or evidence of combination was obtained, although other donor substances, *e.g.* dry pyridine, gave an immediate precipitate with such a solution.

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