

# Tertiary Phosphine Complexes of the Platinum Metals

## PRINCIPLES OF THEIR REACTION MECHANISMS AND USES IN HOMOGENEOUS CATALYSIS

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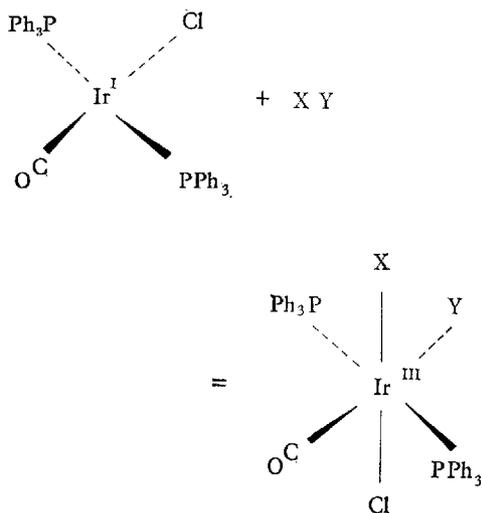
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Complexes of transition metals with tertiary phosphines (and similar complexes with arsines and stibines) both non-chelating, for example,  $(C_2H_5)_3P$  or chelating, for example,  $(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2$  (diphos), have been studied since Hofmann's first preparation of triethylphosphine, arsine and stibine platinum and gold complexes in 1857. An extremely wide range of compounds of most of the transition metals, often in several oxidation states, is now known (1).

Until a few years ago, when some of the complexes began to be of interest as activation for small molecules and as catalysts in organic synthetic reactions, most of the studies concentrated on new types of complexes and especially on the use of phosphine ligands for stabilising low oxidation states of metals, for example,  $Ni(CO)_2(PPh_3)_2$  or  $Mo(diphos)_3$ , and for allowing the stabilisation of rather labile or reactive groups such as H,  $CH_3$ ,  $C_6H_5$  bound to metals as, for example, in  $(Et_3P)_2PtCl(CH_3)$ . This stabilising influence arises from the property of the phosphines to adjust energy levels in the metal atoms of complexes through the  $d_\pi-d_\pi$  bonding capacity of the phosphorus atom. Such  $R_3P$  compounds behave not only as simple donors from electron density of the lone pair on phosphorus but also as acceptors of electron density from electrons in filled orbitals of the metal into vacant  $3d$  orbitals of the phosphorus atom. Phosphines thus fall in that class of ligands, such as carbon monoxide, which have both donor and acceptor properties and which are generally

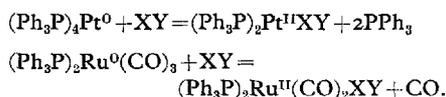
referred to as  $\pi$ -acids. Recent nuclear magnetic resonance studies of  $^{183}W-^{31}P$  coupling constants in phosphine complexes of tungsten, together with infra-red spectroscopic work, have provided sound evidence for the reality of such metal-phosphorus  $\pi$ -bonding (2).

Fairly recently it was recognised that certain square complexes of platinum and iridium may add neutral molecules, whereby the metal is oxidised by +2 units. Thus L. Vaska, using the complex *trans*-bis(tri-phenylphosphine)carbonylchloroiridium(I) confirmed the reaction:

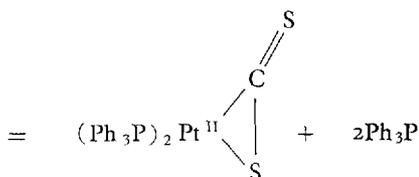
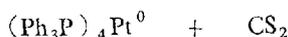


The additions of a molecule XY, examples of which are given below, may involve either *cis* or *trans* addition, depending on the circumstances, but isomerisation of the initial complex to the most thermodynamically

stable system may occur afterwards in solution reactions (3). Such reactions, generally now known as oxidative additions, may proceed as in the above equation for a coordinatively unsaturated complex; however, depending on the stability of a given coordination number in a particular oxidation state, loss of a ligand may occur also. Examples of the latter type of oxidative additions are:



The reactions are best known for complexes of  $\text{Ru}^0$ ,  $\text{Os}^0$ ,  $\text{Rh}^{\text{I}}$ ,  $\text{Ir}^{\text{I}}$ ,  $\text{Ni}^0$ ,  $\text{Pd}^0$ ,  $\text{Pt}^0$ ,  $\text{Pd}^{\text{II}}$  and  $\text{Pt}^{\text{II}}$ , usually though not exclusively with phosphine ligands. Further, there are two other classes of the reaction – those where breaking of the X–Y bond occurs and those where it does not. In both these cases, two new metal bonds, to X and Y, are formed, but for the second class, a three-membered ring is formed. Examples are:

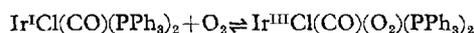


An extremely wide range of XY molecules may be added oxidatively. In the first class we have:  $\text{H}_2$ ;  $\text{Cl}_2$ ,  $\text{Br}_2$ ,  $\text{I}_2$ ;  $\text{HCl}$ ,  $\text{HBr}$ ,  $\text{HX}$ ;  $\text{CH}_3\text{I}$ ,  $\text{RX}$ ;  $\text{C}_6\text{H}_5\text{COCl}$ ,  $\text{RCOCl}$ ;  $\text{RSO}_2\text{X}$ ;  $\text{Me}_3\text{SNEt}_2$ ;  $\text{HgX}_2$ ;  $\text{Cl}_3\text{SiH}$ ;  $\text{R}_3\text{SiH}$ , etc. In the second class:  $\text{O}_2$ ;  $\text{SO}_2$ ;  $\text{C}_2\text{F}_4$ ;  $\text{CS}_2$ ;  $\text{RC}\equiv\text{CR}'$ ;  $(\text{CF}_3)_2\text{C}=\text{O}$ ,  $(\text{CF}_3)_2\text{C}=\text{S}$ ;  $\text{RNCO}$ ,  $\text{RNCS}$ ;  $\text{RN}=\text{C}=\text{NR}$  (carbodiimides);  $\text{R}_2\text{C}=\text{C}=\text{O}$ . The criteria for oxidative addition reactions to occur are not fully understood at present. Among other factors it is clear that the metal atom in the complex must have unused electron density—that is, it can behave as a nucleophile; molecules such as  $\text{H}_2$  or  $\text{O}_2$

*The study of platinum metal complexes of tertiary phosphine ligands has allowed substantial advances to be made in the preparation of new classes of complexes which in turn have contributed to a greater understanding of the stability and reactivity of other ligands such as hydride and alkyl groups bound to metals. Many of these complexes are effective in homogeneous catalyses, such as hydrogenation or isomerisation of olefins, and may be used for a number of other organic syntheses.*

to be “activated” must have acceptor orbitals available—even the hydrogen molecule has anti-bonding orbitals; the promotional energy involved in oxidising the metal from state  $n$  to  $n+2$  must be more than overcome through the formation of new bonds to the added molecule.

Of special interest are the reversible oxygen carriers discovered by Vaska, that is:



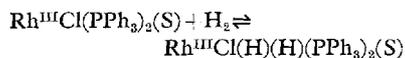
These provide not only the simplest model for biological oxygen carriers but have also provided important X-ray structural data on O–O bond lengths. Such data (4) and that obtained for  $(\text{Ph}_3\text{P})_2\text{PtCS}_2$  (5) have led to the suggestion (5) that when XY is coordinated without bond breaking, the geometry of XY can then be correlated with that determined spectroscopically for electronic excited states of XY.

The oxidative addition reactions may be important steps in many catalytic processes employing tertiary phosphine and other metal complexes, where small molecules are activated at a metal site prior to subsequent attack by other molecules or ions. A second very important general reaction is the so-called “insertion” reaction (6). These are now considered to be transfer reactions of a hydrido, alkyl or other ligand from the metal to a second, briefly coordinated ligand;

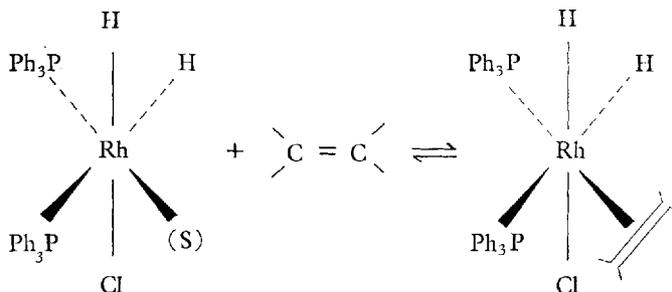
implicit here is the fact that for a ligand to be so activated by coordination, the catalyst species must be coordinatively unsaturated or must have coordination sites only weakly occupied by solvent molecules which can be competitively displaced by the ligand to which a transfer is made.

We can consider here in illustration only a few types of catalytic reactions in which the above principles operate and for which phosphine complexes of platinum metals are especially effective.

Homogeneous hydrogenation of olefins is exceedingly rapid using the complex  $\text{RhCl}(\text{PPh}_3)_3$ —or more properly, in solution, the coordinatively unsaturated, solvated species  $\text{RhCl}(\text{PPh}_3)_2(\text{S})$  where S is a solvent molecule produced by dissociation. This “activates” molecular hydrogen, which adds oxidatively with bond breaking in a reversible reaction:



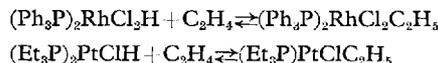
In presence of olefins, a coordinated olefin complex intermediate is postulated:



and the formation of this complex is the rate determining step. Hydrogen transfer rapidly occurs, producing paraffin. The various factors and mechanism involved have been discussed in detail (7). Other complexes, such as  $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ ,  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$  and  $[\text{RuCl}(\text{PPh}_3)_3]_2$  are also effective hydrogenation catalysts, which may have high selectivity. Thus the ruthenium complex is essentially specific for  $\alpha$ -olefins, while the complex  $\text{RhCl}(\text{PPh}_3)_3$  has already found extensive use for selective hydrogenation or deuteration of steroids (8).

For the hydroformylation of olefins ( $\text{olefin} + \text{CO} + \text{H}_2 = \text{aldehyde}$ ) there have been patent claims that the addition of tertiary phosphines to the cobalt carbonyl catalyst usually employed improves the yield of straight chain relative to branch chain aldehydes simultaneously produced. Recent studies using stoichiometric and well established complexes, such as  $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ , have shown that hydroformylation can be achieved under abnormally mild conditions, even at room temperature and pressure (9).

Many platinum metal complexes, including those with phosphine ligands, can catalyze olefin isomerisation and oligomerisation reactions—in these cases, hydrido metal complexes are probably involved as well as unstable alkyls derived from them by reactions with olefins. Fairly simple systems in which both the hydrido and alkyl species can be studied have been reported recently (10), for example:



There are many other catalytic or stoichiometric reactions that may be achieved using  $\text{R}_3\text{P}$  complexes of platinum metals—decarbonylation of aldehydes, polymerisation of acetylenes, hydrosilation of olefins, oxidations using molecular oxygen and so on. One recent example is the polymerisation of allene by  $\text{RuCl}_2(\text{PPh}_3)_2$  and  $\text{RhCl}(\text{PPh}_3)_3$  (11).

Finally, it may be noted that phosphine species have been used in the recent preparation of molecular nitrogen complexes of cobalt (12) and that the hydrido species

(Et<sub>3</sub>P)<sub>2</sub>PtClH has been found to react with a diazonium salt in much the same way that a reducing enzyme is thought to react with a metal complex of molecular nitrogen in biological systems (13).

As will be seen from the reference list, this area of chemistry is currently of great interest and it seems clear that many other reactions of potential use in organic synthesis are as yet undiscovered.

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## Palladium Addition Protects Titanium in Hot Concentrated Chloride Solutions

Titanium is used widely in the manufacture of chemical plant because of its natural resistance to corrosion by oxidants, such as boiling nitric acid, and its use has been extended to reducing conditions, such as with hydrochloric and sulphuric acids, by alloying small amounts of palladium to the titanium, a development due largely to Milton Stern and his colleague at Union Carbide (1, 2). The mechanism by which the addition of palladium affords protection to titanium has been described more recently in this journal by J. B. Cotton of Imperial Metal Industries (3).

Akira Takamura, working at the Central Research Laboratory of Kobe Steel Ltd in Japan, has now shown that the 0.13 per cent palladium-titanium alloy is almost completely free from corrosion by hot concentrated chloride solutions (4). Corrosion problems had been occurring in awkward angles and crevices of titanium heat exchanger tubes, pipe flanges and heater tubes used in circuits carrying, for example, hot copper chloride and ammonium chloride solutions.

Takamura carried out corrosion and electrochemical tests on coupons of titanium and the palladium-titanium alloy in six different

boiling chloride solutions. Although the passivity of titanium was very stable in solutions of low chloride concentration it decreased with increasing chloride and hydrogen ion concentration. No corrosion of titanium occurred in neutral 25 per cent sodium chloride but severe corrosion soon occurred in acidic 33 per cent aluminium chloride solution. Pitting corrosion arose quickly in neutral solutions of 61 per cent calcium chloride and 86 per cent zinc chloride, depending on the surface condition of the specimens. Uniform attack took place after small additions of hydrochloric acid.

No corrosion was observed with the palladium-titanium alloy, the superiority of which is attributed to palladium enrichment at crevice surfaces and the consequent promotion of cathodic passivation. In consequence, equipment with joints and flanges likely to have crevices is now fabricated with the alloy, which has given more than three years successful commercial service.

F. J. S.

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