

Phosphine Complexes of the Platinum Group Metals

By B. W. Malerbi, M.A.

Research Laboratories, Johnson Matthey & Co Limited

Complexes made by reacting the platinum group metals with alkyl or aryl phosphines are of considerable potential interest. Many of them are soluble in aromatic or polar aliphatic solvents and are already finding applications as homogenous catalysts. In this paper the methods available for producing the phosphine complexes are reviewed, and details are given of a range of phosphine stabilised hydrido and phosphine stabilised carbonyl hydrido complexes of the metals, all of which have been produced under controlled conditions and are now available in research quantities.

Just over a hundred years ago Hofmann (1) first reported that platinum and gold compounds could be reacted with triethylphosphine in alcoholic solution to produce phosphine co-ordination complexes. In 1870 Cahours and Gal (2) prepared and characterised complexes of gold, palladium and platinum with tertiary phosphines and arsines. Progress in this field was slow until the thirties when Mann and Chatt (3) stimulated a new interest. This was heightened in the forties and fifties by Hieber (4), Malatesta (5) and Vaska (6). Since then the expansion of effort has been almost explosive, with the result that nearly every possible permutation of ligand and metal has now been prepared.

These phosphine complexes are part of a much larger field of co-ordination complexes in which transition metals are linked to donor atoms or groups of atoms by dative or co-ordinate bonds. Examples of such donor groups of ligands are ammonia, amines, arsines, carbonyls, halogen ions, and olefins.

In co-ordination complexes certain characteristic configurations of atoms are common, for example the square planar (Fig. 1) and the octahedral (Fig. 2). Less common are the halogen-bridged binuclear species (Figs 3 and 4) and the tetrahedral structure found in some nickel complexes. Of the metals under

consideration here, Pd (II), Pt (II), Rh (I) and Ir (I) complexes have the square-planar form, and Ir (III), Rh (III), Ru (III) and Os (II) have an octahedral configuration. Ru (II) and Rh (II) tend to give the bridged structure of Fig. 4.

Most of the platinum metal phosphine complexes known show the structures illustrated in Figs 1 to 4. In phosphine complexes the ligand, shown in the diagram as R_3P , may consist of trialkyl (e.g. Et_3P), triaryl (e.g. Ph_3P), or mixed alkyl aryl tertiary phosphines such as Et_2PhP or $EtPh_2P$.

Several general methods of preparing phosphine complexes of platinum metals are known. The simplest, used by Mann among others, is to stir the metal halide with the tertiary phosphine in ethanol either at room temperature, or with gentle heating up to boiling. Complexes such as $PdCl_2(PPh_3)_2$ or $RhCl_3(PPh_3)_3$ result. If the boiling is prolonged, especially if higher boiling alcohols such as ethanediol or 2-methoxyethanol are employed, reductive carbonylation or hydride formation will result. As an example, Vaska boiled $IrCl_3$ with excess PPh_3 in 2-(β -methoxyethoxy) ethanol and obtained $IrCl(CO)(PPh_3)_2$.

A different approach involves carbonylation of the metal halide, followed by addition of

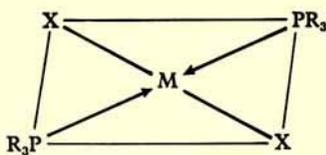


Fig. 1 Square planar
M = Pd (II), Pt (II), Rh (I), Ir (I)
X = Cl, Br, I, NO₂, NO₃, SCN

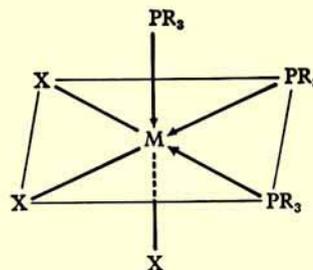


Fig. 2 (above) Octahedral
M = Ir (III), Ru (III), Rh (III),
 Os (II), Ru (II), Ir (II)
X = Cl, Br, I, NO₂, NO₃, SCN

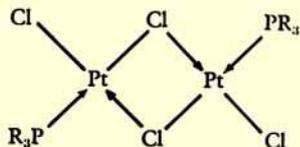


Fig. 3 (left) Dimer with double halogen bridge

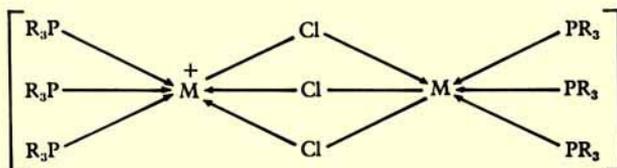


Fig. 4 Dimer with triple halogen bridge
M = Ru (II)
 or Rh (II)

Characteristic structures of the phosphine complexes of the platinum metals

the phosphine to the metal carbonyl halide. Heck (8) prepared $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ from RhCl_3 by this method, and then added PPh_3 to give $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$. The iridium analogue $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$, prepared by Vaska, on treatment with HCl gas yields the hydrido complex $\text{IrHCl}_2(\text{CO})(\text{PPh}_3)_2$. Presumably the analogous rhodium compound would react similarly. In preparing a range of ruthenium complexes Chatt (7) utilised the intermediate $[\text{Ru}_2\text{Cl}_3(\text{PEt}_2\text{Ph})_6]^+\text{Cl}^-$ (prepared by refluxing RuCl_3 with PEt_2Ph in 2-methoxyethanol under nitrogen), and reductively carbonylated it by boiling it with ethanolic potassium hydroxide to give $\text{RuHCl}(\text{CO})(\text{PEt}_2\text{Ph})_3$. In another reaction with $[\text{Ru}_2\text{Cl}_3(\text{PEt}_2\text{Ph})_6]^+\text{Cl}^-$, by shaking an ethanol solution with CO at 75°C and 50 atm, Chatt obtained the dicarbonyl complex $\text{RuCl}_2(\text{CO})_2(\text{PEt}_2\text{Ph})_2$.

Complexing the salts of platinum group metals with phosphines gives them certain

useful properties. The normal salts of these metals are generally not appreciably soluble in organic solvents other than alcohols, and for applications in the field of homogenous catalysis this limits their usefulness. (An exception is the notable reactivity of rhodium trichloride trihydrate in ethanolic solutions; Harrod and Chalk (9) showed that rhodium trichloride in ethanol readily catalysed the isomerisation of hex-1-ene to *cis*-hex-3-ene.) On the other hand the tertiary phosphine complexes of the platinum metals are usually quite soluble in a wide range of organic solvents. The trialkylphosphine derivatives are especially soluble but this causes difficulties in their preparation. A further advantage conferred by the phosphine ligands is the stabilisation of lower, normally unstable, valency states of the platinum metals. If the normal lower valent platinum metal salts, which are very reactive, were used as catalysts there is a danger of their

being reduced to the metal. When associated with phosphines this is less likely. The phosphine ligand has been found to stabilise transition metal hydrides which are otherwise unobtainable. Vaska (6) has prepared $\text{IrH}_2\text{Cl}(\text{PPh}_3)_3$ and $\text{OsHCl}(\text{CO})(\text{PPh}_3)_3$, but simple hydrides of iridium and osmium are unknown. The carbonyl ligand has a similar stabilising effect but it is much weaker. The metal-carbon bond is also strengthened by co-ordinated phosphines, as in the case of $(\text{Et}_3\text{P})_3\text{Pt}(\text{CH}_3)_2$.

It has been reported by Wilkinson, *et al.* (10) that the rhodium complex $\text{RhCl}_3(\text{PPh}_3)_3$ has the ability to promote hydrogenation and hydroformylation (the simultaneous addition of CO and H_2) of olefins and acetylenes under relatively mild conditions. Hydrogenation of hex-1-ene to *n*-hexane occurs at 20°C and less than 1 atmosphere pressure of hydrogen. Hydroformylation of hex-1-ene is effected after twelve hours at 55°C and 90 atmospheres pressure of a 1:1 mixture of carbon monoxide and hydrogen. The products are 20 per cent of 2-methylhexanoaldehyde and 70 per cent of *n*-heptaldehyde. As an aside, it may be noted that Wilkinson (11) reports that ethanolic solutions of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ also catalyse the hydrogenation of olefins.

The work of Harrod and Chalk, referred to earlier, suggests that a metal hydride is a likely intermediate in the case of isomerisation and hydrogenation reactions. The fact that some of these complexes are relatively labile in solution in the presence of air would imply that they may also catalyse organic oxidation reactions under relatively mild conditions.

It seems likely, on the basis of our present knowledge of homogeneous catalytic mechanisms, that many applications of hydride complexes of the platinum metals will soon emerge.

For these reasons the preparation of a number of these complexes has been surveyed in the Johnson Matthey Research Laboratories, and details of seven of the compounds so far prepared are summarised below. All these compounds are now available to potential users in research quantities.

$\text{Pt}[(\text{C}_6\text{H}_5)_3\text{P}]_4$

This is made by reacting K_2PtCl_4 with an excess of triphenylphosphine in a mixture of ethanol and water at 55°C.

The compound consists of orange yellow crystals having a melting point of 120 to 125°C. They are readily soluble in benzene and sparingly so in hexane. Benzene solutions slowly decompose in air, and on standing in the absence of air, they gradually deposit $\text{PtH}_2[(\text{C}_6\text{H}_5)_3\text{P}]_2$. This compound can replace chlorine in CCl_4 by hydrogen.

$\text{PdCl}_2[(\text{C}_6\text{H}_5)_3\text{P}]_2$

This is made by reacting $(\text{NH}_4)_2\text{PdCl}_4$ with triphenylphosphine in ethanol at 20°C.

The compound consists of yellow crystals which decompose at around 250°C. The crystals are soluble in benzene, toluene and chloroform and the resulting solutions are stable in air.

$\text{IrH}_2\text{Cl}[(\text{C}_6\text{H}_5)_3\text{P}]_3$

This is made by reacting $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ with an excess of triphenylphosphine in a mixture of ethanediol and water, boiling the mixture for about four hours.

The compound consists of white crystals having a melting point of 195 to 210°C. The crystals are insoluble in alcohol but soluble in carbon tetrachloride or CHCl_3 ; but the solutions are unstable. The solid slowly turns green on exposure to light.

$\text{IrHCl}_2(\text{CO})[(\text{C}_6\text{H}_5)_3\text{P}]_2$

This is made by passing dry HCl gas into an ether suspension of $\text{IrCl}(\text{CO})[(\text{C}_6\text{H}_5)_3\text{P}]_2$.

The compound is a white crystalline solid having a melting point of 295 to 310°C. It is very sparingly soluble in acetone, chloroform or benzene.

$\text{IrCl}(\text{CO})[(\text{C}_6\text{H}_5)_3\text{P}]_2$

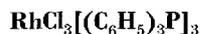
This is made by reacting $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ with excess of triphenylphosphine in a mixture of methyl digol and water. The mixture is boiled for about two and a half hours.

The compound consists of lemon yellow crystals having a melting point of 315 to 320°C. They are soluble in high boiling alcohols and chloroform.



This is made by reacting $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ with an excess of triphenylphosphine in boiling methanol for twenty-four hours.

The compound consists of red-brown crystals having a melting point of 176 to 178°C. The crystals are sparingly soluble in alcohols but readily soluble in acetone, chloroform and benzene. The solutions rapidly change in colour from red to green when exposed to air and the compound is not recrystallisable.



This is made by reacting $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ with a large excess of triphenyl phosphine in ethanol. The solution is brought just to the boiling point and then allowed to cool.

The compound consists of orange red crystals having a melting point of 270 to

280°C. The crystals are soluble in alcohols and benzene, but attempts at recrystallisation result in loss of phosphine.

References

- 1 A. W. Hofmann, *Ann. Chem. Liebigs*, 1857, **103**, 357
- 2 A. Cahours and H. Gal, *ibid.* 1870, **155**, 223, 355
- 3 F. G. Mann and J. Chatt, *J. Chem. Soc.* 1938, p. 1949, 2086; 1939, p. 1622
- 4 W. Hieber and H. Heusinger, *J. Inorg. Nucl. Chem.*, 1957, **4**, 179
- 5 L. Malatesta *et al.*, *J. Chem. Soc.*, 1955, p. 3924; 1958, 2323; 1963, 2080; *J. Inorg. Nucl. Chem.*, 1958, **8**, 561
- 6 L. Vaska *et al.*, *J. Amer. Chem. Soc.*, 1960, **82**, 1263; 1961, **83**, 756, 1262, 2784; 1962, **84**, 679; 1964, **86**, 1944
- 7 (a) J. Chatt and R. G. Hayter, *J. Chem. Soc.*, 1961, 896
(b) J. Chatt and B. L. Shaw, *Chem. Ind.*, 1960, 931
(c) J. Chatt, B. L. Shaw, A. E. Field, *J. Chem. Soc.*, 1964, 3466
- 8 R. F. Heck, *J. Amer. Chem. Soc.*, 1964, **86**, 2796
- 9 J. F. Harrod and A. J. Chalk, *J. Amer. Chem. Soc.*, 1964, **86**, 1776
- 10 J. A. Osborn, G. Wilkinson, J. F. Young, *Chem. Communications*, 1965, 17
- 11 R. D. Gillard, J. A. Osborn, R. B. Stockwell, G. Wilkinson, *Proc. Chem. Soc.*, 1964, 284

Hydrogen Recovery by Palladium Diffusion

AN INEXPENSIVE LARGE-SCALE PROCESS

The big demand for pure hydrogen has encouraged Union Carbide Corporation to develop a large-scale hydrogen diffusion process using thin palladium films. Hydrogen 99.99 per cent pure is being produced at Corporation plants and the Olefins and Linde Divisions are prepared to manufacture units for sale elsewhere. The first nine plants will soon be operating, producing between them 34 million cubic feet of hydrogen per day.

R. B. McBride and D. L. McKinley have described these developments in a paper delivered at the 55th National Meeting of the American Institute of Chemical Engineers at Houston, Texas. Following experiments on the mechanisms of hydrogen diffusion through palladium, a pilot plant was built which operated satisfactorily from 1961 onwards.

Details were given of a 4 million cubic feet per day plant which uses a feed gas containing

50 per cent hydrogen. The diffuser operates at 350 to 400°C and produces hydrogen suitable for catalytic hydrogenation processes.

An important consideration is the availability of feed gases. The Union Carbide plant is designed for using off-gas streams from olefin plants and might also be used with coke oven gas or gas streams from oil refineries. Feed gases from such sources are low in cost and the reforming of other molecules to generate fresh hydrogen is obviated. Only hydrogen sulphide seriously poisons the palladium films and must be removed before the diffusion stage.

Factors which merit favourable consideration of diffusional recovery and purification of hydrogen include high pressure and concentration of feed gas, absence of contaminants, and a requirement for high purity hydrogen at low pressure.