

# Tris(hydroxymethyl)phosphine Platinum Metal Complexes

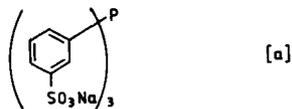
## CATALYSTS FOR WATER-BASED REACTIONS

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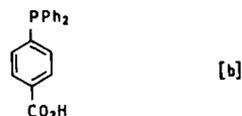
Phosphorus(III) ligands,  $PR_3$ , have been quintessential to the development of modern inorganic chemistry. They are used as stabilising ligands for a huge variety of species including high and low oxidation states, carbonyls, hydrides, organometallics, dinitrogen- and dihydrogen-complexes. Their unique versatility arises from the almost limitless choice of electronic and steric effects that can be engendered by the judicious choice of the R group. The co-ordination complexes of phosphines and phosphites are not just of academic importance since their catalytic properties have found application in bulk industrial synthesis, such as hydroformylation, hydrocyanation and oligomerisation, and increasingly in small scale organic synthesis, for example asymmetric hydrogenation and carbon-carbon bond formation.

With few exceptions, phosphine and phosphite co-ordination chemistry is carried out in non-aqueous solvents because usually the complexes are insoluble in water, or reactive to water. Although water-soluble phosphines are not common, their advantages are amply demonstrated by the hydroformylation process operated by Rhône-Poulenc using the phosphine [a]. In this reaction, the rhodium complex of [a] work is dissolved in water and



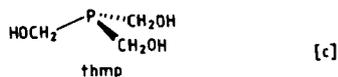
catalysis takes place at the aqueous/organic interface. The separation of the catalyst from the product, so often the major weakness in homogeneous catalysis processes, is achieved simply by separating the liquid layers. The suc-

cess of this process has promoted the study of other water-soluble triarylphosphines such as [b], below (1).

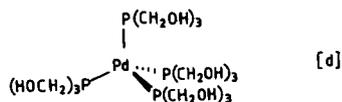


The purpose of almost all of these studies has been the development of two-phase analogues of well-known homogeneously catalysed reactions and surprisingly little attempt has been made to characterise the fundamental chemistry taking place in the water, or to investigate new types of catalysis that may be possible only in water.

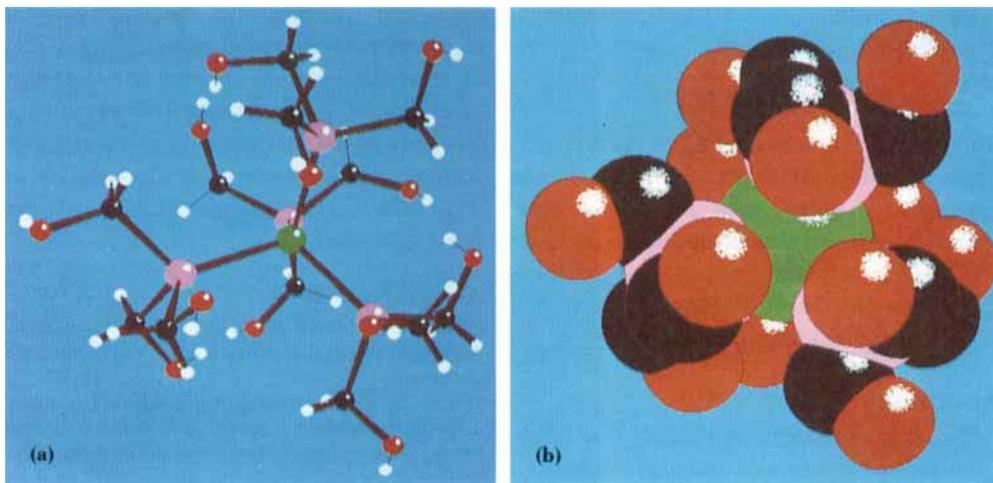
Tris(hydroxymethyl)phosphine, [c], thmp, is



a rare example of a water soluble trialkylphosphine; it can be weighed out in air without any significant decomposition—although like other trialkylphosphines, it has an odious smell!—and has been shown previously to form water-soluble complexes with palladium(II) and platinum(II) (2). In view of its desirable combination of properties, it is surprising to find so little reported co-ordination chemistry. We have embarked on a broad ranging study of the metal complexes of thmp, and have already uncovered some surprises. In [d]



for example, we have made the only fully characterised water soluble palladium(0)



**Fig. 1** Crystal structure of  $[\text{Pd}\{\text{P}(\text{CH}_2\text{OH})_3\}_4]$  (Pd = green, P = purple, C = black, H = white, O = red) (a) ORTEP showing the overall geometry (b) space filling model (H atoms omitted) which illustrates the outer sphere of hydroxyl groups surrounding the  $\text{PdP}_4$  core

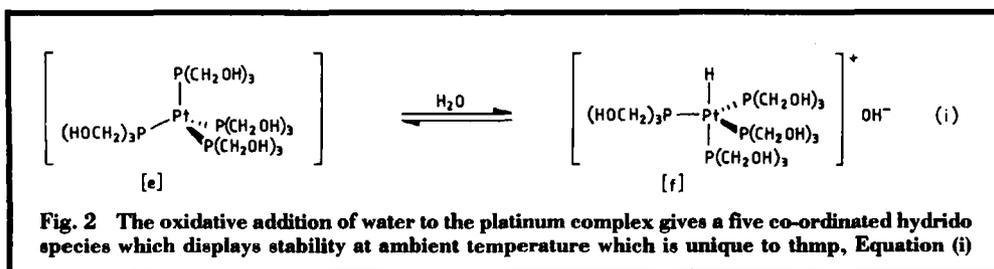
complex whose crystal structure, see Figure 1, shows the palladium co-ordination sphere encapsulated in a sheath of twelve hydroxyl groups, presenting a highly hydrophilic surface to an incoming solvent molecule. The importance in organic synthesis of palladium-phosphine catalysed carbon-carbon bond formation has led to speculation on the use of complex [d] in a two phase organic/aqueous system for the same reaction (3).

The platinum complex [e] is ostensibly similar to [d] but in water it reversibly undergoes addition to give the five co-ordinated hydrido species [f], Equation (i), see Figure 2. The addition of water is characteristic of a trialkylphosphine-platinum(0) complex, but the stability of a five co-ordinated  $[\text{HPt}(\text{PR}_3)_4]^+$  at ambient temperatures is unique to thmp. Thus in these platinum species, thmp is a strong

donor, making the complex basic, and stabilising the high co-ordination number; in short it is behaving as a small trialkylphosphine.

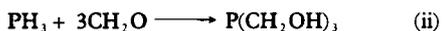
We have also shown that thmp readily forms water soluble complexes with many other transition metals, for example: ruthenium, rhodium, iridium, nickel, silver and gold, and in each case it behaves as a small trialkylphosphine. The synthesis of many of these complexes illustrates the phase-transfer properties of thmp. For example, the palladium(0) complex [d] is conveniently made by adding an aqueous solution of thmp to a dichloromethane solution of  $[\text{Pd}(\text{PPh}_3)_4]$ ; the yellow colour is gradually transferred from the organic to the aqueous phase and the product is isolated from the  $\text{PPh}_3$  by-product by separation of the layers.

The palladium, platinum and nickel thmp



**Fig. 2** The oxidative addition of water to the platinum complex gives a five co-ordinated hydrido species which displays stability at ambient temperature which is unique to thmp, Equation (i)

complexes catalyse the addition of phosphine to formaldehyde, Equation (ii), below:



This reaction is quantitative and is the best synthesis of thmp. However, the need to use phosphine to make thmp may deter some chemists but there is an alternative route from  $[\text{P}(\text{CH}_2\text{OH})_4]\text{Cl}$ ; the method and research quantities of this phosphonium salt are available from Albright and Wilson\*.

### Summary

Tris(hydroxymethyl)phosphine has the following combination of desirable properties:

- white, crystalline, water soluble trialkylphosphine
- easily handled, can be weighed in air
- forms water soluble metal complexes
- small cone angle, between those of trimethylphosphine and triethylphosphine
- readily prepared.

From our work it is clear that unique metal-

phosphine chemistry takes place in water when using tris(hydroxymethyl)phosphine (4). Thus its co-ordination chemistry will be worthy of further study, particularly in areas where water solubility would be an advantageous property, such as homogeneous catalysis, noble metal drug development, metal imaging agents and metal extraction.

### Acknowledgements

We thank Albright and Wilson for supporting this work, and Johnson Matthey for the loan of platinum metal salts.

\*Dr. P. A. T. Hoye, Albright and Wilson Ltd, International Technology Centre, PO Box 80, Trinity Street, Oldbury, Warley, West Midlands B69 4LN.

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## Materials for Higher Density Recording

Last year a short item was published in this journal to draw attention to two papers from scientists at the Philips Research Laboratories, in the Netherlands, and at the E. I. du Pont de Nemours Experimental Station, U.S.A., both of which reported investigations into the magnetic and magneto-optic properties of cobalt/platinum layered structures (1). In the same issue an abstract of a communication from the Sony Corporation Research Center, Yokohama, Japan, on the properties of ultrathin multilayer films was published (2). Now two further papers from these Japanese researchers have appeared (3, 4).

Amorphous rare-earth transition-metal films used as magneto-optical recording media are easily oxidised and an additional element is required to provide resistance to corrosion. For these reasons, and because the magneto-optical properties of currently used media decrease at the shorter wavelengths favoured for higher density recording, investigations to find superior materials are continuing. The recent paper describes the magneto-optical and magnetic properties of ultrathin cobalt/platinum and cobalt/palladium multilayers.

The structure of these multilayered films, their magneto-optical and magnetic properties and the dependence of these on film thickness are reported and discussed, as is the dependence of the magneto-optical properties on light wavelength. Corrosion resistance of these multilayers is high and they are thermally stable at temperatures of up to 400°C.

It is reported that at 780 nm the magneto-optical properties of ultrathin cobalt/platinum films are superior to those of TbFeCo films, while at shorter wavelengths the figure of merit is even better, being 2.5 times larger than that of TbFeCo at 400 nm.

A further communication by the same authors, on the potentially useful magnetic properties of rf magnetron sputtered thin films of cobalt-palladium alloys, is abstracted on page 99 of this journal.

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