

Platinum Metal Complexes of Substituted Aryl Phosphines

IMPORTANT ASPECTS OF THEIR CATALYTIC AND CO-ORDINATION CHEMISTRY

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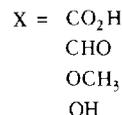
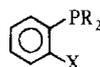
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Highlights of the co-ordination chemistry of platinum metal complexes of phosphorus-oxygen chelating agents are described. The ligands of interest all contain the oxygen bearing substituent (methoxy, hydroxy, formyl, carboxy-) ortho to a phosphine on a benzene ring; complexes of these ligands are efficient homogeneous catalysts for hydrogenation, isomerisation and polymerisation reactions. Furthermore, these studies have revealed structural and reactivity patterns which are suggestive of new and improved strategies towards useful catalytic systems.

Phosphines play a pivotal role in homogeneous catalysis by metal complexes. This class of ligands is particularly useful since their steric and electronic properties can be varied readily, and also because they are relatively unreactive towards the usual catalytic substrates and impart desirable solubility properties to the resultant complexes. The association between the platinum metals and phosphines has been an especially fruitful one, both from historical and applied perspectives and while other transition metals are also effectively co-ordinated by tertiary phosphines, especially the alkyl derivatives, that work is overshadowed by the corresponding chemistry of the platinum metals.

The catalytic chemistry of platinum metal phosphine complexes is largely confined to unidentate tertiary phosphines although recent potentially useful applications of chelating diphosphines have been described (1). This tradition is primarily a consequence of convenience since these simpler ligands, especially the unidentate ones, are readily prepared by established procedures or are available commercially. Recent reports both in the research and patent literature suggest that somewhat more elaborate phosphines may be a richer

source of cocatalysts than the corresponding unidentate ligands. A class of particular interest to the author is the *ortho*-heteroligand arylphosphines depicted below, and this review will be concerned primarily with platinum metal derivatives of the aryl phosphines containing oxygenated substituents.



Phosphinoanisoles (X = OCH₃)

The first report of an *o*-phosphinoanisole complex in the literature was by the Knowles group at Monsanto who used it in the asymmetric hydrogenation of prochiral olefins to chiral products, particularly L-DOPA, used for the treatment of Parkinson's disease, Figure 1. Starting with acylaminoacrylic acid derivatives, optical yields of up to 95 per cent (plus 5 per cent racemate) were obtained (2). These optical yields indicate an energy difference of about 2.1 kcal/mol at 25°C between the two reaction pathways leading to the enantiomeric products from the prochiral precursor. The actual source of this energy difference, be it a consequence of the relative concentrations of

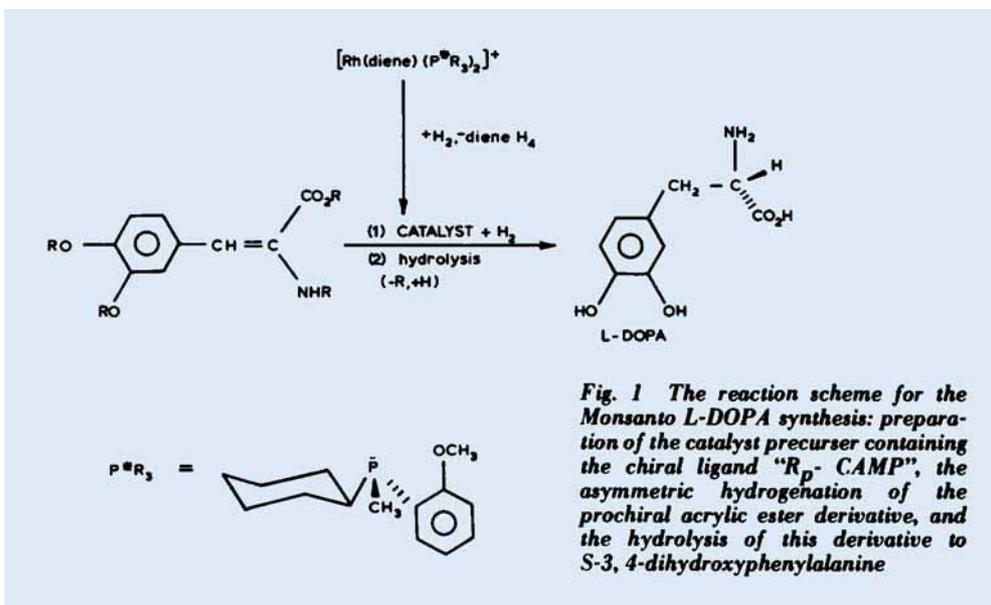


Fig. 1 The reaction scheme for the Monsanto L-DOPA synthesis: preparation of the catalyst precursor containing the chiral ligand "R_p-CAMP", the asymmetric hydrogenation of the prochiral acrylic ester derivative, and the hydrolysis of this derivative to S-3, 4-dihydroxyphenylalanine

the diastereomeric metal olefin complexes or their rates of hydrogenation is not known. More recent improvements of this ligand system involve the synthesis and applications of the chelating ditertiary phosphine, diPAMP (3). The efficiency of these ligands in catalytic asymmetric hydrogenation is impressive especially in light of the alternative methods using achiral catalysts to afford racemic products which must be separated using tedious and time-consuming resolutions.

A curious feature of the Monsanto ligands is the recurring presence of the anisole substituent whose role has yet to be clarified, although it should be noted that there exist several other effective chiral ligands which do not contain this anisole group. Relevant to this problem is the study of other platinum metal complexes of simpler phosphinoanisoles.

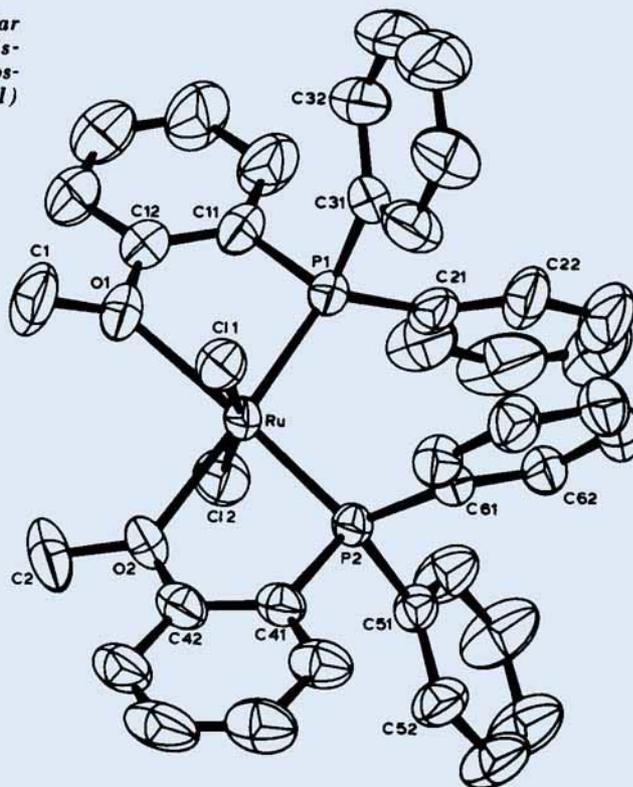
The red complex *trans,cis*-RuCl₂(PO)₂ (where PO = *o*-diphenylphosphinoanisole) can be prepared in high yield from ruthenium trichloride and PO in refluxing ethanol. We recently determined its structure, shown in Figure 2, by X-ray methods, and it indicates that the "hard" ether group effectively functions as a ligand for the "soft" ruthenium(II) (4). The structure further indicates that the ethers are only weakly

co-ordinated ($r_{\text{Ru-O}} = 2.23$) and this is suggestive that the ligand may be quite labile and consequently the complex has potential as a catalyst wherein substrate would displace the weakly co-ordinated ethers. In practice the red complex was found to be completely inactive for hydrogenation; however, the addition of a small amount of basic ethanol resulted in its rapid conversion to a yellow, very active catalyst for the isomerisation of 1-hexene and the hydrogenation of 1-hexene, cyclohexene and benzaldehyde*. While the yellow complex is quite air sensitive, its red precursor is completely robust both thermally and oxidatively. Its ease of preparation and handling, coupled with its simple conversion to an active catalyst, renders this complex an attractive alternative to the RuCl₂(PPh₃)₃₋₄ system.

The red RuCl₂(PO)₂ represents an unusual example of a **completely** aerobically stable complex which reacts efficiently with carbon monoxide. This reaction is accompanied by a

* Typical catalytic conditions: 10 ml of a 5×10^{-3} M solution of RuCl₂(PO)₂ in 10:1 toluene/ethanol is pretreated with 0.05 ml 20% aqueous NaOH. This solution isomerises 1-pentenes (10⁻¹M) with t_{1/2} of 5 min at 26°C. Under 1 atm H₂, isomerisation is still dominant as internal olefins (2-pentenes, cyclohexene) require H₂ pressures of about 4 atm for efficient (t_{1/2} ≈ 90 min) hydrogenation.

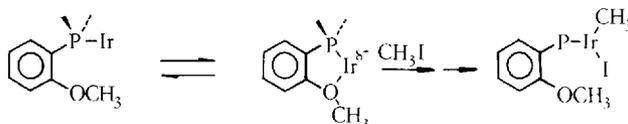
Fig. 2 The molecular structure of *trans,cis-dichlorobis(o-diphenylphosphinoanisole) ruthenium (II)*



dramatic change to the yellow colour of $\text{RuCl}_2(\text{PO})_2(\text{CO})$ and $\text{RuCl}_2(\text{PO})_2(\text{CO})_2$, a colour change which can be used for the detection of carbon monoxide. We have found, for instance, that automobile exhaust effects the clean conversion of the red precursor to the yellow carbonyls.

The work of Shaw's group on iridium and rhodium anisole phosphines is also enlightening. It was found that the complexes of formula *trans*- $\text{MCl}(\text{CO})(o\text{-CH}_3\text{OC}_6\text{H}_4\text{Pme}_2)_2$, which resemble the well-known derivatives of unsubstituted tertiary phosphines, undergo oxidative addition at extraordinarily rapid rates (5). A sensible explanation of these rates, especially in view of the fact that the *para*-methoxy analogues react normally, involves the transient formation of a P-O chelate. Since the ether oxygen is an exclusive σ -donor, its co-

ordination enhances the reactivity of the metal centre towards the oxidative addition substrate.



In view of these results it would be very interesting to determine the rates of hydrogenation of transition metal anisole phosphine analogues of currently employed tertiary phosphine catalyst systems.

Phosphinophenols (X = OH)

The connection between the phosphinoanisoles and the phosphinophenols was first made by Shaw and co-workers who found that the thermolysis of the complexes *cis*- $\text{PtCl}_2(\text{R}_2\text{PC}_6\text{H}_4\text{OCH}_2)_2$ resulted in ether dealkylation affording complexes derived from phosphinophenols (6). Again, it is reasonable to

assume that these reactions involve the initial co-ordination of the methoxy group to the metal ion. Simpler routes to these ligands by acid cleavage of phosphinoethers now represent the most convenient preparation of these ligands; indeed, we recently devised a synthesis of the *o*-diphenylphosphinophenol from phenol itself (7).

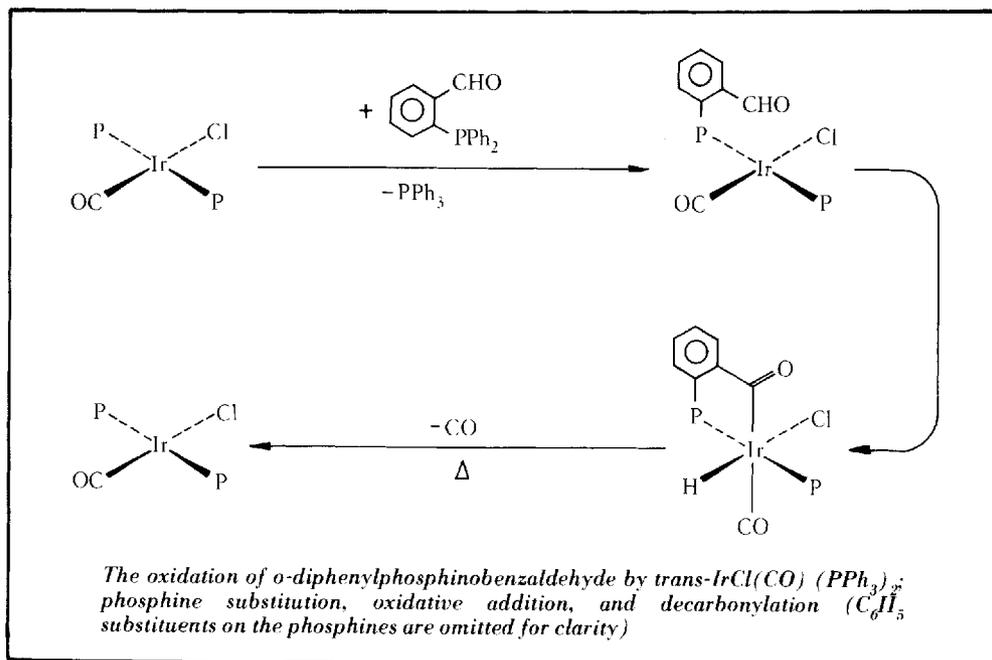
Why are we interested in these ligands? Two reasons, first they represent phosphine analogues of salicylaldehyde ligands whose Co(II) complexes are known to function as oxygen carriers. For instance it has been known for some time that derivatives of 1,2-ethanebis(salicylaldehyde)cobalt(II) (Co(salen)) can be used for the collection and storage of molecular oxygen as well as oxidation catalysts (8). More recently it has been found that *o*-di(*tert*-butyl)phosphinophenoxide forms stable mononuclear iridium(II) complexes which reversibly oxygenate (9), possibly binding the O₂ in an end-on manner like Co(salen). There is the prospect that these end-on bonded complexes may evolve into more effective oxidation catalysts than the side bonded O₂ adducts which are derived from iridium(I).

Another reason for examining the phosphinophenols is that by virtue of the hard phenolate component they may prove useful for the exploration of the phosphine derivatives of the early transition elements.

Phosphinobenzaldehydes (X = CHO)

This class of ligands was reported in 1973 by Schiemenz and Kaack (10); however, the associated co-ordination chemistry has not received any attention except from our laboratories.

There are two noteworthy features about this ligand which are particularly interesting to us: first, the co-ordination chemistry of the phosphinoaldehydes with catalytically active metals, particularly the platinum group, allows one to examine the interactions of the formyl group with model catalyst systems. Information of this sort is rare and we have taken full advantage of the chelate effect to delineate several different reaction pathways available for the metal ion activation of the formyl group. This work is important since platinum metals are efficient catalysts for the hydrogenation



(11), hydroacylation (12), hydrosilylation (13), and decarbonylation (14) of aldehydes. It is particularly interesting to note that the chelate effect promotes the oxidative addition of the aldehydic C-H bond yet inhibits the decarbonylation sufficiently to allow the isolation of the acyl hydride as illustrated in the Scheme (15). This is remarkable when one realises that iridium(I) is an effective decarbonylation catalyst.

A second reason for studying the phosphinoaldehydes is their synthetic flexibility; for instance these ligands can easily be converted to a wide range of derivatives by simple manipulations of the formyl group (16). We are actively pursuing several lines of research utilising these and related compounds

with a goal of preparing asymmetric and bimetallic complexes.

Diphenylphosphinobenzoic Acid (X = CO₂H)

This potentially chelating ligand has been described primarily in patents covering work done at the Shell Development Laboratory where it was found that in combination with Ni(1,5-cyclooctadiene) it forms a very active ethylene polymerisation catalyst (17). Curiously, little other work with this ligand has been reported, although its ease of synthesis from the inexpensive *o*-chlorobenzoic acid coupled with its impressive, albeit brief, catalytic track record suggests that a study of its co-ordination chemistry may prove fruitful.

References

- 1 W. C. Cristopfel and B. D. Vineyard, *J. Am. Chem. Soc.*, 1979, **101**, (15), 4406, and references therein
- 2 W. S. Knowles, M. J. Sebacky and B. D. Vineyard, *Am. Chem. Soc.*, Homogeneous Catalysis Volume II, *Advances in Chemistry*, 1974, (132), 274, ed. D. Forster and J. F. Roth, and references therein
- 3 B. D. Vineyard, W. S. Knowles, M. J. Sebacky, G. L. Backman and D. J. Weinkauff, *J. Am. Chem. Soc.*, 1977, **99**, (18), 5946
- 4 J. C. Jeffery and T. B. Rauchfuss, *Inorg. Chem.*, 1979, **18**, (10), 2658
- 5 E. M. Miller and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1974, (5), 480
- 6 C. E. Jones, B. L. Shaw and B. L. Turtle, *J. Chem. Soc., Dalton Trans.*, 1974, (9), 992
- 7 T. B. Rauchfuss, *Inorg. Chem.*, 1977, **16**, (11), 2966
- 8 L. Vaska, *Acc. Chem. Res.*, 1976, **9**, (5), 175
- 9 R. Mason, K. M. Thomas, H. D. Empsall, S. R. Fletcher, P. N. Heys, E. M. Hyde, C. E. Jones and B. L. Shaw, *J. Chem. Soc., Chem. Commun.*, 1974, (15), 612
- 10 G. P. Schiemenz and H. Kaack, *Justus Liebigs Ann. Chem.*, 1973, (9), 1480
- 11 B. R. James, "Homogeneous Hydrogenation", Wiley-Interscience, New York, 1973
- 12 J. W. Suggs, *J. Am. Chem. Soc.*, 1979, **101**, (2), 489. C. F. Lochow and R. G. Müller, *J. Am. Chem. Soc.*, 1976, **98**, (5), 1281
- 13 R. J. P. Corriu and J. J. E. Moreau, *J. Organomet. Chem.*, 1975, **85**, (1), 19
- 14 D. H. Doughty and L. H. Pignolet, *J. Am. Chem. Soc.*, 1978, **100**, (22), 7083
- 15 T. B. Rauchfuss, *J. Am. Chem. Soc.*, 1979, **101**, (4), 1045
- 16 T. B. Rauchfuss, *J. Organomet. Chem.*, 1978, **162**, (2), C19. J. E. Hoots, T. B. Rauchfuss, D. A. Wroblewski: unpublished results. J. C. Jeffery, T. B. Rauchfuss, P. A. Tucker, manuscript in preparation
- 17 D. M. Singleton, P. W. Glockner and W. Keim, *German Offen.*, 2,159,370 to Shell Oil Co., *Chem. Abs.*, 1972, **77**, 89124; R. F. Mason, *U.S. Patent* 3,676,523 to Shell Oil Co., *Chem. Abs.*, 1972, **77**, 100710. See also K. Issleib and H. Zimmermann, *Z. Anorg. Allg. Chem.*, 1967, **353**, (3-4), 197

The Chemistry of the Platinum Group Metals

An international conference organised by the Dalton Division of the Royal Society of Chemistry is to be held at Bristol, England, during 19-24th July, 1981. The chemistry of all six platinum group metals is to be discussed at sessions devoted to: the biological aspects of the platinum group metals, homogeneous catalysis, co-ordination and organometallic chemistry, metal cluster complexes, the

platinum group metals in organic synthesis, structure and bonding, and the role of the platinum group metals in technological chemistry.

Many important contributions have already been offered; others wishing to contribute, or to receive further information, should contact the Organising Secretary: Dr. P. L. Goggin, School of Chemistry, University of Bristol, England.