

# Catalytic Aspects of Some Phosphine Complexes of the Platinum Metals

PAPERS AT THE RECENT NORTH AMERICAN SYMPOSIUM

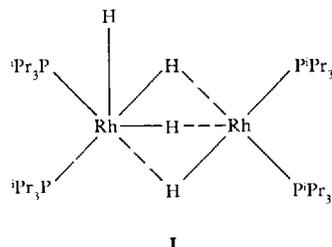
By Professor F. R. Hartley

The Royal Military College of Science, Shrivenham, England

*The 1980 Biennial Symposium jointly organised by the Inorganic Divisions of the Canadian Institute of Chemistry and the American Chemical Society, held in Guelph, Ontario, from the 5th to 7th June, was entitled "Catalytic Aspects of Metal Phosphine Complexes". This article concentrates on the contributions presented there that were particularly concerned with the platinum group metals.*

The symposium began by considering the application of  $^{31}\text{P}$  NMR to the investigation of the structure of phosphine complexes. A. Pidcock, of the University of Sussex, England, discussed the origins of metal-phosphorus coupling and showed the dominance of the Fermi term. P. S. Pregosin of ETH, Zurich, Switzerland used  $^1\text{H}$ ,  $^{31}\text{P}$ ,  $^{119}\text{Sn}$  and  $^{195}\text{Pt}$  NMR to study the hydrogenation catalyst formed between *cis*- $[\text{Pt}(\text{PR}_3)_2\text{Cl}]$  and  $\text{SnCl}_2$ ; in particular he reported  $^{119}\text{Sn}$ - $^{195}\text{Pt}$  coupling constants in excess of 20,000Hz. an order of magnitude greater than the already large couplings associated with phosphorus-metal interactions. C. A. Tolman of du Pont, Wilmington, U.S.A., described the history of the development of the cone angle, which provides a simple measure for the steric bulk of a phosphine. G. Ferguson, of the University of Guelph, Canada, described one method of extending this to provide a ligand profile that is of value with very bulky phosphines that mesh like cogs and leave only a limited region around the metal ion where other ligands may co-ordinate. B. L. Shaw, of the University of Leeds, England, emphasised the importance of the non-bonded interactions between bulky groups in promoting large ring formation; the effect is variously known as the "Thorpe-Ingold effect" or "stereopopulation control". R. V. Kastrup of Exxon, Linden, N.J.,

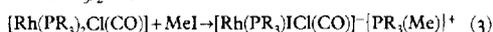
U.S.A., showed that the equilibrium between  $[\text{Rh}(\text{PPh}_3)_3\text{H}(\text{CO})]$  and  $[\text{Rh}(\text{PPh}_3)_2\text{H}(\text{CO})]$  strongly favours the former. Replacing  $\text{PPh}_3$  by  $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$  ( $n = 2$  or  $3$ ) results in a decrease of the ratio of *n*:*iso* aldehyde formed on olefin hydroformylation from about 4.5 to 1.3. L. H. Pignolet, of the University of Minnesota, Minneapolis, U.S.A., reported the decarbonylation of benzaldehyde in the presence of  $[\text{Rh}\{\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2\}_3]^+$ ; the complex with  $n = 3$  was particularly effective but the mechanism is complex depending on the number of methylene groups in the phosphine backbone. The decarbonylation of optically active aldehydes occurs with retention of configuration and a mixture of  $\text{C}_6\text{H}_5\text{CDO}$  and *p*- $\text{CH}_3\text{C}_6\text{H}_4\text{CHO}$  gives exclusively  $\text{C}_6\text{H}_5\text{D}$  and  $\text{CH}_3\text{C}_6\text{H}_5$  eliminating a free radical mechanism. D. L. Thorn, currently at du Pont, Wilmington, U.S.A., reported a novel rhodium-hydride, **I**, in



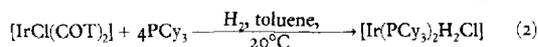
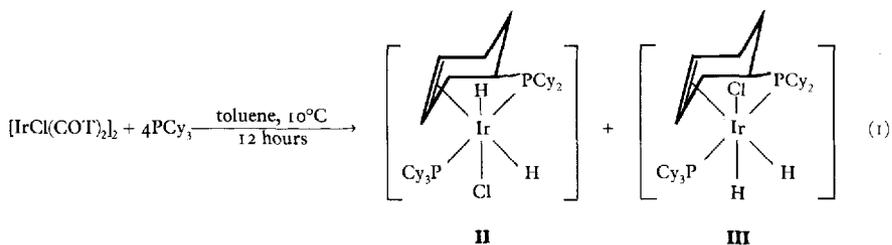
which one rhodium is formally in the +3 oxidation state and the other in the +1 oxidation

state. The  $^1\text{H}$  NMR of **I** in  $\text{C}_6\text{D}_6$  shows no hydride resonances due to rapid H/D exchange. S. Otsuka, Osaka, Japan, reported that  $[\text{Rh}(\text{P}^i\text{Pr}_3)_3\text{H}]$  and  $[\text{Pt}(\text{P}^i\text{Pr}_3)_2]$  undergo oxidative-addition of water in the presence of pyridine to yield both  $[\text{Rh}(\text{P}^i\text{Pr}_3)_2(\text{pyr})_2\text{H}_2]^+\text{OH}^-$  and  $[\text{Pt}(\text{P}^i\text{Pr}_3)_2(\text{pyr})\text{H}]^+\text{OH}^-$  respectively. The platinum systems catalyse the hydration of activated olefinic bonds and H/D exchange of activated  $>\text{CH}_2$  and  $-\text{CH}_3$  groups in  $\text{D}_2\text{O}$ ; the rhodium systems are even more versatile and catalyse H/D exchange between  $\text{H}_2$  gas and  $\text{D}_2\text{O}$  and between aromatic hydrocarbons and  $\text{D}_2\text{O}$ . B. R. James, of the University of British Columbia, Canada, reported the interesting dehydrogenation of  $\text{PCy}_3$  ligands by iridium (Reaction 1). Neither **II** nor **III** react with further  $\text{H}_2$  although the potential hydrogenation product can be prepared by Reaction 2.

amines in which the carbon chains can be extended by between 2 and 6 carbon atoms. F. R. Hartley, of the R.M.C.S., England, described the preparation of two series tertiary phosphines with long alkyl chains  $\text{PR}_3$  and  $\text{P}(\text{---}\text{C}_6\text{H}_4\text{---}\text{R})_3$  that are very soluble in simple hydrocarbon and chlorinated solvents. The platinum(II) complexes of these ligands in conjunction with  $\text{SnCl}_2$  gave highly selective catalysts for the hydrogenation of poly-olefins to mono-olefins. When  $[\text{Rh}(\text{PR}_3)_2\text{Cl}(\text{CO})]$  is dissolved in methyl iodide, anionic rhodium(I) complexes are formed by Reaction 3; these anionic complexes undergo oxidative-addition and then CO insertion to form rhodium(III) acyl complexes more rapidly than neutral  $[\text{Rh}(\text{PR}_3)_2\text{Cl}(\text{CO})]$ .



R. J. Puddephatt, of the University of

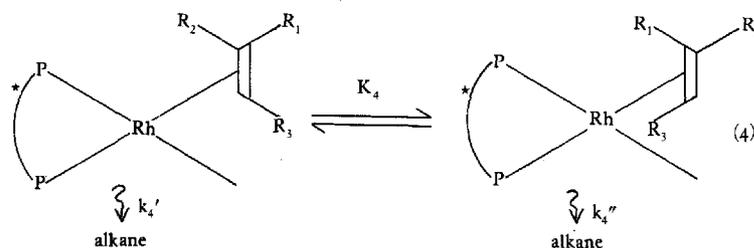


M. A. Bennett, of the Australian National University, reported that the decarbonylation of acid chlorides by  $[\text{Ir}(\text{PPh}_3)_3\text{Cl}]$  is accompanied by secondary to normal isomerisation of the alkyl group. The stability of  $[\text{Pt}\{\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2\}\text{CH}_3(\text{OH})]$  complexes is greater when  $n=3$  than when  $n=2$ ; CO (1 atmosphere pressure) can insert into the Pt—OH bond to yield  $[\text{Pt}\{\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2\}\text{CH}_3(\text{COOH})]$  which has no acidic properties and does not lose carbon dioxide on heating in contrast to the formate complex  $[\text{Pt}\{\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2\}\text{CH}_3(\text{OCO})]$ . R. F. Heck, of the University of Delaware, U.S.A., reported the syntheses of a wide range of valuable organic compounds by the palladium-tris(*ortho*-tolyl)phosphine catalysed reactions of vinylic halides with olefins and

Western Ontario, Canada, and A. L. Balch, of the University of California at Davis, U.S.A., described a range of binuclear platinum and palladium complexes of  $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ . It was apparent that the platinum complexes are often less reactive than other mononuclear platinum complexes; palladium complexes are catalytically more active than platinum complexes, for example  $[\text{Pd}(\text{Ph}_2\text{PCH}_2\text{PPh}_2)\text{Cl}]_2$  catalyses the cyclotrimerisation of  $\text{MeOCC}\equiv\text{CCO}(\text{Me})$ . D. W. Meek, of the Ohio State University at Columbus, U.S.A., summarised the advantages of using polyphosphine ligands as enabling the stoichiometry, stereochemistry and electronic ground state to be controlled as well as stabilising unusual co-ordination numbers and inhibiting inter- and intra-molecular exchange. He then

described the use of  $[\text{Rh}(\text{ttp})\text{Cl}] + \text{AlEt}_3$ ,  $\text{ttp} = \{\text{Ph}_2\text{P}(\text{CH}_2)_3\}_2\text{PPh}$  which is an active olefin hydrogenation catalyst that is more active than  $[\text{Rh}(\text{PPh}_3)_3\text{Cl}]$  for terminal olefins but which does not hydrogenate internal olefins. L. Sacconi of Florence, Italy, described a number of polydentate phosphine complexes with  $\text{P}_3$  and  $\text{P}_4$  ( $\text{P} = \text{elemental phosphorus}$ ) ligands, and R. B. King, of the University of Georgia at Athens, U.S.A., reviewed advances in polyphosphine syntheses since 1972.

The final day of the conference was devoted to asymmetric catalysis. W. S. Knowles of Monsanto, St Louis, U.S.A., reviewed the asymmetric hydrogenation of enamide precursors of  $\alpha$ -amino acids demonstrating that the optical yield depends on the catalyst used, particularly the asymmetric phosphine, the substrate, solvent, temperature and hydrogen pressure. B. Bosnich, of the University of Toronto, Canada, demonstrated that while the asymmetry is cast at the stage of co-ordination by the equilibrium constant  $K_4$ , the enantiomeric excess will depend on the relative rates,  $k_4'$  and  $k_4''$  at which the



two olefin complexes subsequently react. P. A. Chaloner, of the University of Oxford, England, undoubtedly provided the high spot of the conference by an extremely elegant NMR demonstration that in the hydrogenation of  $\text{PhCH}=\text{C}(\text{COOMe})\text{NHCOMe}$  in the presence of  $\text{Rh}[(\text{Ph}(m\text{-MeOC}_6\text{H}_4)\text{PCH}_2)_2(\text{norborna-diene})]^+\text{BF}_4^-$  it is indeed the minor isomer that is hydrogenated the faster and gives rise to the observed enantiomeric excess. J. Halpern, of the University of Chicago, U.S.A., confirmed that his group have reached a similar conclusion. It enables us to understand why increasing the hydrogen pressure often decreases the observed optical yield because it results in the minor isomer being rapidly consumed so that

the major isomer is then hydrogenated. The fact that it is the minor isomer that dominates the catalytic cycle should not be a surprise. It is very likely that the species we can detect in solution are too unreactive to be part of a catalytic cycle, rather they are stable reservoirs of catalyst that are essential to the continued retention of activity. P. Pino of ETH Zurich, Switzerland, showed that the optical yields that can be achieved in hydroformylations are much lower than in hydrogenations, the best being 69 per cent for the hydroformylation of  $\alpha$ -methylstyrene to *t*-butyl-3-phenylbutanoate using a palladium(II)-DIOP catalyst. Even predictions of the conformation of the enantiomeric excess based on the dominance of repulsive interactions for aliphatic olefins and attractive interactions for aromatic olefins only give the correct result in 84 per cent of cases. L. Markó, of the University of Veszprem, Hungary, reported that 80 per cent optical yields can be achieved for the asymmetric hydrogenation of aromatic ketones such as  $\text{PhCOCH}_3$  using  $[\text{Rh}(\text{norborna-diene})\text{Cl}]_2 +$

DIOP as the catalyst precursor. The best solvents were alcohols although these slowly poison the catalyst due to transfer of hydrogen from alcohol

to olefin and subsequent decarbonylation of the aldehyde to form inactive rhodium(I)-carbonyl complexes.

It is planned to publish the full proceedings of this conference, as a volume in the American Chemical Society's *Advances in Chemistry Symposium Series*.

### Triarylphosphine-Palladium Complexes

To clarify a statement headed "Catalyst Availability" that appeared in *Platinum Metals Review*, 1980, 24, (2), 63, please note that licensing of the Heck patents is to be arranged with the Office of Research and Patents at the University of Delaware, Newark, Delaware 19711. Information about catalyst availability can be obtained from Johnson Matthey Incorporated.