

# The Chemistry of the Platinum Group Metals

## A REVIEW OF THE THIRD INTERNATIONAL CONFERENCE

*Sponsored by the Dalton Division of the Royal Society of Chemistry, the Third International Conference on the Chemistry of the Platinum Group Metals, was held at Sheffield University in July 1987. The first meeting in this series was held at Bristol in 1981 and the second in Edinburgh in 1984. Over three hundred and fifty delegates from academia and industry attended with more than half from abroad and with over twenty countries represented. During the week forty-five lectures were presented along with over one hundred and seventy posters.*

The conference opened with the Dalton Presidential Address given by Professor P. M. Maitlis from the University of Sheffield who described an interesting new area of platinum group metal chemistry in his talk on metal-containing liquid crystals. The inclusion of metals in these systems may give rise to new magnetic and electrical properties, as well as non-linear optical effects. The first compounds prepared contained platinum or palladium complexed by biphenyl nitrile ligands and the work has been extended to gold and palladium complexes with liquid crystal-forming pyridine derivatives and palladium dithiocarboxylic acid complexes.

The T. A. Stephenson Memorial Lecture was given by one of his former students Professor D. J. Cole-Hamilton of the University of St. Andrews, who described some recent work on the production of hydrogen from alcohols. Hydrogen is an important raw material in the chemical industry, used mainly for production of methanol and ammonia, and is usually produced by steam reforming of natural gas. An alternative route would be from renewable fermentation products such as ethanol. The known homogeneous catalysts for ethanol dehydrogenation give hydrogen and acetaldehyde, and not the thermodynamically favoured products from ethanol and water which are alkane, carbon dioxide and hydrogen. However  $[\text{Rh}(\text{bipyridyl})_2]^+$  with

sodium hydroxide at 120°C catalyses the latter reaction, through a combination of alcohol dehydrogenation, aldehyde decarbonylation and the water-gas shift reaction.

### Clusters and Dinuclear Complexes

The synthesis of metal chain compounds was described by Professor F. G. A. Stone from Bristol University. Chains are constructed by complexation of two metal atoms (nickel(0) or platinum(0)) to tungsten or molybdenum carbyne compounds where the carbyne ligand bridges two metal atoms. Up to eleven metal atoms have been joined together in this manner. Professor H. D. Kaesz from U.C.L.A. presented some reactions of acetylenes with edge double-bridged trinuclear ruthenium and osmium clusters, and Professor R. Usón from the University of Zaragoza, Spain, described the preparation of unusual platinum compounds starting from binuclear anions of the type  $[\text{Pt}(\mu\text{-X})(\text{C}_6\text{X}'_5)]_2^-$ , where X = Cl, Br; X' = F, Cl. Complexes with Pt-Pt bonds with no bridging ligands were illustrated and reaction with silver salts gave platinum-silver clusters with bridging silver atoms.

Many attempts have been made to use cluster compounds as homogeneous catalysts, but they are usually unstable under the reaction conditions and catalysis is by monomeric species. A new approach where clusters were stabilised by a central carbon atom was described by H.

Yamazaki, of the Institute of Physical and Chemical Research, Japan. Thus the well-known cluster anion  $[\text{Ru}_6\text{C}(\text{CO})_{16}]^-$  gave  $[\text{Ru}_6\text{C}(\text{CO})_{16}\text{Me}]^-$  on treatment with methyl iodide at  $130^\circ\text{C}$ . The alkyl, on treatment with hydrogen at 100 atm and  $100^\circ\text{C}$  gave the hydride  $[\text{Ru}_6\text{C}(\text{CO})_{16}\text{H}]^-$ , which was shown to be a catalyst for the hydrogenation of olefins at 1 atm  $\text{H}_2$  and room temperature with no apparent dissociation of the cluster. Unusual cluster compounds of main group elements and platinum group metals was the subject of the lecture by P. Stoppioni of the University of Florence, Italy. As an example Vaska's complex  $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$  with  $\text{P}_4\text{S}_3$  gave a di-iridium species with each iridium co-ordinated by a  $\text{P}_4\text{S}_3$  ligand, and one phosphorus atom in each ligand bridging to the other iridium atom.

Professor F. A. Cotton from Texas A&M University has worked with binuclear complexes for many years. He pointed out that although binuclear rhodium complexes of the type exemplified by  $[\text{Rh}_2(\text{CH}_3\text{COO})_4]$  are well known, attempts to make iridium analogues by the same methods invariably fail. His group has recently been investigating formamide ligands, of the type  $\text{tolNCHNtol}$ , ( $\text{tol} = 4\text{-methyl phenyl}$ ) from which  $[\text{Ir}_2(\text{tolNCHNtol})_4]$  can be prepared. This is the first binuclear iridium complex directly analogous to the binuclear rhodium complexes. With other metals the ligand gives  $[\text{M}_2(\text{tolNCHNtol})_4]$ ,  $\text{M} = \text{Co}$  with the shortest Co-Co bond length ever observed, and  $[\text{M}_2(\text{tolNCHNtol})_4]^+$ ,  $\text{M} = \text{Ni, Pd}$ . There is a weak metal-metal bond in the nickel complex but not in the palladium complex.

Professor P. H. Dixneuf from the University of Rennes discussed his approach to the incorporation of carbon dioxide into an organic substrate. Vinylcarbamates are usually prepared using phosgene but a number of ruthenium complexes catalyse the reaction of acetylenes with secondary amines and carbon dioxide to give these synthetically useful intermediates. For catalyst precursors of the type  $[\text{RuCl}_2(\eta^6\text{-aryl})\text{PR}_3]$ , ruthenium vinylidene complexes are intermediates as shown by trapping experiments

with alcohols. Professor E. Singleton from C.S.I.R., South Africa also described some new ruthenium chemistry using versatile, reactive intermediates, including  $[\text{RuH}(\text{cycloocta-1,5-diene})(\text{H}_2\text{NNMe}_2)]^+$ . A number of routes to new compounds were shown involving displacement of labile ligands, as well as an improved synthesis of ruthenocene by reaction of  $[\text{RuCl}_2(\text{COD})]_n$  with acetonitrile to give  $[\text{RuCl}_2(\text{COD})(\text{MeCN})_2]$  which with  $\text{TICp}$  gave  $[\text{RuCp}_2]$  in more than 90 per cent yield.

## Hydrides and Hydrogenation

The first two papers of this session described the use of NMR to study dihydrogen ligands. Professor R. H. Crabtree from Yale University discussed the chemistry of non-classical  $\text{H}_2$  bonding. Detection of dihydrogen complexation in metal polyhydride species is problematic, for example their structures in solution and in the solid state may be different and their fluxionality gives rise to only one  $^1\text{H}$  NMR resonance. However it has been found that the temperature dependence of the relaxation time  $T_1$  can be used to identify structures and obtain H-H distances. Correction for temperature is carried out by taking measurements at the minimum of the  $T_1$  versus temperature curve. These non-classical polyhydrides are mainly found for  $d^6$  metal ions and a high oxidation state is required. One possible industrial application is for the preparation of heavy water via H/D exchange.

Professor R. H. Morris of the University of Toronto has looked at analogies between  $\text{N}_2$  and  $\text{H}_2$  chemistry using NMR and labelling experiments. Dihydrogen complexes such as  $t\text{-}[\text{M}(\eta^2\text{-H}_2)(\text{H})(\text{PEt}_2\text{CH}_2\text{CH}_2\text{PEt}_2)_2]\text{BPh}_4$  where  $\text{M} = \text{Fe, Ru, Os}$  have been prepared and the half-life for incorporation of deuterium in acetone- $d^6$  solutions has been measured in conjunction with NMR spectra. The H/D interchange mechanism appears to have a number of possibilities and a typical value for the free energy of transfer of H between a dihydrogen and a classical hydride ligand on an osmium complex is of the order of 50–55 kJ/mol at a temperature of 300 K.

The use of H<sub>2</sub>/O<sub>2</sub> mixtures for oxidations catalysed by rhodium complexes was described by Professor B. R. James, University of British Columbia. The selective oxidation of dimethylsulphoxide (dmsO) to the sulphone using [RhCl<sub>3</sub>(dmsO)<sub>3</sub>] and of cyclooctene using an iridium(III) system were given as examples. In each case the stoichiometry corresponds to:

Substrate (X) + O<sub>2</sub> + H<sub>2</sub> = X(O) + H<sub>2</sub>O  
and the driving force for the reaction is the formation of water.

The mechanism of this type of reaction does not involve the formation of free radicals. When dimethylacetamide (dma) is used as a solvent, the dma is selectively oxidised at 50°C to the hydroperoxide. Spectroscopic and kinetic data indicate oxygen transfer via a rhodium(III)peroxide intermediate and dihydrogen is required to reduce rhodium(III) to rhodium(I).

Professor J. L. Spencer's lecture was concerned with work at the University of Salford on electron deficient platinum clusters such as [Pt<sub>4</sub>H<sub>x</sub>(PBU<sup>t</sup>)<sub>4</sub>]<sup>+</sup> (x = 3,7). The metallic core is stabilised by co-ordination to tri-*t*-butylphosphine but small molecules such as dihydrogen react rapidly and reversibly, regenerating the polyhydrido clusters. Characterisation of these species has been carried out using a variety of techniques including X-ray diffraction, <sup>31</sup>P and <sup>195</sup>Pt NMR, fast-atom bombardment mass spectroscopy and cyclic voltammetry.

The use of co-ordinatively unsaturated clusters as models for chemisorption and catalysis on platinum surfaces was discussed by Professor R. J. Puddephatt, University of Western Ontario. To mimic a surface using clusters one requires systems that are co-ordinatively unsaturated, can accept extra ligands and be capable of regeneration. Thus for example the clusters [Pt<sub>3</sub>(μ<sup>3</sup>-CO)(μ-dppm)<sub>3</sub>]<sup>2+</sup> and [Pt<sub>3</sub>(μ<sup>3</sup>-H)(μ-dppm)<sub>3</sub>]<sup>+</sup> where dppm = Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub> serve as models for reactions at the 3-fold sites on a platinum{111} surface. Special attention has been given to the reactions of acetylene on platinum, such as

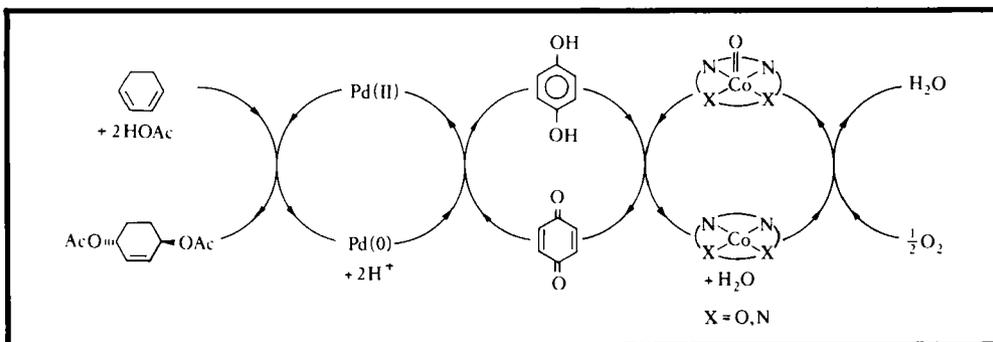
hydrogenation. Interestingly no C<sub>3</sub> or C<sub>4</sub> species have been detected during these reactions.

Hydrogenation reactions using binuclear rhodium complexes were discussed by Professor R. Eisenberg from the University of Rochester, New York. NMR has been used to assign structures to these species and detect the presence of a radical pair mechanism, and the use of deuterated substrates provides additional data. The results originally suggested that for styrene hydrogenation a radical pair mechanism was involved with a metal-based radical pair. However, a more extensive analysis showed that the chemically induced dynamic nuclear polarisation effects observed were due to products from reaction of para-hydrogen with the olefin, where the ortho/para equilibrium was shifted in favour of the para-form by storage at liquid nitrogen temperatures.

Use of the RhCl<sub>3</sub>-methyltrioctylammonium chloride ion pair as a hydrogenation catalyst was discussed by Professor J. Blum of the Hebrew University, Jerusalem. This system was reported to hydrogenate aromatics at ambient temperatures and pressures, and also proved potentially useful in selectively hydrogenating double and triple bonds and aromatics in preference to vulnerable groups such as nitro and carbonyl derivatives. B. F. G. Johnson of the University of Cambridge described the formation of large osmium clusters of ten metal atoms and beyond. These complex systems are influenced by the degree of protonation, with the hydrogen located in tetrahedral and octahedral structures raising the overall cohesive energy.

The presentation of the recent work on clusters at Cambridge was continued by P. P. Edwards who considered these species to be a potential link between microscopic and macroscopic regimes and that successful experimental probing could allow monitoring of the evolution of bulk properties from the atomic and molecular level.

J. F. Stoddart of the University of Sheffield discussed the nature of the bonding between outer sphere ligands such as crown-ethers or



cyclodextrins and a variety of platinum group metal complexes including  $cis\text{-}[\text{PtCl}_2(\text{NH}_3)_2]$ . This second sphere co-ordination was interpreted as a molecular recognition phenomenon and bonding is believed to be non-covalent with stable molecular adducts being observed in solution as well as in the solid state. This expanding area of extra-molecular chemistry offers potential applications in drug delivery of platinum anti-tumour agents and also to novel catalytic systems. M. Schröder presented work recently carried out at the University of Edinburgh aimed towards applying the chemistry of macrocyclic complexes of the platinum group metals towards homogeneous and electrocatalysis. The structures of octahedral tetra-aza complexes were discussed and it was shown that square planar complexes of palladium(II) could be reduced electrochemically to produce highly reactive palladium(I) species. A range of homoleptic hexathia complexes were described and it was shown that the ability of the polythia crown ligands to stabilise mononuclear platinum(III), palladium(III) and rhodium(II) species was related to the stereochemical and electronic properties of these products.

### Palladium Compounds in Organic Synthesis

Organic chemists are increasingly turning to palladium compounds to give high yield, selective syntheses under mild conditions. A half day session was devoted to this important area of palladium chemistry. Professor A. Yamamoto from the Tokyo Institute of Technology presented results of a mechanistic

investigation into palladium catalysed carbon-carbon bond formation from alkyl and aryl halides and Grignard reagents. Possible intermediates were prepared and their reactions to give organic products were discussed. The syntheses of bicyclic and tricyclic systems were illustrated by Professor G. P. Chiusoli from the University of Parma, Italy. In a versatile method, palladium complexes were used to catalyse the co-cyclisation of terminal olefins with alkenes, alkynes, nitriles or carbon monoxide, giving cyclic systems in high yield.

Professor J.-E. Bäckvall from the University of Uppsala, Sweden presented a fairly general method for the highly specific 1,4 functionalisation of 1,4-dienes. In this reaction the palladium(II) acetate catalyst is reduced to palladium(0), but as shown in the Scheme, for catalysis to take place oxygen acts as an oxidant via cobalt complexes which oxidise hydroquinone, which in turn re-oxidises the palladium. This type of triple catalysis is common in biological reactions and may be expected to be more widely used in homogeneous catalysis over the next few years. Asymmetric Wacker reactions, giving chiral products, have not yet reached the almost perfect enantioselectivity encountered in rhodium-catalysed asymmetric hydrogenations and, as explained by T. Hosokawa of Osaka University, optical yields are rarely more than 20 per cent. In his work, palladium  $\pi$ -allyl complexes derived from  $\beta$ -pinene were used to cyclise derivatives of allyl phenol with excellent chemical yield but moderate optical yields.

W. P. Griffith from Imperial College has

recently been investigating the application of high oxidation state ruthenium complexes in organic synthesis. One novel, particularly selective system is  $(Pr_4N)[RuO_4]/4$ -methylmorpholine N-oxide in dichloromethane. This is simple to prepare from ruthenium trichloride and oxidises primary alcohols to aldehydes and secondary alcohols to ketones, leaving sensitive groups such as epoxides, olefins and silyl ethers unaffected.

### Platinum in Biology

Professor B. Lippert from the University of Freiburg began his lecture on platinum-nucleobase interactions with a brief description of what is known of the mechanism of action of the anti-tumour drug Cisplatin and its binding to DNA and then showed examples of a number of different types of platinum nucleobase complexes prepared in his laboratory. M. J. Cleare from the Johnson Matthey Technology Centre was the first person to prepare Carboplatin [diammine(cyclobutane-1,1-dicarboxylato)platinum(II)] which has recently been launched in the U.K. and elsewhere as a second generation platinum anti-tumour drug. He gave the rationale for its selection and illustrated its much reduced toxicity when compared with Cisplatin. Recent clinical data was also discussed particularly on the use of Carboplatin against ovarian and small cell lung cancer.

The kinetics of reaction of platinum anti-tumour complexes with typical nucleophiles found in biological systems have been studied by I. A. G. Roos of the Peter MacCallum Cancer Institute, Melbourne, Australia who found that the conversion of Carboplatin to Cisplatin by chloride ion was pH dependant. F. Joó from the Hungarian Academy of Sciences described his use of water soluble platinum group metal complexes as hydrogenation catalysts for double bonds in intact biological membranes, and the effects of such hydrogenations. H. A. O. Hill from the University of Oxford discussed the modification of gold and platinum electrodes with various ligands which facilitate electron transfer to proteins. This

technique was originally used to study protein electrochemistry but now finds a place in sensor electrodes such as the recently launched blood glucose monitor intended for use by diabetics.

### Surfaces and Catalysis

Professor D. A. King of Liverpool University reported on chemisorption studies on Pt{110}, Pd{110} and Cu{110} surfaces. Relatively simple, well-understood systems such as those formed by carbon monoxide adsorption were investigated initially and formed a basis for understanding more complex processes such as the adsorption and decomposition of H<sub>2</sub>NCO and CH<sub>3</sub>NCO. A range of techniques were employed for this work, mainly based on particle spectroscopy, which included vibrational spectroscopy, thermal desorption spectroscopy and angle-resolved ultraviolet photoelectron spectroscopy; the latter being used to prove an angular surface positional configuration of carbon monoxide on Pt{110}. The work has also shown that considerable reconstruction of a metal surface can take place following adsorption which depends on the chemical properties of both the metal and adsorbate. Co-adsorption of potassium with other adsorbates onto several metal surfaces was also described and it was shown that, in some cases, for instance with Cu{110} stable salt formation can occur, whereas with Pd{110} a more complex system evolves. This may have a bearing on the application of these metals to certain processes such as Fischer-Tropsch catalysis. Professor P. B. Wells of the University of Hull described collaborative work carried out between the Chemistry and Physics Departments of Hull University and I.C.I. Chemical and Polymers Group on the structure and catalytic chemistry of osmium clusters at oxide and sulphide surfaces. The eventual goal is that as metal clusters can be highly characterised, catalytic site fabrication via metal clusters may lead to well understood catalyst systems which can perhaps be easily optimised towards site configuration of a desired activity and/or selectivity. Although that goal remains distant, carbonyl clusters of osmium with nuclearity 3,4,6 and 10

have been impregnated from non-aqueous solutions onto a variety of oxide or sulphide supports, and then rendered catalytically active by heating to 523K in helium to give an even distribution of osmium on the surfaces. The work has shown that for a relatively demanding process, such as ethane hydrogenolysis where a multi-nuclear site is required, cluster catalysts are more active than conventional catalysts and their performance is remarkably reproducible. The specific catalytic activities of the supported osmium clusters for ethene hydrogenation and for ethane hydrogenolysis were found to vary by more than two orders of magnitude depending upon the support and this was interpreted as an electronic effect resulting from direct chemical interaction between support and cluster. Structural evidence was presented for such an interaction between Os-Al in the osmium-alumina system.

The topic of cluster chemistry was continued by Professor A. Ceriotti of the University of Milan, Italy who described investigations into a new high nuclearity anion  $[\text{Ni}_{36}\text{Pt}_4(\text{CO})_y]^{6-}$ . This cluster structure was found to be a  $\text{Pt}_4$ -tetrahedron fully encapsulated in a nickel atom skin and confirmed the theory that such clusters mimic the structure found in small bimetallic particles where, under certain conditions, the phase with lower surface energy will envelop the other phase giving rise to the so-called "Cherry" model. This led to conclusions similar to those of Professor Wells, and it was proposed that metal clusters may be useful models for metal crystallites, and that investigations of their properties should lead to an improved understanding of the role played by metal particles in heterogeneous catalysis. The topic of high nuclearity carbonyl clusters was also discussed by Professor B. T. Heaton of Liverpool University. In this talk, some of the problems in characterising these species were covered, in particular beam damage following examination by analytical electron microscopy (AEM). A large nickel-platinum cluster  $[\text{Ni}_{38}\text{Pt}_6(\text{CO})_{48}\text{H}]^{5-}$  however suffered little damage following a low beam intensity examination, and the structural and elemental

information obtained was consistent with that expected for this anion. This contrasted with a similar treatment of a gold cluster  $[\text{Au}_{55}(\text{PPh}_3)_{12}\text{Cl}_6]$  which readily lost all ligands on electron impact. The mode of destruction of the nickel-platinum cluster following AEM at higher beam intensities was then described and involves agglomeration to give uniform size spots of approximately  $40\text{\AA}$  followed by loss of carbon monoxide with concomitant formation of a graphite skin around a nickel-platinum alloy.

The session was completed by D. S. Cameron of the Johnson Matthey Technology Centre who reported on new developments in platinum alloy catalysts for fuel cells. Fuel cell power generators are capable of converting chemical energy directly to electrical energy and this is effected by reaction of hydrogen with oxygen over electrodes comprising platinum or platinum alloy catalysts. The units are compact, highly efficient, non-polluting and they require little maintenance. Their cost can be a disadvantage and to minimise this, much effort has been expended on improving the efficiency, activity and durability of the carbon supported electrode catalysts. The use of certain platinum alloys as opposed to monometallic platinum as the active centres on the oxygen reduction electrode has resulted in improved activity and also minimises sintering and consequently this increases catalyst lifetimes. These improvements should result in commercially available fuel cell systems in the near future.

## Clusters and Catalysis

Professor B. C. Gates from the University of Delaware discussed molecular organometallic chemistry on surfaces with reference to the reactivity of metal carbonyls of osmium, ruthenium and rhodium on silica, magnesia and alumina. The reactions of these organometallic compounds on surfaces are strikingly similar to their solution chemistry. The main goal of this research is to prepare catalytic sites with metal carbonyl clusters of controlled nuclearity. Reactions of surface-bound metal carbonyls include

oxidative fragmentation, giving ensembles of mononuclear complexes, and reductive carbonylation of metal ions to generate surface-bound metal carbonyl clusters.

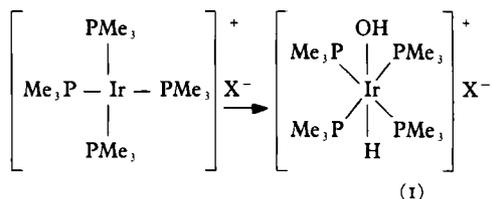
Professor M. Ichikawa of Hokkaido University reported on the problems of improving selectivity in the Syngas reaction. Rhodium is well-known as a good catalyst for this reaction and it has been shown that the addition of transition metals such as titanium, zirconium and manganese have a marked promotional effect on CO + H<sub>2</sub> conversion. However, selectivities alter dramatically on changing from for instance, rhodium-molybdenum to rhodium-iron and a wide range of techniques including EXAFS, Mössbauer and i.r. spectroscopy have been used to understand this behaviour. The rhodium-iron system was carefully investigated since it was found that almost complete conversion of carbon monoxide and hydrogen to ethanol could be achieved under certain conditions. Clusters such as [Fe<sub>2</sub>Rh<sub>4</sub>(CO)<sub>16</sub>]<sup>2-</sup> give good efficiencies for ethanol formation while the cluster [Pt<sub>12</sub>(CO)<sub>25</sub>]<sup>2-</sup> gives 100 per cent conversion. For the platinum-rhodium-iron system, iron exists as both Fe(0) and Fe(III). The iron seems to act as a breaker to divide rhodium and platinum clusters, and provides active bifunctional sites for acid-promoted CO insertion. B. D. Dombek talked about Union Carbide's recent work on the Syngas conversion. Useful products from this reaction include ethylene glycol, ethanol, higher alcohols and acetic acid. For this reaction ruthenium catalysts give two types of reaction: the production of methanol in non-basic solvents, and the formation of methanol, ethylene glycol and other alcohols in the presence of basic promoters. In an effort to produce a catalytic system with high selectivity for ethylene glycol formation with high conversion rates, model compounds such as [HRu(CO)<sub>4</sub>]<sup>-</sup> were investigated in the presence of basic promoters such as iodide using spectroscopic and kinetic studies. The addition of rhodium complexes to the ruthenium catalyst substantially enhances the selectivity to ethylene glycol. A novel system for methanol homologation to ethanol

has recently been identified and is the subject of a patent application.

## Novel Organometallic and Co-ordination Chemistry

Some aspects of conjugated diene complexes including their co-ordination geometry and the nature of the bonding were described by Professor A. Nakamura of Osaka University. According to a structural and theoretical analysis, the chemical properties of the diene complexes of electron-rich platinum group metals contrast markedly with those of electron-deficient early transition metals and of actinides. M. A. Bennett from the Australian National University reported research carried out into the chemistry of diplatinum complexes containing bridging orthometallated aryl phosphine ligands. The synthesis of mono-oxo and di-oxo alkyl complexes of osmium(VI) has been investigated by Professor P. Shapley from the University of Illinois at Urbana Champaign. The reaction of trans-[Os(O)<sub>2</sub>Cl<sub>4</sub>][PPh<sub>4</sub>]<sub>2</sub> with R<sub>2</sub>Mg or RMgX (where R = CH<sub>3</sub>, CH<sub>2</sub>SiMe<sub>3</sub>, CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>, or C<sub>6</sub>H<sub>5</sub>, and X = Br or I) produces [Os(O)R<sub>2</sub>] in yields of approximately 50 per cent depending on R. These oxo alkyl complexes of osmium(VI) are remarkably stable to ligand loss and substitution and only react under extreme conditions.

J. G. Jeffrey from Oxford University described the synthesis and some chemistry of trifluoromethyl and difluorocarbene mononuclear complexes of osmium, ruthenium and rhodium. D. Milstein from E.I. du Pont de Nemours & Co. gave a lecture entitled "Activation of O-H and N-H Bonds by Ir(I)". The reaction of [IrL<sub>4</sub>]X with water, where L = PMe<sub>3</sub>, proceeds readily even at low temperatures to give the hydroxy complex (I) (X = PF<sub>6</sub><sup>-</sup>, Cl<sup>-</sup>):



The mechanism of this oxidative addition was followed by  $^{31}\text{P}$  NMR which shows that the trans OH species is formed first and then rearranges to form the more thermodynamically stable cis complex. There is a very strong trans effect which follows the order  $\text{H} > \text{P} > \text{SH} > \text{OCH}_3 > \text{OH}$ . The cis Ir-O-H angle is unusually small ( $91^\circ$ ). The reaction with methanol is different from that for water and the end product is the protonated complex  $[\text{IrH}_2\text{L}_3]^+$  and formaldehyde, although the products do depend on the initial concentration of the reactants. The addition of ammonia to alkenes would be a useful reaction and thus analogies with the above reactions have been sought. The reaction of ammonia with the complex  $[\text{Ir}(\text{PEt}_3)_2(\text{C}_2\text{H}_4)_2]\text{Cl}$  in THF at  $25^\circ\text{C}$

produces an ammine-bridged bi-iridium complex, with the release of  $\text{Cl}_2$  and ethene.

### The Fourth Conference

During the week the oral presentations gave an insight into the current state of research on the chemistry of the platinum group metals. Some of the most recent work was presented in the poster sessions which gave an opportunity for informal discussion. The continued high level of academic interest in this area may well result in new opportunities for commercial developments, and can be expected to lead to further useful discussions at the fourth conference in the series, which is to be held in Cambridge in 1990.

B.A.M.

G.G.F., R.J.P.

## Weldability Test for Thin Iridium Sheet

The use of iridium alloys doped with thorium to encapsulate the  $^{238}\text{PuO}_2$  radioactive heat sources used in thermoelectric generators which provide stable electrical power during outer planetary missions has been reported here previously (1, 2). These iridium alloys possess high melting point, good high temperature strength, resistance to oxidation, and are compatible with both the fuel and the surrounding insulation materials. The thorium serves as a grain boundary strengthener, segregating to the grain boundaries and inhibiting intergranular fracture.

A container is formed by joining together two hemispherical cups and, because of the application, the equatorial weld is required to be totally reliable. An improved method of welding has been developed for this purpose (3).

Iridium alloys may suffer from hot cracking during welding, and experience indicates that even when approved specifications and welding procedures are followed variations in weld quality can occur. Clearly defective welds represent a waste of both materials and fabrication costs. Thus if the weldability of a material can be established prior to or early in the manufacturing process, significant savings will result.

Standard tests to determine the hot cracking tendency of metals and alloys do exist, but these are most suitable for sections thicker than 2.5 mm. Now, however, workers at the Oak Ridge National Laboratory have developed a simple modified circular plate test which will

successfully determine hot cracking susceptibility (4).

Sheet specimens 50 mm in diameter and 0.63 mm thick are held in a test fixture which is designed to restrain them at the centre and the periphery. Using a gas tungsten arc welding procedure under an inert atmosphere, two circular concentric autogenous welds are made, then the disc is removed, turned over, replaced, and the procedure repeated. The first weld is 35 mm in diameter and the other 22.3 mm; after inversion the welds are repeated in the same order.

The first welding sequence produces a microstructure which is susceptible to cracking and it also increases the stress in the specimen. If cracking does not occur, the disc is then inverted and the process repeated. After the second sequence, a lack of evidence of cracking in either of the two circular welds is taken to indicate a weldable alloy. If the smaller but not the larger diameter weld shows cracking the material is regarded as being susceptible to cracking, but if both welds are cracked the material is classified as highly susceptible to cracking.

### References

- 1 *Platinum Metals Rev.*, 1979, 23, (1), 16
- 2 H. Inouye, *Platinum Metals Rev.*, 1979, 23, (3), 100
- 3 *Platinum Metals Rev.*, 1985, 29, (1), 11
- 4 S. A. David and J. J. Woodhouse, *Weld. J.*, 1987, 66, (5), 129s