

The Chemistry of the Platinum Group Metals

A REVIEW OF THE SECOND INTERNATIONAL CONFERENCE

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Following a successful meeting held in Bristol in 1981, the second international conference to deal entirely with the chemistry of the platinum group metals was held at the University of Edinburgh in July 1984, sponsored by the Dalton Division of the Royal Society of Chemistry. The conference attracted over three hundred participants from both academic and industrial organisations in twenty three countries. There were twenty seven lectures, and in excess of one hundred posters presented during the week. The lectures are summarised here, while a book containing abstracts of the posters only is available from the Royal Society of Chemistry.

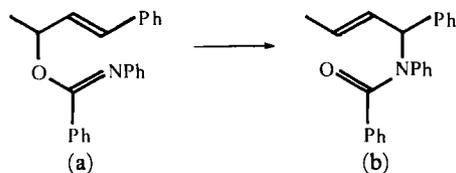
Topics covered at Edinburgh included cluster and organometallic chemistry, catalysis, biological aspects and physical methods. The conference was opened by Professor Joseph Chatt of the University of Sussex, who gave his impressions of progress since he first became involved in this field. It was particularly appropriate that Professor Chatt should address the conference as it was he who had organised the first small conference on the co-ordination chemistry of the platinum group metals some thirty five years ago. From that time onwards the interest in their organometallic chemistry has increased enormously, leading to the development of the industrially important area of homogeneous catalysis, to a far greater understanding of cluster chemistry and, more recently, to the successful use of platinum group metal compounds in medicine. His introduction was also enlivened by reminiscences of some of the leading personalities formerly involved in these areas of research.

The first lectures of the conference considered homogeneous catalysis; Professor J. Halpern of the University of Chicago presented the results of his investigations of the mechanism of homogeneous hydrogenation by

anionic ruthenium hydride complexes. The activity of the orthometallated species $K^+[RuH_2(PPh_3)_2(PPh_2\overset{\ominus}{C}_6H_4)]^-$ in homogeneous hydrogenation was reported in 1980 when it was shown to reduce ketones, esters, nitriles and polycyclic aromatics as well as olefins. Originally this unusual reactivity was ascribed to the hydride groups in the anionic catalyst but Professor Halpern went on to show that this is not the case as for instance, hydrogenation of anthracene to 1,2,3,4-tetrahydroanthracene proceeds via a co-ordinated 1,3-diene intermediate. A number of anionic ruthenium hydride phosphine complexes were isolated and all gave the same activity, showing that the original orthometallated complex, formed by ruthenium insertion into the C-H bond of an *ortho* carbon in a triphenylphosphine ligand, is probably not itself involved in the catalytic cycle. These anionic species decompose with protonic reagents so the hydrogenation of ketones and nitriles, which yields alcohols and amines, respectively, as products is not likely to involve them to any great extent. By examination of single steps, Professor Halpern showed that two catalytic cycles operate with the common intermediate being a solvated form of

[RuH₂(PPh₃)₃]. In the course of this work straightforward syntheses of catalytically active compounds were developed and it is hoped that their unusual selectivity will make them useful laboratory reagents.

Professor B. Bosnich of the University of Toronto discussed his work on metal-catalysed Claisen and Cope rearrangements. These rearrangements are highly stereospecific and widely used in synthetic organic chemistry, but are generally very slow requiring several hours at 200°C to go to completion. Such harsh treatment may cause decomposition so a catalysed reaction would be very useful and leads to the possibility of using optically resolved (chiral) ligands on the metal catalyst to achieve asymmetric synthesis. Bosnich screened a number of noble metal complexes and found that [PdCl₂(PhCN)₂] gave a remarkable rate acceleration (reaction complete in a few hours at room temperature) with the same stereochemical control as in the uncatalysed rearrangement. The Pd⁰ complex [Pd(PPh₃)₄], gave considerable deuterium scrambling but the stereochemistry of the starting material was still preserved. This was explained in terms of a dissociation of the imidate ester starting material (a) to a palladium π-allyl complex and an amide anion followed by their recombination to give the amide (b).



In conclusion, Professor Bosnich emphasised that Pd^(II) catalysis can be widely applied in organic syntheses and that further work will be aimed at introducing chiral centres into the products.

In his lecture entitled *Reactivity and Selectivity in Catalysis* Dr. J. M. Brown of the University of Oxford described some of his more recent work on homogeneous hydrogenation catalysis. Results from model compound studies and NMR evidence suggested that a *cis-bis*-phosphine rhodium complex could be an inter-

mediate in the hydrogenation of olefins with Wilkinson's catalyst [RhCl(PPh₃)₃]. The asymmetric hydrogenation of olefins with catalysts with chiral ligands to give optically active products was also discussed, with particular emphasis on the use of stable iridium complexes as models for the corresponding transient rhodium complexes which are intermediates in the reaction.

One of the most interesting new developments in organometallic chemistry and of considerable potential in commercial terms, is the activation of C-H bonds in saturated hydrocarbons. This was reviewed by Professor W. A. G. Graham from the University of Alberta who then described his own work in the area. In his laboratory the activation of cyclohexane was discovered by accident, as irradiation of a solution of the pentamethylcyclopentadienyl complex [Ir(CO)₂η⁵-C₅Me₅] in cyclohexane under hydrogen was expected to give a trihydride, but instead gave a cyclohexyl derivative where iridium had inserted into a C-H bond. The presumed 16-electron intermediate in this case, either [Ir(CO)η⁵-C₅Me₅] or [Ir(CO)₂η³-C₅Me₅], is so reactive that Professor Graham stated that he has yet to find a hydrocarbon with which it does not react. A similar osmium complex [OsH₂(CO)η⁶-C₆Me₆] also gave products of insertion in photolysis in alkane solvents, but with some decomposition. Direct conversion of hydrocarbons to functionalised derivatives is possible but a commercially viable system is some way off as yet.

Organometallic Chemistry

Professor R. Poilblanc of CNRS, Toulouse described the synthesis and reactions of iridium and rhodium bi- and trimetallic species where the metal atoms were bridged with sulphur-based ligands and Dr. A. J. Deeming of University College, London reviewed the occurrence of metallocarboxylic acids and their role in the homogeneously catalysed water gas shift reaction (CO + H₂O = H₂ + CO₂). He then presented his work on iridium complexes for instance *cis,cis,trans*-[IrCl₂(COOH)(CO)(PPhMe₂)₂], prepared by addition of methyl

chloroformate to the square planar *trans*-[IrCl(CO)PPhMe₂]₂ and subsequent hydrolysis of the ester. In the presence of base, the carboxyl group was lost to give an iridium hydride via an Ir^I intermediate, and in acid an iridium carbonyl was obtained via protonation of the carboxyl group and loss of water. In his lecture on organic transformations at ruthenium centres Dr. S. A. R. Knox of Bristol University illustrated the conversion of a bridging carbonyl ligand in a metal-metal bonded diruthenium compound to a bridging methylene ligand. This could then be converted to a bridging methyl group by protonation or to a bridging methyne by hydride abstraction. The bridging methyne ligand reacted readily with alkyllithium reagents to give substituted bridging methylene groups which may possibly be thought of as model compounds for the Fischer-Tropsch reaction on metal surfaces.

Professor H. Werner of the University of Würzburg described the preparation of rhodium cyclopentadienyl complexes with small, normally highly reactive organic molecules as ligands. Complexes of thio-, seleno- and telluroformaldehyde were prepared by reaction of NaSH, NaSeH or NaTeH with [RhI(CH₂I)η⁵C₅H₅(PMe₃)]. With nucleophiles (pyridine, phosphines, sulphides) this compound gave ylid complexes such as [RhI(CH₂PR₃)η⁵C₅H₅(PMe₃)]⁺ by attack of the nucleophile on the co-ordinated iodomethyl group. A similar rhodium compound with a co-ordinated vinylidene ligand could be converted to complexes with thioketene and thioacetaldehyde ligands. Professor G. van Koten of the University of Amsterdam described his work on the oxidative addition of alkyl halides to platinum complexes where reversible alkyl shifts from platinum to a carbon atom of the ligand were observed.

Cluster Chemistry

The session on cluster compounds was opened with a lecture by Professor Sir Jack Lewis of Cambridge University who gave an overall view of the cluster chemistry of ruthenium and osmium. Professor Lewis

showed that synthetic methods for homo- and heterometallic clusters are now becoming rationalised, particularly since the introduction of tertiary amine oxides for the stepwise removal of carbonyl ligands. With the aid of molecular models he then demonstrated how clusters can be built up and taken apart to give a wide variety of new metal atom frameworks. Large cluster compounds particularly those containing large proportions of metal atoms may be analogous to bulk metals and Dr. A. Ceriotti of the University of Milan described the synthesis and characterisation of some very large platinum and platinum/nickel clusters such as [Pt₃₈(CO)₄₄H₂]²⁻. Heating this platinum cluster gave a larger cluster which is not yet fully characterised but had a diameter of 20.5 Å by high resolution electron microscopy, which would correspond to about 100 platinum atoms.

Professor S. G. Shore from Ohio State University presented his results on the synthesis of the anions of ruthenium carbonyl clusters and discussed their relevance in catalysis of the water gas shift reaction. Treatment of [Ru₃(CO)₁₂] or [H₄Ru₄(CO)₁₂] with potassium hydride or an alkali metal together with benzophenone gave high yields of anionic clusters, the structure of which could be altered by varying the stoichiometry. Reaction of these anions with clusters of other metals gave mixed metal clusters. Catalysis of the water gas shift reaction by anions containing four ruthenium atoms did take place but the overall reaction was extremely slow (approximately 3 turnovers per day at 100°C under 0.9 atm carbon monoxide). The activity could be improved slightly by the addition of chelating biphosphines. This could be a true example of catalysis by an intact cluster, as the mononuclear anion [HRu(CO)₅]⁻ does not survive the reaction conditions.

The synthesis of mixed metal clusters containing palladium and platinum by reaction of square planar d⁸ *trans*-dichloro complexes containing a variety of ligands with a number of sodium carbonylmetallates such as Na[Mn(CO)₅] was described by Dr. P. Braunstein of the Université Louis Pasteur,

Strasbourg. A mixed metal cluster $[\text{Pd}_2\text{Mo}_2\text{Cp}_2(\text{CO})_6(\text{PPh}_3)_2]$ on a support of alumina gave an active and selective catalyst for the carbonylation of nitrobenzene to phenylisocyanate.

Heterogeneous Catalysis

The importance of the surface topography of a supported catalyst and the state and effect of adsorbed hydrocarbons was discussed by Dr. G. Webb of Glasgow University in his lecture entitled "Transformations of Hydrocarbons Catalysed by Platinum Group Metals". Dr. Webb described the two extreme types of reactions: those which are structure insensitive, such as olefin hydrogenation where the catalyst dispersion and type of support have little effect on the activity per metal atom and those which are structure sensitive such as hydrogenolysis where more than one metal site is believed to be involved. He then described some of his recent work which showed that in the hydrogenation of ethylene with a palladium/silica catalyst the surface is rapidly and irreversibly covered by a monolayer of carbonaceous material which is not itself hydrogenated. There is a growing body of evidence that for most reactions of hydrocarbons the catalyst surface is almost completely covered with an organic layer which has a significant effect on catalytic activity. The exact role of this layer is not yet defined but in some cases it acts as a slow poison, perhaps due to graphitisation, whereas in other cases it dramatically enhances the catalytic activity. The layer may also act as a hydrogen reservoir or even as an electron donor, hence lowering the work function of the metal. In conclusion, Dr. Webb stressed that the organic layer is a vital part of a catalyst and that models used for supported catalysts should take account of this monolayer coverage of carbonaceous material.

Dr. B. Harrison of the Johnson Matthey Group Research Centre in his lecture on the preparation of noble metal catalysts began with a survey of uses of heterogeneous platinum group metal catalysts and pointed out that the amount of noble metal used in pollution control systems, particularly catalytic converters on

automobiles, will soon exceed that used for catalysis in the petrochemical industry. He then illustrated the importance of selecting the correct catalyst precursor in the preparation of supported metal catalysts and the relevance of the control and understanding of the firing procedure to obtain the required dispersion. Dr. Harrison concluded with a description of two applications of catalyst technology, automobile emission control and fuel cells, where a deep understanding of the catalyst preparation is necessary in designing and developing a successful catalyst.

Photolysis of Water

In his lecture on platinum group metals and the photodissociation of water, Dr. A. Harriman of the Royal Institution reviewed the different approaches to water photolysis and commented that there has been a recent slackening of interest in this area although the problems are by no means solved. He then went on to describe his work with metalloporphyrins as stable photosensitisers which absorb in the visible spectrum and can be readily modified. During a hydrogen evolution catalysis test an aqueous solution of a zinc metalloporphyrin with methyl viologen and EDTA as hydrogen donor gave 200ml hydrogen per hour from one litre of solution on the roof of a building in London. Metalloporphyrins were also successfully used as redox catalysts in the oxygen evolution reaction.

Dr. D. J. Cole-Hamilton of the University of Liverpool discussed his recent work on low valent platinum complexes, especially $[\text{HPt}(\text{PEt}_3)_3]^+$. Ultraviolet irradiation of a solution of this complex in dilute sulphuric acid leads to the catalytic production of hydrogen, together with the formation of persulphate. Silver ion catalyses the decomposition of persulphate to oxygen and sulphate, giving catalytic water photolysis. The disadvantages with this system are that it requires u.v. illumination and the turnover number is very low. A similar platinum complex $[\text{PtHCl}(\text{PEt}_3)_2]$ was shown to be active for the conversion of glucose to hydrogen and carbon dioxide in

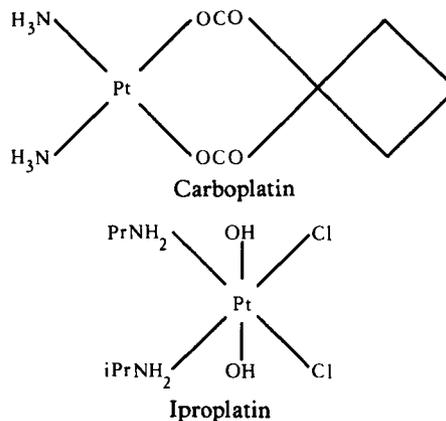
alkaline solution and this may have potential uses in conversion of waste carbohydrate.

Medical Uses of the Platinum Group Metals

The increasingly important use of the platinum group metals in medicine was comprehensively covered in three lectures. Dr. E. W. Stern of Engelhard Industries gave an overview of their applications. In addition to the well known use of platinum compounds in cancer chemotherapy the radioactive isotope ^{192}Ir may be used in radiotherapy, when a small amount of the metal inside a plastic tube is placed inside or close to a tumour. The dose of radiation is then contained within a small area, minimising damage to the patient and increasing the safety of medical personnel. Another iridium isotope is used in autoradiography. In this case ^{190}Os is irradiated with neutrons to give ^{191}Os which is then converted to $[\text{OsCl}_6]^{2-}$. A solution of this relatively long-lived isotope is injected into the patient where the short-lived decay product $^{191\text{m}}\text{Ir}$ ($t_{1/2} = 4.9$ s) emits γ -radiation which is detected in autoradiography. The highly toxic OsO_4 has a surprising use in treatment of inflammatory arthritis of the knee. A solution of the reagent is injected into the knee where some precipitates as insoluble oxides. This gives relief of pain and swelling in 60 to 70 per cent of patients with few side effects. The treatment has been used in Sweden and Norway since 1978. Dr. Stern concluded with a list of potential medical uses for platinum group metals as a variety of compounds have been shown to be effective as radiosensitisers, antiviral and antiparasitic agents and bacteriocides.

Dr. P. Sadler of Birbeck College began with a summary of the metal compounds which have been tested for antitumour activity by the National Cancer Institute. Of 13,000 compounds tested (remarkably few compared with the number of organic compounds screened) about one thousand were active. Of these, thirteen platinum complexes have entered clinical trials but there are indications that ruthenium complexes may also be effective with

about 20 per cent of the compounds tested showing some activity. The characterisation and some reactions of two of the latest platinum drugs in clinical trials, Carboplatin [JM8, diammine-1,1-cyclobutanedicarboxylato-platinum(II)] and Iproplatin [JM9, *cis*-dichloro-*trans*-dihydroxo-*bis*(2-aminopropane)platinum (IV)] were then illustrated followed by a description of the preparation of platinum complexes with nitroimidazole ligands for use as radiosensitisers.



Dr. H. Calvert of the Institute of Cancer Research gave a clinician's eye view of the development and use of platinum complexes in cancer chemotherapy. He described the remarkable results obtained with Cisplatin [*cis*-diamminedichloroplatinum(II)] in the treatment of testicular cancer and its uses against other types of cancer. However, the major side effects of this drug, nephrotoxicity and prolonged nausea and vomiting, limit its use. Two second generation drugs, Carboplatin and Iproplatin, developed in conjunction with Johnson Matthey Research are currently being evaluated as less toxic analogues. Carboplatin is being used at the Royal Marsden Hospital in single agent therapy for advanced ovarian cancer in a randomised comparison with high dose Cisplatin. Results to date show equivalent activity with greatly reduced side effects, particularly elimination of kidney toxicity and hearing loss and reduced nausea and vomiting. Iproplatin which is being used for the treatment of ovarian cancer at the Christie Hospital,

Manchester is showing similar results though with slightly greater toxicity than Carboplatin. Additional trials of Carboplatin at the Royal Marsden Hospital suggest that its reduced toxicity will allow platinum therapy to be used for a wider range of cancers, where results for small cell lung cancer has been promising.

Physical Techniques

Three lectures illustrated the use of NMR to solve a wide variety of problems in platinum group metal chemistry. Professor J. W. Faller of Yale University described a novel method of determination of the structure of palladium π -allyl complexes by NMR spectroscopy of complexes with a paramagnetic, encapsulated Co^{2+} ion incorporated into a phosphine ligand. The use of high pressure NMR in the determination of rates of solvent and electron exchange reactions of platinum group metal solvates was discussed by Professor A. E. Merbach of the University of Lausanne. Dr. C. A. Fyfe of the University of Guelph, Ontario reviewed the theory of high resolution solid state NMR, a technique of rapidly growing importance in diverse areas of chemistry. The use of solid state NMR was illustrated with a study of supported homogeneous catalysts, where phosphine ligands could be shown to be almost fully oxidised, and hence become inactive, during some methods of catalyst preparation.

Dr. J. A. Harrison of the University of Newcastle-upon-Tyne began with a summary of electrode kinetics and went on to describe the range of instrumental methods available to investigate the electrode reactions of inorganic compounds and electrocatalysis on electrodes based on platinum group metals. The technique of resonance Raman spectroscopy was described by Professor R. J. M. Clark of University College, London and its use illustrated in the study of mixed valence platinum chain compounds. Dr. J. Evans from the University of Southampton in his lecture on the role of EXAFS (extended X-ray absorption fine structure) in platinum group metal chemistry showed how this technique could be used to

determine the distances of atoms from a central metal atom. Examples were given from homogeneous catalysis (the orientation of ligands in a rhodium catalyst for asymmetric hydrogenation), heterogeneous catalysis and surface science. One of the strengths of the technique is that samples may be solid, in solution, on a surface or even in the gas phase. Professor N. Sheppard of the University of East Anglia discussed the use of vibrational spectroscopy to characterise metal surfaces and its relevance to the study of noble metal catalysts on oxide supports. Two recent developments have greatly aided work in this area: Fourier transform and computing techniques and electron energy loss spectroscopy. By a combination of these techniques and comparison with model metal cluster compounds, Professor Sheppard was able to show that the major species resulting from ethylene adsorption on platinum/silica have one carbon atom bridging two or three metal atoms.

The use of thermodynamics in the extraction and refining of the platinum group metals was discussed by Dr. J. R. Taylor of the Johnson Matthey Group Research Centre. The various processes were presented as far as possible in thermodynamic terms, relating the process reactions to the basic thermodynamic properties of the platinum group metals and associated minerals. Refining was discussed in terms of a possible hydrometallurgical route, and the smelting and converting operations, where ways of modelling the complex matte phase using thermodynamic data based on the component binary systems, were described.

The talks at the conference provided an excellent overview of the current state of knowledge in platinum metals chemistry, and the posters gave an opportunity for presentation of very recent results. The high concentration of academic research in this area is revealing opportunities for more commercially orientated work particularly in the area of catalysis. Representatives from academia and industry from many different parts of the world were able to discuss their mutual interests, and subsequent collaborative work is likely to result.