

The Chemistry of the Platinum Group Metals

A REVIEW OF THE FOURTH INTERNATIONAL CONFERENCE

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Sponsored by the Dalton Division of the Royal Society of Chemistry, the fourth International Conference on the Chemistry of the Platinum Group Metals was held at the University of Cambridge on 9th to 13th July 1990. Previous meetings in this series have been held in Bristol (1981), Edinburgh (1984) and Sheffield (1987). More than three hundred delegates, over one third from overseas, attended the meeting for a programme of twenty-seven lectures and almost two hundred poster presentations.

The opening lecture by Lord Lewis of the University of Cambridge set the main theme for the conference with a review of metal cluster chemistry, an area to which he has made a major contribution over many years. While concentrating on the structural aspects of cluster compounds, his lecture also illustrated a variety of synthetic routes to the compounds, their redox behaviour and the fluxionality of ligands in large clusters.

Careful analysis of the products of pyrolysis of $[M_3(CO)_{12}]$ or $[M_3(CO)_{10}(MeCN)_2]$ ($M = Ru$ or Os) has led to the identification of series of compounds ranging from M_5 species up to M_{20} species. While the structures of small clusters ($M \leq 6$) can be predicted by electron counting rules as described by Mingos, for larger clusters the rules do not predict a unique structure. Large cluster compounds can also undergo a significant number of redox changes without corresponding major structural changes, for example nine redox states have been identified for an $[Os_{20}(CO)_{40}]$ core. In the search for larger metal clusters, substitution reactions generating mixed metal species have proved useful. The coupling of osmium or ruthenium clusters with mercury salts yields compounds such as $[Ru_{18}Hg_3C_2(CO)_{42}]^{2-}$ where two Ru_9 units are linked by a Hg_3 bridge. The compounds readily undergo an unusual reversible rearrangement to form a Hg_2 -bridged

species and elemental mercury. More details on the structures of these complexes and other clusters were given by Professor M. McPartlin of the Polytechnic of North London. By studying related series of compounds, an insight has been gained into how smaller clusters react to form larger units. While early efforts to synthesise large clusters of osmium and ruthenium emphasised the role of interstitial atoms in providing additional electrons to stabilise the structure, they are not essential, as indicated by the recent characterisation of the dianion $[Os_{17}(CO)_{36}]^{2-}$.

Cluster compounds stabilised by the incorporation of boron were described by C. Housecroft of the University of Cambridge. These species, for example $[HRu_4(CO)_{12}(AuPPh_3)BH]$, may be characterised by multinuclear NMR spectroscopy (1H and ^{11}B), and in addition by X-ray crystallography when suitable crystals can be formed. The variation in reactivity of Ru_4 cluster compounds containing B, C or N atoms was illustrated by reactions with diphenylacetylene. Mixed metal clusters containing platinum were discussed by Professor R. Adams of the University of South Carolina. A number of such compounds may be obtained from the reaction of bis(cyclooctadiene)platinum(0) with metal carbonyls $M(CO)_5$ ($M = Fe, Ru$ or Os). Although the majority of the products are small clusters (3 to 7 metal atoms), reaction with $[Os_3(CO)_{10}(MeCN)_2]$,

where the acetonitrile ligands are readily substituted, yields high nuclearity clusters such as $[\text{Pt}_5\text{Os}_6(\text{CO})_{21}(\text{COD})_2]$. Reduction of $[\text{PtOs}_2(\text{CO})_9]_2$ with hydrogen yields three cluster products each containing six bridging hydrogen atoms.

The kinetics of substitution reactions of metal carbonyl clusters were discussed by Professor A. J. Poë of the University of Toronto. The effect of phosphine ligands (L) in complexes $[\text{Ru}_3(\text{CO})_{11}\text{L}]$ on the further substitution behaviour of these compounds can be analysed in terms of electronic and steric factors. Very good correlations between reaction rates and phosphine basicity (corrected where necessary for steric effects) were obtained. Increased electron donation into the cluster promotes further substitution as would be expected. A wide range of cluster complexes may be obtained by these reactions, providing many interesting opportunities for future investigations.

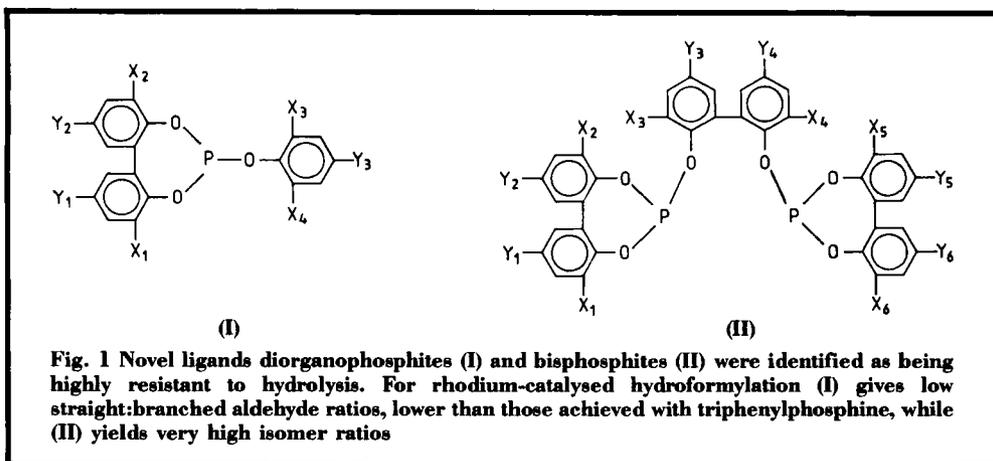
The molecular recognition processes contributing to crystal packing and growth were discussed by Professor D. Braga of the University of Bologna, using metal cluster compounds as examples. Differences in the solid state structures of $[\text{Ru}_3(\text{CO})_9(\text{C}_6\text{H}_6)]$ and $[\text{Os}_3(\text{CO})_9(\text{C}_6\text{H}_6)]$ may be attributed to crystal packing and intermolecular interactions. Intramolecular interactions affecting solid state motions such as the rotation of co-ordinated organic fragments were also considered. The motions of benzene and ethene ligands of $[\text{Os}_3(\text{CO})_8(\text{C}_2\text{H}_4)(\text{C}_6\text{H}_6)]$ can be explained by the different shapes of the potential energy surfaces for rotation of the two ligands.

Recent advances in the characterisation of small metal particles were described by Professor J. M. Thomas of the Royal Institution. Using high angle Rutherford scattering rather than the normal low angle diffraction technique, electron microscopy can detect metal particles of only 3 or 4 atoms. Information on particle structure can also be obtained by temperature-dependent EXAFS. Using this technique the giant metal clusters $[\text{Pd}_{561}\text{L}_{60}(\text{OAc})_{180}]$ (L = bipy or phen) first described by Russian workers have been characterised. These molecules are soluble in

water and do not show colloidal effects such as light scattering. For larger metal clusters (about 1000 atoms) low temperature (1 K) NMR spectroscopy provides information on the electronic properties of the particles. This technique was described by P. P. Edwards of the University of Cambridge for copper and platinum colloids. As the size of the particles decreases their electronic properties deviate from the normal metallic behaviour associated with large arrays of atoms, and so by studying a range of particles, details of this transition from metallic to non-metallic behaviour may be obtained.

Catalysis

Low pressure hydroformylation using rhodium catalysts (LP-oxo) was jointly developed during the 1970s by Union Carbide, Davy McKee and Johnson Matthey and now accounts for over half of the world capacity for butyraldehyde production. Recent developments in the extension of this technology to butene feedstocks through the use of novel phosphite ligands were described by D. Bryant of Union Carbide. Simple phosphite ligands were initially discarded by Union Carbide during their development work on the LP-oxo process due to their instability to hydrolysis under reaction conditions. The more stable phosphines, in particular triphenylphosphine, were selected to provide suitable reaction rates, selectivity and catalyst stability. However a re-examination of the factors responsible for phosphite hydrolysis led to the identification of novel ligands, see Figure 1, highly resistant to hydrolysis. Furthermore, using these ligands hydroformylation rates were greatly superior to those for phosphine-based catalysts, thus allowing these systems to be considered for hydroformylation of higher (C_4+) olefin feedstocks. Olefin isomerisation from internal to terminal double bonds is also catalysed in these reactions, allowing mixed butene feedstocks (now widely available as a by-product of MTBE production) to be used. Diorganophosphites (I) give low straight:branched aldehyde ratios, lower than those achieved with triphenylphosphine, but the bisphosphites (II) yield very high isomer ratios. The production of *n*-valeraldehyde by a



bisphosphite-modified rhodium catalyst is thus an economically attractive proposition. The aldehyde would find a market as a precursor to 2-propylheptanol used in the preparation of didecylphthalate which has advantages over dioctylphthalate in its use as a plasticiser. Development work is continuing at Union Carbide with the aim of commercialising this process over the next few years.

The use of other chelating ligands with the potential for promoting chiral selectivity in homogeneous catalysis was discussed by Professor L. Venanzi of ETH, Zurich. Rhodium pyrazolylborate complexes have been examined in alkene hydrogenation reactions and their performance compared with rhodium-phosphine systems. Catalysis of acetalisation reactions, Equation (i), by rhodium-triphos complexes

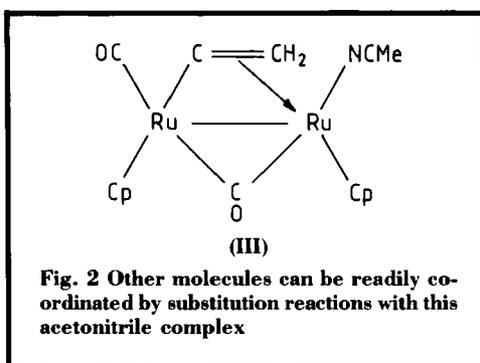


allows such reactions to be carried out on acid sensitive molecules with significant diastereochemical selectivity.

Developments in the field of heterogeneous catalysis for automobile exhaust emission control were described by T. J. Truex of Johnson Matthey. The oxidation catalysts (for converting hydrocarbons and carbon monoxide to carbon dioxide and water) introduced in 1975 were replaced by three-way catalysts (which in addition achieves simultaneous reduction of nitrogen oxides, NO_x) in the early 1980s. Over the past

10 years significant improvements have been made to the performance and durability of the catalyst through better understanding of the contribution and interaction of the various components of the catalytic system; namely the platinum group metals, promoters and the support. A key feature in maintaining NO_x reduction performance while also achieving carbon monoxide oxidation through the water-gas shift reaction has been an increase in the use of ceria. With ever tighter specifications proposed for future legislation, the difficulties in obtaining good catalyst performance under cold start conditions will become more important. This may eventually lead to a requirement for heating the catalyst (for example, electrically) before starting the engine.

Hydrocarbon oxidation reactions represent one of the major uses of heterogeneous catalysis in the chemical industry. These reactions generally involve the use of oxygen-rich catalysts (like metal oxides), a point that has generally been ignored in mechanistic studies to date. An attempt to overcome this deficiency was presented by Professor W. G. Klemperer of the University of Illinois. Model compounds were synthesised by the reaction of organometallic cations with polyoxoanions such as $[(C_5Me_5)TiW_5O_{18}]^{3+}$ and $(P_3O_9)^{3-}$. Studies of reactions with molecular oxygen were illustrated for the case of a cyclooctadiene iridium complex. This reaction results in the initial formation of a 4-membered oxygen-



bonded metallocycle which subsequently re-arranges to give a hydroxyl-substituted C-bonded metallocycle.

Mechanistic studies of carbon chain growth which may be applicable to Fischer-Tropsch catalysis were discussed by Professor S. A. R. Knox of Bristol University. Di-ruthenium μ -vinyl complexes were chosen as model compounds with ^{13}C labelling of one of the atoms of the vinyl group allowing the point of linking for C-C bond formation to be established. By substitution reactions with the acetonitrile complex, see Figure 2, other molecules can be readily co-ordinated. Reaction with diazomethane leads to carbene addition at the β -carbon of the vinyl group, and alkynes also link to this carbon to yield μ -butadiene complexes. However, ethene links to the α -carbon of the vinyl group. The spatial arrangement of the ligands may contribute to this change in point of attachment but the situation is complicated by the possibility of migration of the vinyl group from one metal centre to the other.

A third, less conventional, area of platinum group metals catalysis that was discussed by D. T. Thompson of Johnson Matthey is the effect first claimed by Fleischmann and Pons as involving low temperature nuclear fusion. Detailed analytical studies of palladium electrodes obtained from cells reported to have generated "excess" heat in "cold fusion" experiments showed various anomalous features. These included changes in the microstructure of the rods, suggesting high thermal stress (temperatures of up to at least 300°C) in local areas, and an unusual

lithium isotope ratio in material deposited on the electrode surface during electrolysis. As long as the possibility remains of energy generation by this technique, whatever the mechanism, experimentation will continue to identify the numerous factors that need to be controlled before the phenomenon can be obtained reproducibly.

Professor J. Grobe of the University of Munster described the electrochemical generation of platinum group metals compounds active for homogeneous catalysis. The inertness of the platinum group metals can be overcome giving reasonable current yields by three methods: low temperature cathodic dissolution, high temperature anodic dissolution in the presence of halide ions, and dissolution using a biased alternating current (DC imposed on AC). Typical electrolyte/solvent combinations found useful were MeOH/NaOMe and DMF/ NBu_4Cl . Low valent complexes such as $[\text{RhCl}(\text{CO})(\text{PPh}_3)_2]$ were obtained when the electrolysis was carried out in the presence of CO and PPh_3 ligands.

Oxidative Addition

Routes to the intramolecular activation of C-H bonds have only recently been identified. Studies of iridium and rhodium complexes which undergo C-H oxidative addition to yield stable alkyliridium hydride products were described by Professor R. G. Bergman of the University of California. Irradiation of dihydride complexes such as $[\text{Ir}(\text{C}_3\text{Me}_3)(\text{H})_2(\text{PMe}_3)]$ at low temperature results in the elimination of hydrogen and the formation of a solvent-stabilised intermediate. This intermediate reacts with C-H bonds ($1^\circ \gg 2^\circ > 3^\circ$) to yield stable products. A consequence of this high level of activity was that the choice of an inert solvent for kinetic studies was difficult, and liquefied inert gases (xenon or krypton) were finally selected. Even these solvents interact with the irradiation products to form intermediates which may then undergo an exchange reaction with the alkane followed by the C-H insertion reaction. Through the use of inert gas solvents, iridium complexes were shown to activate adamantane (2° C-H insertion) and cubane (3° C-H insertion).

The effect of metal-metal bonds on the oxidative addition reactions of dimeric compounds was considered by J. P. Fackler of Texas A and M University and Professor M. Cowie of the University of Alberta. Reactions of gold(I) dimers were reviewed by J. P. Fackler. A range of starting materials for this work was readily available in dithiocarbamate and phosphorus ylide complexes. Although the stable species isolated were $\text{Au}^{\text{I}} - \text{Au}^{\text{III}}$ asymmetric products, these were formed by rearrangement of $\text{Au}^{\text{II}} - \text{Au}^{\text{II}}$ intermediates. The interaction between the metal atoms is also evidenced by the reductive elimination from $\text{Au}^{\text{III}} - \text{Au}^{\text{III}}$ dimeric complexes which in the absence of metal-metal bonding is forbidden by orbital symmetry rules. Professor Cowie presented the results of the study of low valent dimeric metal compounds containing bis(diphenylphosphino)methane (DPM). The short bridging ligand allows interaction between the metal atoms, which for a series of rhodium complexes is best described as a dative bond giving the rhodium a formal oxidation state of +1, for example in $[\text{Rh}^{\text{I}}(\text{CO})(\text{DPM})_2\text{M}(\text{CO})_n]$. This interpretation is supported by X-ray crystallography which shows the rhodium atom to have essentially square planar co-ordination. Oxidative addition reactions occur readily at this rhodium centre and subsequent interaction with the second metal yields the final products. Thus hydrogen sulphide reacts to yield sulphur-bridged products.

Linear Clusters

The properties of different types of linear ruthenium cluster compounds were discussed by Professor K. Vrieze of the University of Amsterdam and Professor F. A. Cotton of Texas A and M University. Professor Vrieze described the structures and fluxional behaviour of a series of tetranuclear compounds containing monoazadiene ligands, $\text{R}^1\text{CH}=\text{CH}-\text{CH}=\text{NR}$ (MAD). The complexes are readily prepared by the reaction of the ligand with $[\text{Ru}_3(\text{CO})_{12}]$. Four enantiomeric forms of the product $[\text{Ru}_4(\text{CO})_{10}(\text{MAD})_2]$ exist and have been separated and characterised. The interconversion of terminal and bridging carbonyl groups of the

central $\text{Ru}_2(\text{CO})_4$ unit were studied at low temperature with the process occurring much faster for the *trans*-(SS) isomer than the other forms. At higher temperatures the *cis* and *trans* forms interconvert due to rotation about the central metal-metal bond. Finally, at higher temperatures still, the SS and SR isomers interconvert by an intermolecular process thought to proceed via cleavage of the central Ru-Ru bond.

Professor Cotton dealt with a series of chloride-bridged dimeric and trimeric complexes. Structurally these complexes may be viewed as arising from edge-sharing or face-sharing of octahedra formed around each metal atom by the chloride ligands. In general these complexes do not contain metal-metal bonds, although the mixed oxidation state $\text{Ru}^{\text{II}} - \text{Ru}^{\text{III}}$ dimeric compounds have short Ru-Ru distances consistent with a bond order of one half. EPR studies of Ru^{III} have allowed characterisation of the three isomers of $[\text{Ru}_2\text{Cl}_5(\text{PR}_3)_4]$. For trimeric species representatives of all four oxidation states ($\text{Ru}^{\text{II}} - \text{Ru}^{\text{II}} - \text{Ru}^{\text{II}}$, $\text{Ru}^{\text{II}} - \text{Ru}^{\text{III}} - \text{Ru}^{\text{II}}$, $\text{Ru}^{\text{III}} - \text{Ru}^{\text{II}} - \text{Ru}^{\text{III}}$ and $\text{Ru}^{\text{III}} - \text{Ru}^{\text{III}} - \text{Ru}^{\text{III}}$) have been characterised and their interconversion by redox reactions investigated.

The development of novel polymers containing metal-metal bonds was discussed by Professor M. H. Chisholm of Indiana University. A number of metals (for example rhodium, ruthenium, molybdenum and tungsten) form dimeric compounds of the type $[\text{M}_2(\text{O}_2\text{CR})_n]$. Liquid crystal phases exist for some of these compounds, but this is metal dependent, discotic regions being formed by molybdenum and ruthenium complexes but not by those of tungsten. When reacting molybdenum carboxylate complexes with oxalic acid, ligand exchange yields polymeric materials. The products have a perpendicular arrangement of the metal dimers relative to the direction of the chain. Products where metal dimers are linked in a parallel arrangement can be prepared using anthracene dicarboxylates. Molybdenum and tungsten polymers give different degrees of conductivity on oxidation. While the molybdenum materials give products with only partial delocalisation of

the metal-metal bonding, the tungsten analogues are more easily oxidised and give fully delocalised systems. Ligand exchange reactions with rhodium complexes are unsuccessful due to their inertness and therefore rhodium-based polymers cannot be prepared in this way. However, studies of complexes containing weakly bound ligands ($[\text{Rh}_2(\text{O}_2\text{CR})_2(\text{MeCN})_6]^{2+}$) showed that the rate of substitution in the equatorial sites can be significantly enhanced by the presence of potentially bidentate ligands in the axial sites, which may provide a suitable opportunity for further investigations.

Monomeric Complexes

The chemistry of Rh^{II} was further explored by Professor K. R. Dunbar of Michigan State University. Reaction of $[\text{Rh}_2(\text{MeCN})_{10}]^{4+}$ with tris(2,4,6-trimethoxyphenyl)phosphine (TMPP) yields a monomeric complex $[\text{Rh}(\text{TMPP})_2]^{2+}$ where each ligand is bound through one phosphorus and two oxygen atoms. The oxygen bonding is weak and dissociation provides binding sites for other ligands. Mononuclear complexes of Rh^{II} are rare and this compound therefore offers a useful starting material for exploring the chemistry of this oxidation state of rhodium. Reaction with carbon monoxide involves a series of reversible steps including oxidation of the starting material by $[\text{Rh}(\text{CO})_2(\text{TMPP})_2]^{2+}$. Loss of carbon monoxide from the $\text{Rh}(\text{I})$ dicarbonyl complex yields a product which has a lower oxidation potential and can be re-oxidised by $[\text{Rh}(\text{TMPP})_2]^{3+}$.

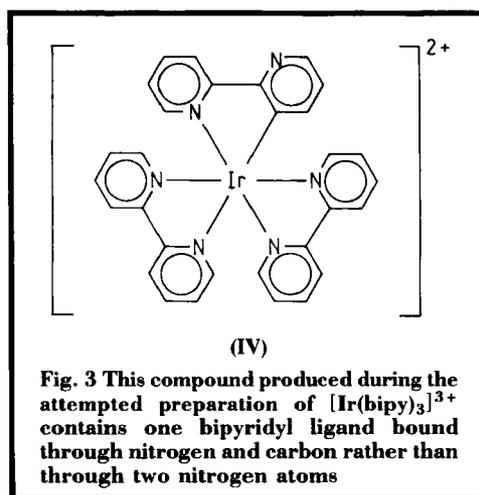
A study of the varying co-ordination modes of a group of substituted pyridine ligands was presented by E. C. Constable of Cambridge University. This work arose from an interest in the use of bipyridine complexes as catalysts for the photolysis of water. Careful analysis of the products obtained from the attempted preparation of $[\text{Ir}(\text{bipy})_3]^{3+}$ identified one compound which was surprisingly found to contain one bipyridyl ligand bound through nitrogen and carbon rather than through two nitrogen atoms, see Figure 3. Using phenylpyridinemercury chloride as a ligand transfer reagent, similar complexes bound through nitrogen and carbon may be

prepared for a variety of metals. On extending the study to more complex ligands, incorporating thiophene rings, the products formed continue to show a preference for cyclometallation rather than co-ordination through the heteroatom.

The application of 2d NMR spectroscopy to the study of tertiary structure in solution was discussed by Professor P. S. Pregosin of ETH, Zurich. Cross-peaks are observed in the 2d patterns when nuclear Overhauser effects influence peak intensity. This occurs when two protons are less than 2.5\AA apart but is negligible for distances greater than 3\AA . By complexing "marker" ligands, such as phenanthroline, where some protons are held close to the metal, the spatial arrangement of the atoms around the metal can be determined. Comparisons with X-ray crystallography can identify structural differences between solution and the solid state. The use of the technique was illustrated by a study of palladium allyl complexes where the relative positions of the syn- and anti-protons, with respect to palladium, were identified.

Metal Films

The formation of thin metal films is a topic of increasing interest in the electronics industry. The generation of platinum group metals films by metal organic chemical vapour deposition (MOCVD) was described by Professor H. D. Kaesz of the University of California. Early



attempts using $[\text{Pt}(\text{acac})_2]$, $[\text{PtCl}_2(\text{CO})_2]$ or $[\text{Pt}(\text{PF}_3)_4]$ gave films contaminated with carbon or phosphorus. Organometallic platinum group metals complexes are suitable alternatives when hydrogen is used to react with the carbon species formed to prevent contamination of the film. Compounds such as $[\text{PtCpMe}_3]$ and $[\text{Pt}(\text{Cp-Me})\text{Me}_3]$ give bright reflective films composed of small crystallites. Bright films can also be made for rhenium, rhodium, iridium and nickel but are amorphous in structure. The problem of alloy formation between a coating and gallium is a significant problem for the use of gallium arsenide as a semiconductor material. This could be avoided by depositing alloy films such as CoGa or PtGa_2 . The synthesis of novel compounds containing the metals in these ratios should allow these films to be prepared.

Biological Aspects

The final lectures of the conference were devoted to the biological aspects of platinum group metals compounds. The allergic response which can occur as the result of exposure to ionic platinum halogeno-complexes was discussed by C. W. Bradford of Johnson Matthey. Sensitisation by platinum salts is restricted to this class of compounds but is none the less important as these are key species in the refining of platinum and are common starting materials for the synthesis of co-ordination compounds. The symptoms of the allergic response are mainly rhinitis, conjunctivitis and asthma, and sensitisation can be confirmed by a simple skin test. Smokers and those sensitive to common allergens such as grass pollen and house dust are more at risk of being sensitised by platinum salts. The routine health monitoring carried out for workers in platinum handling areas of Johnson Matthey sites was described, these procedures now having been adopted into regulatory guidelines. The mechanism of the sensitisation is believed to involve binding of platinum to protein via sulphur atoms in methionine groups. The platinum-protein conjugate is the antigen which stimulates lymphocytes to produce Pt-specific IgE and induces the symptoms on re-exposure. The sensitisation is not produced by salts of the other

platinum group metals, although for platinum sensitive cases there may be some cross reaction on skin testing.

In the closing lecture Professor S. J. Lippard of the Massachusetts Institute of Technology addressed the question of the mechanism of action of platinum anti-cancer complexes, and in particular why there is a marked difference in the activities of the *cis* and *trans* isomers of $[\text{PtCl}_2(\text{NH}_3)_2]$. The key cellular target for platinum complexes was identified as DNA some 20 years ago. The exact details of this interaction have now been identified using ^{195}Pt NMR spectroscopy and X-ray crystallography. Studies of the reaction of the two $[\text{PtCl}_2(\text{NH}_3)_2]$ isomers with nucleosomes indicated that there is little difference in the rate at which they form difunctional adducts. Cisplatin binds most readily to two adjacent guanines on a single strand of DNA while *trans*- $[\text{PtCl}_2(\text{NH}_3)_2]$ binds to purines (guanine and adenine) separated by one or two other bases. By studying the way in which DNA duplex oligomers combine to form extended units it was shown that cisplatin binding causes DNA to bend by $30\text{--}40^\circ$, while there is no directed bending for the *trans* isomer. Binding of both the *cis* and *trans* complexes to DNA inhibits replication and it seems likely that the inactivity of the *trans* isomer is due to these lesions being more readily repaired.

Further work has now identified a protein present in normal cells which binds to cisplatin-DNA lesions. Efforts are now being made to determine the structure of this protein and assess its level in different types of cell. It may be that this will contribute to the understanding of the spectrum of activity of cisplatin and suggest how compounds active against different tumours may be developed.

Posters

In addition to the oral presentations almost 200 posters were exhibited in three sessions during the conference. Although the display area was restricted, the posters attracted considerable interest from participants at all levels and contributed greatly to a successful conference. Most of the posters described new chemistry which was

principally of academic interest, but some also had applications in mind. R. J. Haines of the University of Natal described the use of substituted ruthenium carbonyl cluster systems as electrocatalysts for the reduction of carbon dioxide to methanol, formaldehyde, and carbon monoxide, the product ratios being dependent both on the potential of the electrode and the pH of the electrolyte. Applications for platinum metals as catalyst systems in phosphoric acid fuel cells were described by G. A. Hards and colleagues of Johnson Matthey, who have studied the impact of surface area on the activity of platinum alloy catalysts compared with supported platinum systems. P. G. Pitcher of Johnson Matthey has demonstrated that superconducting YBCO films ($T_c \approx 100$ K) have been produced on polycrystalline alumina substrates coated with 2000 Å thick DC sputtered platinum films; the platinum interlayer acts as an effective diffusion barrier to substrate aluminium. A poster on the development of orally active platinum(IV) anti-tumour agents was

presented by C. F. J. Barnard of Johnson Matthey Technology Centre, while a display by S. G. Warren of Johnson Matthey Materials Technology Division featured advances in the industrial applications of tetraammine platinum(II) compounds for use both as catalyst precursors and for electroplating systems.

Throughout the conference a high standard of presentation was maintained by the lecturers, with their willingness to deviate from their previously submitted abstracts to present recent research results much to be welcomed. The dominance of multi-nuclear chemistry at this conference might suggest that the study of the organometallic and co-ordination chemistry of mono-nuclear species is of declining interest and it is to be hoped that this will be seen as a challenge to workers in these fields to redress the balance at the next Royal Society of Chemistry International Platinum Group Metals Conference. Current plans are for the next conference to be held in 1993 at the University of St. Andrews, in Scotland.

Further Studies of Platinum Mineral Deposits

Although this Journal does not set out to present a comprehensive record of the available information on the occurrence, geology, mineralogy or extraction of the platinum-group elements, from time to time an opportunity is taken to draw the attention of readers to some significant new contribution to the literature concerning these topics. The proceedings of the Fifth International Platinum Symposium, which was held in Helsinki, Finland, from 1st to 3rd August 1989, have recently been published and will be of interest to researchers seeking up-to-date information on the results of recent investigations of platinum deposits world-wide.

Edited by E. F. Stumpfl and H. Papunen, eighteen papers have now appeared in the journal *Mineralogy and Petrology*, 1990, 42, (1-4). Reflecting the recent success of Finnish geologists in identifying several platinum-group element concentrations the first four papers in the major section devoted to "Layered Igneous Complexes" were concerned with the Proterozoic intrusions which are widespread over a large area of the northeastern part of the Fennoscandian Shield, and which are encountered in Finland, Sweden and the Soviet Union.

Thus geologists from each of these countries contributed to the first paper. Three major platinum-group element-bearing mineralisation zones have been found in the early Proterozoic Penikat layered intrusion, and a separate paper was devoted to each. It is suggested that the traditional concepts of platinum genesis cannot explain these deposits, where the platinum-sulphide association is apparently not essential, and where platinum-group minerals may or may not be associated with chromite. There followed significant contributions on platinum-group element mineralisation and distribution in the Bushveld Complex of Southern Africa, the Dumont Sill in Quebec, Canada, the Duluth Complex of Minnesota, U.S.A., and the Munni Munni Complex of Western Australia. This 195 page section was concluded with a paper on the mineralisation potential of the Longwood Igneous Complex of South Island, New Zealand.

Occurrences of platinum-group minerals in ophiolite suites in Cyprus, Morocco, Norway and Spain are featured in the second, 67 page, section, while placer deposits in Burma and France are included in the final section.