The Chemistry of the Platinum Group Metals

## A REVIEW OF THE SIXTH INTERNATIONAL CONFERENCE

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The Dalton Division of the Royal Society of Chemistry held the Sixth International Conference on the Chemistry of the Platinum Group Metals at the University of York from the 22nd to the 26th July 1996. Previous meetings have been held in St. Andrews (1993), Cambridge (1990) and Sheffield (1987). Over 250 delegates from 26 countries attended the programme of 41 lectures and 190 posters.

This conference, covering the whole spectrum of platinum group metals chemistry, was opened by Professor R. Perutz of the University of York. It clearly demonstrated the breadth and quality of the research currently being undertaken, and the many areas of chemistry in which the platinum group metals form a major part. As in past conferences, many delegates emphasised the relevance of their work to industry.

Homogeneous Catalysis

The opening keynote lecture, given by Professor M. Brookhart and colleagues of the University of North Carolina, U.S.A., discussed a new palladium and nickel catalysed alkene polymerisation reaction. The catalyst initiators are based on diimine complexes:
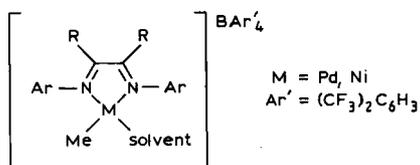
The sterically demanding substituents on the aryl groups block the axial sites of the 4 co-ordinate square planar metal complex; more traditional bulky phosphines are far less effective. Thus the active catalyst has only two potentially reactive sites for co-ordination which activate alkene molecules and assemble them into polymers with a very narrow molecular weight distribution. Once attached to the metal centre the alkene undergoes a migratory insertion reaction into the Pd-Me bond and thus allows further alkene co-ordination, insertion and subsequent polymer formation. The rate determining step is the relatively slow migratory insertion. The palladium catalysts also copolymerise ethylene and methyl acrylate; although in this case the migratory insertion is faster, possibly due to chelation with the acrylate C=O fragment.

A new approach to activating carbon-carbon bonds was described by Professor D. Milstein and co-workers of The Weizmann Institute of Science, Israel. A chelating diphosphine ligand is used to bring an aromatic methyl group into close proximity to a rhodium hydride. The addition of hydrogen eliminates methane and allows the rhodium to insert directly into the aromatic methyl bond. This could ultimately lead to a system for inserting $-CH_2-$ into a variety of bonds.

The known reserves of methane and ethane are as least as abundant as petroleum, but the compounds themselves are much less reactive. Thus selective functionalisation of these potential chemical building blocks is of great interest. Professor A. Sen of The Pennsylvania State University, U.S.A., detailed the latest findings of a rhodium catalysed oxidation system that can selectively activate methane and ethane.

Methane reacts with oxygen in the presence of $RhCl_3$, iodide and chloride ions and carbon monoxide. The system can produce either acetic acid or methanol, depending on solvent. Higher hydrocarbons, such as butane and isopentane, give mostly C-C cleavage products.

Water soluble transition metal catalysts are always of interest and there is much activity towards producing such materials to ease catalyst separation, recycling and effluent disposal. T. Malmström and C. Andersson from Lund University, Sweden, described two strategies for synthesising water soluble polymer ligands. Polyacrylic acid reacts with $Ph_2PC_6H_4NHCH_3$ to give a polymer which is soluble in basic conditions. Alternatively, polyethyleneimine is condensed with $Ph_2PC_6H_4CHO$ to yield an acid soluble polymer. Rhodium complexes of both ligands were prepared, characterised and used in a range of hydrogenation reactions. Enantioselective hydrogenation of cinnamic acid derivatives is also possible, using chiral ligands.

Heterogeneous Catalysis and Materials

Professor G. Ertl of the Fritz-Haber-Institute in Germany spoke on the use of surface analytical techniques, such as scanning tunnelling electron microscopy, (STEM) to investigate elementary steps in heterogeneous catalytic reactions. Oxidation of carbon monoxide on a Pt(110) crystal surface shows differing modes of molecular interaction. As the CO lattice is denser than that of adsorbed oxygen, oxidation cannot occur in a CO-rich zone until O diffuses to its boundary. Adsorbed oxygen atoms can organise into "islands" of oxygen, and subsequent reaction with CO can occur in concentric ring patterns, as the adsorbed molecules combine and then dissociate as CO_2. Research on the new ruthenium catalysed ammonia synthesis reaction details the elementary processes occurring as nitrogen and hydrogen adsorb onto a ruthenium surface and ultimately combine as ammonia. Alkali metal promoters, such as potassium and caesium, act by weakening the N-N bond and promoting dissociation into adsorbed nitrogen atoms.

CeO_2 and ZrO_2 both play important roles in automotive pollution control catalysis. CeO_2 can store and release oxygen to enhance oxidation activity, while the thermal stability of ZrO_2 maintains catalyst surface area under high temperature conditions. Professor M. Graziani and colleagues of the University of Trieste, Italy, examined the use of CeO_2-ZrO_2 solid solutions as supports for platinum, palladium and rhodium catalysts in the reduction of NO by CO. Incorporation of ZrO_2 into CeO_2 creates thermally stable materials which act as good supports for platinum or rhodium. The noble metal component enhances the reduction from Ce^{4+} to Ce^{3+}, and once formed the Ce^{3+} readily reduces NO. Thus the role of the platinum group metal can be to ease CeO_2 reduction, rather than having a direct role in the CO/NO reaction.

Platinum catalysed hydrosilylation is an important reaction for forming C-Si bonds, but little is known about the active catalytic species formed during the reaction. Although colloidal platinum has been implicated from transmission electron microscopy of final reaction solutions, there is no *in-situ* evidence. L. N. Lewis and colleagues of GE Corporate Research, U.S.A., described the characterisation of the catalyst formed during the reaction using X-ray absorption fine structure (EXAFS) analysis. The active catalyst is formed after a poorly understood induction period and can contain either Pt-C or Pt-Si bonds, depending upon the reaction conditions and whether the reaction mixture is alkene- or silane-rich. It is only at the end of the reaction that Pt-Pt bonds formed and colloids are present.

Theoretical Chemistry and Physical Methods

The use of ab-initio calculation in describing and predicting metal-ligand interactions can increase understanding of experimental work. This was proved by O. Eisenstein of the University of Montpellier, France. The geometry of most 4 co-ordinate d^8 complexes is square planar, with the exception of some $M(CO)_4$ complexes. By examining the series of d^8 complexes: RuL_4, $Ru(CO)_2L_2$ and $[Rh(CO)_2L_2]^+$ (L = phosphine) it was shown that the π^* orbital of each carbonyl ligand has enhanced bonding ability once the C-M-C bond angle is perturbed

away from a square planar geometry. Further work has extended the understanding toward the 5 co-ordinate complex, $Ru(CO)_2L_3$, which has isomers with CO in either equatorial or axial sites. Simple calculations for $L = PH_3$ do not fully describe the experimentally observed behaviour. However, the real phosphines ($L = PEt_3$ and P^iPr_2Me) can be incorporated by combining ab-initio methods with molecular mechanics. This technique reveals the important steric effects the ligands have on the geometry of the complexes.

Proton nuclear magnetic resonance (NMR) spectroscopy is a standard technique for the characterisation of compounds. However, S. B. Duckett and co-workers from the University of York, U.K., have extended the practice by exposing ruthenium, iridium and rhodium complexes to para enriched hydrogen which enhances hydride signals by up to 1000 times. This allows rapid, facile NMR analysis of very small amounts of compounds, such as $Rh(H)_2(PMe_3)_3Cl$ and $[Rh(H)_2(PMe_3)_4]$-Cl. The signal enhancement can also help detect minor isomers of hydride complexes at low concentrations and may prove useful for detecting previously unobserved catalytic intermediates.

Organometallic Chemistry

The insertion of isocyanides into metal-carbon bonds yields a diverse range of organometallic chemistry. E. Carmona from the University of Seville, Spain, introduced some aspects of
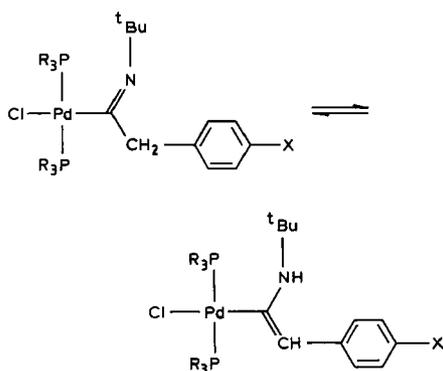
this area. The complexes $Pd(CH_2C_6H_4-p-X)(PR_3)Cl$ (R = Me, Et; X = H, CF_3) readily react with 'BuNC to give the unusual tauto-

merisation of derivatives shown below. The position of the equilibrium depends on the ligand and the aryl substituent, X.

Unusual reactivity of platinum group metal complexes can be stimulated by using bidentate ligands which force complexes into uncommon geometries. This was illustrated to good effect by Professor P. Hofmann of the University of Heidelburg, Germany. The ligand chosen was $^tBu_2PCH_2P^tBu_2$ (P~P) which forms a complex (P~P)Pt^0. The tertiary butyl substituents play an important role in blocking co-ordination to the axial sites.

Ligand
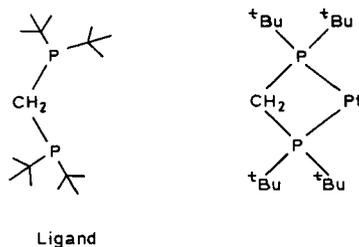
The complex activates C-Si bonds reacting with $SiMe_4$ to give (P~P)Pt(SiMe_3)Me. It can also react with Et_3SiH, but in this case activates a C-H bond yielding (P~P)Pt(SiEt_3)H. The hydride complex will then insert ethylene to give (P~P)Pt(SiEt_3)Et, which can eliminate $SiEt_4$. The rhodium complex (P~P)Rh(PMe_3)Me reacts with H_2 and then CO_2 to give the formate (P~P)Rh(PMe_3)(OCHO), a model reaction for the formation of formic acid from H_2 and CO_2.

Alkyne activation can yield carbon-rich organometallics incorporating -C≡C- and =C=C= fragments which have interesting physical and chemical properties. Professor P. H. Dixneuf of the University of Rennes, France, detailed some versatile ruthenium chemistry involving such alkyne activation. The complex $[(dppe)_2RuCl]PF_6$ (dppe = $Ph_2PCH_2CH_2PPh_2$) activates HC≡C-C_6H_4-C≡CH to give the extended system $[Cl(dppe)_2Ru-C≡C-C_6H_4-C≡C-Ru(dppe)_2Cl]$. Incorporation of palladium gives mixed metal containing polymers of the form {-C≡C-C_6H_4-C≡C-Ru(dppe)_2-C≡C-C_6H_4-C≡C-Pd(PBu_3)_2}_n. The dppm ($Ph_2PCH_2PPh_2$) analogue reacts with HC≡C-CR_2OH to give the cumulene $[(dppm)_2Ru=C=C=CR_2]$.

Professor M. Cowie and colleagues from the University of Alberta, Canada, gave a lecture centred on methyl C-H activation. The complex $[Ir_2(CH_3)(CO)(\mu\text{-}CO)(dppm)_2]SO_3CF_3$ exhibits fluxional behaviour as the methyl group transfers from metal to metal via an $Ir\text{-}CH_2\text{-}Ir\text{-}H$ bridge. The complex reacts with a variety of π acceptor ligands activating the methyl C-H bond, giving $[Ir_2H(CO)_2(L)(\mu\text{-}CH_2)\text{-}(dppm)_2]SO_3CF_3$ (L = CO, SO_2, CNR). However, reaction with alkenes or activated alkynes gives the adducts $[Ir_2(CH_3)(CO)_2(L)(dppm)_2]SO_3CF_3$ (L = C_2H_4, C_2F_4, RC≡CR; R=CF_3, CO_2Me).

A different approach to C-H activation was illustrated by Professor W. D. Jones of the University of Rochester, U.S.A. Reactive rhodium trispyrazolyl borate complexes readily activate a variety of C-H bonds. Reaction with cyclopropane gives C-H activation followed by C-C cleavage to give a metallobutane. The relative strengths of a variety of Rh-C bonds in activated complexes was compared with C-H activation parameters and gave a good correlation.

Organic Applications

A wide range of organic reactions was reviewed by Professor H. Alper of the University of Ottawa, Canada. $RhCl_3.H_2O$, cyclooctadiene (COD) and $NaBPh_4$ combine in aqueous methanol to give the zwitterionic complex:
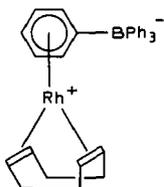
The complex shows good activity for the hydroformylation of alkenes, such as $p\text{-}R\text{-}C_6H_4\text{-}CH_2=CH_2$ to iso aldehydes. The positively charged rhodium atom binds to the alkene and can stabilise a carbonium intermediate to give the iso-isomer. The BPh_4^- ligand acts as a steric barrier to reinforce the electronic effect of the rhodium centre. Incorporation of $[Rh(COD)Cl]_2$ into montmorillonite allows the support to act as a bulky ligand and a Lewis acid. This

heterogeneous catalyst allows hydroformylation of substituted alkenes without leaching of the rhodium – a common problem with such supported complexes.

Palladium catalysed C-C coupling chemistry is an important and emerging area as new catalytic reactions are regularly being reported. Chiral C-C bond formation was introduced by J. M. J. Williams of Loughborough University, U.K. Chiral oxazoline ligands, such as the one shown below, combine with $[Pd(allyl)Cl]_2$ to catalyse the chiral Tsuji-Trost reaction in good enantiomeric purity:
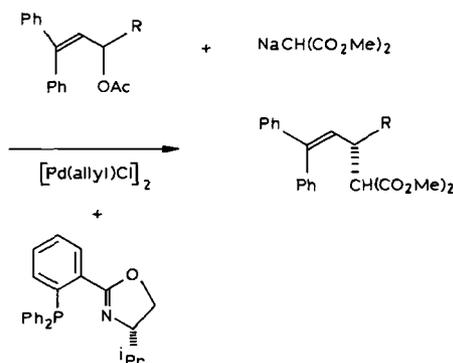
Palladium, as $PdCl_2(MeCN)_2$, also catalyses racemisation of chiral allyl acetates. This allows enzymic resolution to an enantiomerically-enriched allyl alcohol which is then unreactive to both enzyme and the palladium catalyst.

Another example of C-C coupling, but using ruthenium catalysis, has recently been reported by Professor S. Murai of Osaka University, Japan. Aromatic ketones couple with alkenes, as shown below, in good yield, under moderate conditions, and allow a range of functionalities.
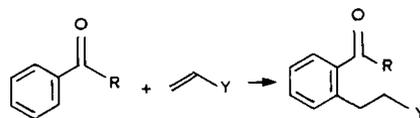

Catalytically active compounds, such as $Ru(H)_2(CO)(PPh_3)_3$ and $Ru(CO)_2(PPh_3)_3$ activate a C-H bond, adjacent to the ketone, forming an intermediate which is stabilised by co-ordination of the ketone oxygen atom. Further co-ordination of the alkene to this cyclometallated intermediate allows the coupling to occur.

This reaction has been extended to activate aromatic imines and to produce diketones by combined coupling and carbonylation.

The Heck reaction is an important method of coupling aromatic halides with alkenes, but its mechanism is not fully understood. This was addressed by K. K. Hii and J. M. Brown of the University of Oxford, U.K. Carbon-13 labelled methyl acrylate ($^{13}CH_2$=CHCO$_2$Me) was coupled with [(P~P)Pd(Ar)(solvent)]$^+$ (P~P = bis(diphenylphosphino)ferrocene) to examine the insertion reaction, and gave [(P~P)Pd-(CH(CO$_2$Me)^{13}CH$_2$Ar)(solvent)]$^+$. This alkyl product rearranges to a transient palladium hydride which can react with more methyl acrylate to give the coupled organic compound Ar^{13}CH=CHCO$_2$Me and [(P~P)Pd-(CH(CO$_2$-Me)^{13}CH$_3$)(solvent)]$^+$. The choice of solvent, aryl group and ligand all have an important effect on the observed reactivity.

Although catalytic asymmetric hydrogenation of C=C double bonds using chiral platinum group metal compounds is a rapidly advancing field, there is little mechanistic information on the analogous reaction of C=O bonds. Thus asymmetric hydrogenation of ketones has proved a fruitful line of research for J.-F. Carpentier and co-workers of CNRS, Lille, France, when they compared experimental results with theoretical predictions. Chiral diphosphine ligands are readily synthesised from naturally occurring amino alcohols and act as good ligands for rhodium complexes:

R = cyclohexyl, cyclopentyl
Ligand

Complex
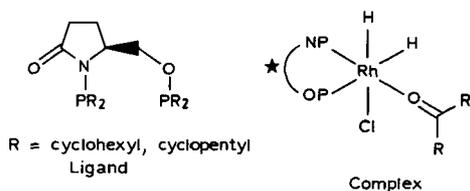
Prochiral ketones, such as ketopantolactone and β-amino acetophenone, are hydrogenated to give chiral alcohols in high enatiomeric purity (90 to 99 per cent). Molecular modelling in conjunction with extended Hückel analysis reveals the importance of dihydrido rhodium complexes and shows that hydride *trans* to the N-PR$_2$ part of the bidentate ligand is more likely to react

with the co-ordinated substrate ketone. This approach can correctly predict the chiral configuration of the product alcohol, but tends to over-predict the observed chiral purity.

Bioinorganic and Supramolecular Chemistry

The role of platinum complexes in cancer treatment is very significant. Cisplatin and carboplatin are widely used as anticancer drugs and there are several other platinum compounds in clinical trials, including an orally active Pt(IV) compound (JM-216).

Cisplatin   Carboplatin

JM – 216
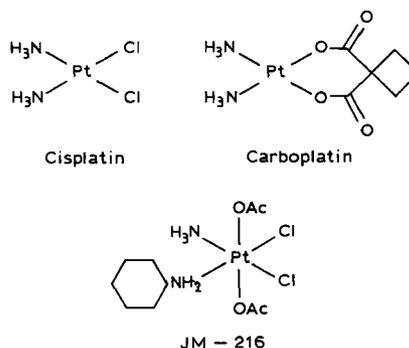
Professor P. J. Sadler of the University of London, described how platinum complexes interact with biological systems. The use of nuclear magnetic resonance (NMR) allows the observation of N-H protons to follow aquation and deprotonation of platinum complexes. These complexes can then react with DNA and the adducts have been detected. The role of the sulphur compound methionine in these systems may also be important. Methionine can bind to cisplatin via the sulphur atom, increasing its rate of reaction with DNA, and enhancing ammonia release due to the high *trans* effect of the sulphur. Methionine can also activate carboplatin, opening the chelate ring to form surprisingly stable adducts.

Although Pt(II) amine compounds can have anti-tumour activity they cannot usually be orally administered. In contrast, Pt(IV) prodrugs are inherently less reactive and can be effective if given by mouth, as the active Pt(II) compound forms prior to interaction with DNA. C. F. J. Barnard, Johnson Matthey Technology

Centre, lectured on the synthesis and characterisation of the Pt(IV) prodrug JM-216 and some of its isomers. As part of the regulatory requirement to identify any impurities found in such syntheses, reverse phase high performance liquid chromatography (HPLC) can identify a variety of *cis* and *trans* isomers of JM-216 and also mixed chloro and acetato derivatives. The independent synthesis of these complexes is challenging and involves the use of light catalysed substitution reactions and oxidation with hypervalent iodine reagents. For example, *cis*-[Pt(CyNH$_2$)(NH$_3$)Cl$_4$] reacts with light and KOAc to yield *all-cis*-[Pt(CyNH$_2$)(NH$_3$)-(OAc)$_2$Cl$_2$], whereas *trans*-[Pt(CyNH$_2$)(NH$_3$)-Cl$_2$] is oxidised by PhI(OAc)$_2$ to *cis,trans*-[Pt(CyNH$_2$)(NH$_3$)(OAc)$_2$Cl$_2$] where the chloro ligands are *trans* to each other (Cy = cyclohexyl).

A further use of the square planar geometry of platinum(II) complexes was introduced by Professor B. Lippert and colleagues of the University of Dortmund, Germany. Open molecular boxes are made using uracil nucleobases as heterocycle ligands with Pt(II) at the corners and ligands as walls. By extending the principle, squares are made with the ligand at the corner and the platinum in the sides.

## Supramolecular and Co-ordination Chemistry

To show that chiral ligands are not the exclusive preserve of catalytic chemists, Professor A. von Zelewsky and co-workers of the University of Fribourg, Switzerland, described the formation of chiral co-ordination complexes using a variety of pinene based ligands:

B = -(CH$_2$)$_{\overline{n}}$, m-xylyl
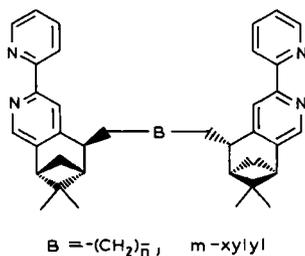
Complexation with ruthenium gives Ru(ligand)Cl$_2$ which has labile chloride ligands and can be used as a precursor for a range of poly-nuclear complexes. Chiral chelating ligands can also induce chirality at square planar metal centres such as platinum and palladium, which is retained during oxidative addition reactions. The control of chirality at a metal centre could have applications in molecular materials besides catalysis, (see *Platinum Metals Rev.*, 1996, 50, (3), 102).

Mixed hydride/dihydrogen complexes often exhibit interesting reactivity, and S. Sabo-Etienne and co-workers from CNRS, Toulouse, France, detailed the remarkable activity of RuH$_2$(H)$_2$(PCy$_3$)$_2$ (Cy = cyclohexyl) toward alkenes and silanes. The ruthenium complex is a catalytic precursor for the silylation of ethylene giving synthetically useful vinylsilanes. The PCy$_3$ ligand can bond via phosphorus and also with an η^3-cyclohexenyl link (**A**). Reaction of RuH$_2$(H)$_2$-(PCy$_3$)$_2$ with a siloxane O(SiMe$_2$H)$_2$ gives a new, air sensitive complex with bonds between the Si-H bonds and the ruthenium centre (**B**):

A   **B**
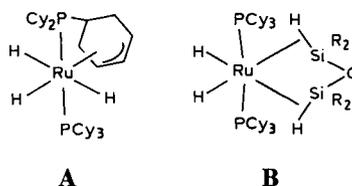
Hydrodesulphurisation (HDS) of petroleum-based fuels uses transition metal catalysis on a massive scale. However, current HDS technology cannot reduce sulphur levels below the 5 ppm soon to be required. As platinum group metals form very effective HDS catalysts, J. J. Garcia and co-workers from the University of Mexico and the University of Sheffield, discussed model reactions of platinum(0) complexes with thiophenes. Pt(PEt$_3$)$_3$ readily reacts with thiophenes:

Pt(PEt$_3$)$_3$ +
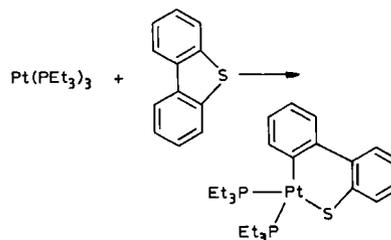
The resulting thiaplatinacycle can react with H$^+$

to yield the RSH sulphide in which one S-C has been broken. However, reaction with H⁻ gives the free hydrocarbon and H_2S, completing the HDS process. The reaction has now been extended to methyl thiophenes which are more resistant to HDS.

Photochemistry and Electrochemistry

The efficient conversion of light to electricity has always been a challenging area of chemistry. A new system using ruthenium- and osmium-based sensitisers was introduced by Professor M. Grätzel of the Swiss Federal Institute of Technology, Switzerland. The complex of choice is cis-[Ru(SCN)₂(2,2'-bipyridyl-4,4'-dicarboxylate)₂] which is attached to a fine suspension of titania. Once light has been 'harvested' by the ruthenium complex the titania allows facile electron conduction. The redox processes are completed by using an iodine/iodide electrolyte to re-reduce the ruthenium after photooxidation. As the light conversion is wavelength-dependent and tails off at high wavelength, new ligands are being designed to extend the range of light conversion. This technology allows a simple ruthenium based photovoltaic cell to compete with more expensive silicon based products, also see *Platinum Metals Rev.*, 1994, **38**, (4), 151.

An alternative use for light energy was outlined by Professor R. Eisenberg and colleagues of the University of Rochester, U.S.A. Square planar platinum(II) complexes with dithiolate and diimine ligands display photoluminescence in solution. The aim is to produce a photocatalytic system for generating hydrogen. The synthesis of extended systems with multi metal centres can be performed with bridging ligands.
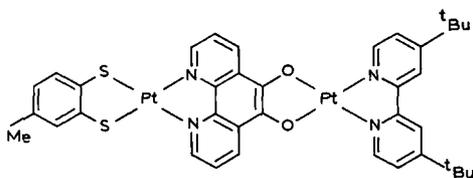
A large number of dithiolate and diimine ligands have been synthesised and the photoluminescence properties compared with molecular orbital calculations. This shows that the Lowest Unoccupied Molecular Orbital (LUMO) is based on the diimine ligand and the Highest Occupied Molecular Orbital (HOMO) has platinum and thiolate character. By varying these ligands the electrochemical properties of the complexes can be fine tuned.

The process of electron transfer from one metal centre to another was described by Professor W. Kaim and co-workers of the University of Stuttgart, Germany. The known ability of [Cp*RhCl(N~N)]⁺ (Cp* = pentamethylcyclopentadienyl, N~N = α-diimine) to eliminate chloride, giving the highly reactive [Cp*Rh(N~N)], has been utilised. This co-ordinatively unsaturated species readily accepts protons to give reactive Rh(III) hydrides which are good hydride transfer catalysts. Combining two of the fragments with the bis chelating ligands shown below gives complexes which have a range of electron transfer and chemical processes.
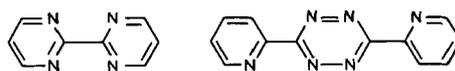
Poster Sessions

Almost 200 posters added to the scientific content of the meeting and contributed greatly to a successful conference. These sessions were an excellent opportunity to learn about new developments in many areas, and interact with other platinum group metal specialists.

The palladium catalysed synthesis of polyketones from alkenes and CO is an important area of research which is of great industrial interest. B. Milani and co-workers from the University of Trieste, Italy, have explored the role of the cocatalyst for the reaction, [(N~N)H]X (N~N = substituted bipyridyl or phenanthroline derivatives; X = PF₆⁻, BF₄⁻). The cocatalyst increases both the polymer yield and its molecular weight. It also allows easy catalyst precursor synthesis by the reaction.

Pd(OAc)₂ + 2 [(N~N)H]X → [Pd(N~N)₂]X₂

Changing the [(N~N)H]⁺:N~N ratio in the reaction solution modulates the overall

acidity, and this has a significant effect on the catalytic system.

Rhodium catalysed low pressure hydroformylation was developed over 20 years ago by Union Carbide, Davy McKee and Johnson Matthey to produce butyraldehyde from propene, CO and H_2. Although the standard industrial process uses triphenylphosphine as a ligand for the catalyst, there is much interest in alternative phosphines. Professor A. M. Trzeciak and colleagues of the University of Wroclaw, Poland, have used π acceptor ligands based on pyrrole, $PPh_x(NC_4H_4)_{3-x}$ (x = 0–2) to form rhodium based complexes such as $Rh(2,4-$pentanedionato$)(CO)(P(NC_4H_4)_3)$. These precursors readily form $HRh(CO)L_3$ with H_2 and CO and can perform hydroformylation reactions with excellent selectivity.

Iridium catalysed methanol carbonylation has recently been commercialised by BP in conjunction with catalyst supplier Johnson Matthey. Unlike the existing rhodium system, the mechanistic detail behind the new *Cativa* process is an unexplored area. However, the situation is being remedied by Professor P. M. Maitlis and A. Haynes and their group at the University of Sheffield, U.K. Both rhodium and iridium form analogous active catalytic species, $[M(CO)_2I_2]^-$ (M = Rh, Ir), but their reactivity is very different. Although both readily react with the MeI cocatalyst, only the rhodium complex undergoes a very rapid migratory CO insertion to the acyl $[Rh(CO)(COMe)I_3]^-$. The iridium forms a relatively stable methyl complex $[MeIr(CO)_2I_3]^-$, which can undergo the essential CO insertion reaction when promoted by protic solvents or tin(II) iodide.

Nitric oxide (NO) has been implicated in a variety of disease states such as septic shock, epilepsy and arthritis. E. Slade, B. A. Murrer and colleagues of Johnson Matthey Technology Centre, U.K., have shown that the ability of ruthenium (III) complexes to bind NO can be used to clear NO from biological systems. Ligand systems involving polyaminocarboxylates give ruthenium compounds with good water solubility, low toxicity and allow rapid *in vivo* removal of NO. Infrared spectroscopy is a useful tool for determining the mode of bonding of NO to ruthenium.

Although first line anti-tumour therapy uses cisplatin, $Pt(NH_3)_2Cl_2$, and carboplatin, $Pt(NH_3)_2(C_3H_6C(COO)_2)$, cisplatin resistance can develop after initially successful treatment. C. F. J. Barnard and B. A. Murrer from the Johnson Matthey Technology Centre, U.K., introduced JM-473, *cis*-$Pt(NH_3)$(2-methylpyridine)Cl_2 which shows activity against resistant tumour xenograft models. The alkyl substituted pyridine ligands slow ligand substitution and can reduce thiol deactivation, which is an important mechanism in resistance.

Addendum

The next conference in this comprehensive series of platinum group chemistry is presently scheduled to take place in the U.K. at Nottingham University, in 1999.

Controlling the Shape of Colloidal Platinum

Colloidal metal particles find use in optical, electronic and magnetic devices, as catalysts and photocatalysts. Their catalytic activity depends on the size and shape of the nanoparticles, so the ability to control these parameters is very desirable. Some success has been achieved in controlling the size distribution, stability and catalytic activity of the nanoparticles, but controlling shape has been more difficult.

Now, however, researchers from the Georgia Institute of Technology, Atlanta, U.S.A., and Hahn-Meitner Institut, Berlin, Germany, have synthesised colloidal platinum nanoparticles with controlled shapes (T. S. Ahmadi, Z. L. Wang, T. C. Green, A. Henglein and M. A. El-Sayed, *Science*, 1996, **272**, (5270), 1924–1926).

Platinum nanoparticles were prepared from a solution of K_2PtCl_4 and sodium polyacrylate (capping agent) in various concentrations of capping polymer to platinum cation. The platinum ions were then reduced by hydrogen gas. On changing the ratios of the concentrations at room temperature under the same conditions, the distribution of platinum nanoparticle shapes could be changed. Tetrahedral, cubic, irregular-prismatic, icosahedral and cubo-octahedral particle shapes were observed, with cubic and tetrahedral being predominant in some cases.