

# The Chemistry of the Platinum Group Metals

## A REVIEW OF THE FIFTH INTERNATIONAL CONFERENCE

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*Organised by the Dalton Division of the Royal Society of Chemistry, the fifth International Conference on the Chemistry of the Platinum Group Metals was held at the University of St. Andrews, Scotland, on 11th to 16th July 1993. Previous meetings in this series have been held in Bristol (1981), Edinburgh (1984), Sheffield (1987) and Cambridge (1990). More than four hundred delegates from thirty-three countries, attended the meeting for a programme of forty-two lectures and over two hundred poster presentations.*

The opening keynote lecture by Professor R. Noyori of Nagoya University, Japan, set the tone for the conference, with the emphasis on the need to concentrate research towards real industrial applications. Indeed, throughout the entire meeting, many speakers were keen to emphasise the relevance of their research to industry.

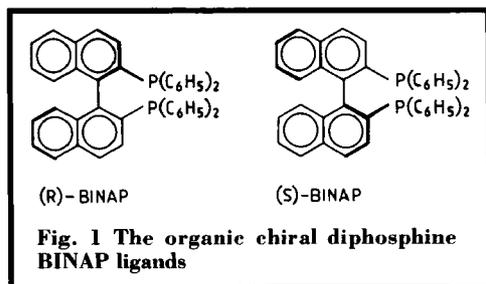
### Catalysis and Oxidative Addition

In his lecture, entitled "Asymmetric Catalysis: Science and Opportunities", Professor Noyori illustrated the use of ruthenium and rhodium complexes with chiral organic ligands, such as BINAP, see Figure 1, which can discriminate between enantiomeric atoms, groups or faces in achiral molecules, and can catalyse the production of a broad array of chiral compounds with excellent enantiotopic purity. One

compound  $[\text{Rh}(\text{BINAP})_2]\text{ClO}_4$  is used in the production of multi-ton quantities of (-)-menthol each year.

The use of a number of ruthenium complexes as active homogeneous catalysts, with suitable co-oxidants, for the oxidation of organic substrates was described by W. P. Griffith, of Imperial College of Science, Technology and Medicine. Primary alcohols, primary aromatic halides and nitro compounds can be oxidised to carboxylic acids, and secondary alcohols and halides can be oxidised to ketones by aqueous solutions of  $[\text{RuO}_4]$  with bromate, *trans*- $[\text{Ru}(\text{OH})_2\text{O}_3]^{2-}$  with persulphate, and *trans*- $[\text{RuO}_2\{\text{IO}_5(\text{OH})\}_2]^{6-}$  with periodate. In non-aqueous solution more regioselective oxidations are effected with  $(^{\text{Pr}_4\text{N}}[\text{RuO}_4])$ , with N-methylmorpholine-N-oxide as co-oxidant. This reagent can be used in the synthesis of the anti-parasitic agent Avermectin B<sub>1</sub>, and the antibiotic Rutiennocin.

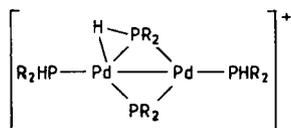
The theme of homogeneous catalysis was continued by E. Drent, of Shell Research, Amsterdam. He discussed the efficient carbonylation catalysis by cationic palladium(II) complexes. These complexes derive their ability of activating nucleophilic substrate molecules, such as alkenes, alkynes, carbon monoxide, hydrogen and alcohols, from the



electrophilic nature of the palladium centre. He also highlighted the use of a palladium(II) complex containing 2-pyridyldiphenylphosphine  $[P(C_6H_5)_2(C_5H_4N)]$  as a catalyst in the selective production of methylmethacrylate (which had a world production of 1.2 Mega tonnes in 1989) by methoxycarbonylation of propyne. The original process generated two and a half tons of waste per ton of product. High turnover rates of 40,000 mole per mole palladium per hour and selectivities of up to 99.95 per cent can be obtained under mild conditions.

The insertion reactions of carbon monoxide and alkenes were discussed by Professor K. Vrieze from the University of Amsterdam, with particular regard to the alternating coupling of carbon monoxide and ethene to produce a polyketone, catalysed by palladium complexes. He described the synthesis of these complexes with a variety of bidentate and terdentate ligands. For the bidentate ligands it was shown that the rate of carbon monoxide insertion proceeded much faster in the order  $N-N \gg P-P > N-P$ , while the rate of alkene insertion increased in the order  $P-P > N-N$ . Professor Vrieze highlighted the somewhat surprising observation that complexes of type  $\{(N-N'-N)Pd(CH_3)\}-Y$  ( $N-N'-N$  = symmetric trinitrogen ligand;  $Y = Cl^-, CF_3SO_3^-$ ) are not only stable but also very reactive towards insertion of carbon monoxide. The products of this reaction,  $\{(N-N'-N)Pd(C(O)CH_3)\}Y$ , react rapidly with norbornene, norbornadiene and dicyclopentadiene.

Novel C-H, N-H and P-H agostic bonds were the subject of the talk by Professor P. S. Pregosin of ETH-Zentrum, Switzerland. In his talk he suggested that, just as for C-H types, there are several different categories of M-H-N bonds. In particular he discussed the chemistry of a palladium complex, shown below, which



contains the first Pd-H-P interaction, and the unique intramolecular dynamics associated with

the movement of the "hydride type" proton across the molecule.

The reactions of methane with platinum group metal complexes were discussed by Professor A. E. Shilov, Institute of Chemical Physics, Russia. Methane and its homologs react with electron rich complexes of the platinum group metals, such as platinum(II), rhodium(I) and iridium(I). The initial step appears to be one of oxidative addition. Professor Shilov provided evidence in the form of kinetic results and data for the isotope exchange with the solvent (water), which were obtained for the reaction of ethane with platinum(II) and the decomposition of  $Cs_2[PtCl_4(CH_3)_2]$ , to show that the reactions involve a similar intermediate, namely a platinum(IV) alkyl hydride complex, confirming that the mechanism proceeds via oxidative addition.

Anionic promoters such as alkoxy, amido, acetate and chloride ions have been shown to enhance the activity and selectivity of  $Ru_3(CO)_{12}$  in the hydroesterification of ethylene by methyl formate, providing an amide solvent is used. P. Kalck and his co-workers, Institut National Polytechnique de Toulouse, France, have undertaken a detailed investigation of this mechanism in the presence of added chloride. In their work, they have shown that mixtures of  $Ru_3(CO)_{12}$  and  $[(PPh_3)_2N]Cl$  as well as the preformed anionic species,  $[(PPh_3)_2N][Ru_3(Cl)(CO)_{12-n}]$  ( $n = 1, 2, 3$ ), exhibit a comparable efficiency. Using this approach, the addition of methyl formate to ethylene can be achieved under rather mild conditions (using dimethylformamide for 12 hours at  $160^\circ C$ ), in the presence of  $Ru_3(CO)_{12}$  activated by chloride, to give  $CH_3CH_2CO_2Me$  in 100 per cent yield and 99 per cent associated selectivity.

A successful radio-labelling technique which has helped to resolve reaction pathways in synthesis gas chemistry was described by D. G. Parker of ICI. Currently some 90 per cent of the total methanol manufactured worldwide is made by utilising a  $Cu/ZnO/Al_2O_3$  catalyst. By labelling with  $^{14}C$  it is possible to show that the methanol is derived from carbon dioxide and *not* from carbon monoxide. This technique has

been further utilised to show that the production of alcohols from carbon monoxide/hydrogen mixtures using ruthenium dioxide as catalyst occurred via a direct growth mechanism rather than alcohol homologation.

Novel modifications of carbon-unsaturated polymer compounds was discussed by Professor M. Tanaka, from the Tsubuka Research Centre, Japan. Treatment of silicon-silicon bonds with low valent palladium and platinum complexes, such as  $\text{Pt}(\text{PPh}_3)_4$ , affords bis(silyl)metal species. Elaboration of these and other elemental reactions in the presence of carbon unsaturated compounds has led to the development of novel silicon containing polymer backbones.

The development and mechanism of a palladium catalysed synthesis of a carbon-unsubstituted stannole  $\text{C}_4\text{H}_4\text{SnR}_2$ , where  $\text{R} = \text{CH}(\text{SiMe}_3)_2$ , was described by K. R. Pörshke, Max-Planck Institute, Germany. The catalysis was most effective ( $-30^\circ\text{C}$ ; yield 87 per cent) when  $(\text{Pr}_2\text{P})_2\text{Pd}(\text{C}_2\text{H}_2)$  was used as the catalyst.

A rhodium-based system that effectively catalyses, under carefully controlled conditions, the selective coupling of enolisable  $\text{C}_n$  aldehydes ( $\text{RCH}_2\text{CH}=\text{O}$ ) to saturated  $\text{C}_{2n}$  monoaldehydes ( $\text{RCH}(\text{CH}=\text{O})\text{CH}_2\text{CH}_2\text{R}$ ) was reported by M. Fontaine, University of Liege, Belgium. Furthermore, these  $\alpha$ -disubstituted aldehydes can be easily oxidised *in situ* to  $\text{C}_{2n-1}$  ketones ( $\text{RC}(\text{O})\text{CH}_2\text{CH}_2\text{R}$ ). The most efficient and selective catalysts were those containing at least one phosphine ligand, with Wilkinson's catalyst  $\text{RhCl}(\text{PPh}_3)_3$ , proving to be the best for the system where  $\text{R} = \text{phenyl}$  with an 80 per cent yield of  $\text{PhCH}(\text{CH}=\text{O})\text{CH}_2\text{CH}_2\text{Ph}$ .

The discovery of the co-ordination of dihydrogen without dissociation on a tungsten complex has stimulated a renewed interest in the study of transition metal hydride derivatives and led to the reformulation of a number of polyhydride complexes. B. Chaudret and co-workers, CNRS, Toulouse, have reformulated  $\text{RuH}_6(\text{PCy}_3)_2$  as  $\text{RuH}_2(\text{H}_2)_2(\text{PCy}_3)_2$ , the only thermally stable *bis* dihydrogen derivative. The ready substitution of hydrogen by very weakly co-ordinating ligands such as dinitrogen, main

group hydrides or even freons was emphasised together with reactions with hydrocarbons by Professor B. R. James, University of British Columbia, Canada. He reported on the syntheses of  $[(\eta^2\text{-H}_2)(\text{dppb})\text{Ru}(\mu\text{-Cl})_2\text{RuCl}(\text{dppb})]$ , (A), where  $\text{dppb} = \text{PPh}_2(\text{CH}_2)_4\text{PPh}_2$ , and species of the type  $[\text{L}_2(\eta^2\text{-H}_2)\text{Ru}(\mu\text{-Cl})_2(\mu\text{-H})\text{RuH}(\text{PR}_3)_2]$ , (B), where  $\text{L}_2 = \text{a ferrocene (P-N) ligand or } (\text{PR}_3)_2$  with  $\text{R} = \text{Ph}$  or *p*-tolyl, along with a range of analogues. Kinetic evidence supports a role for (A) in a catalytic hydrogenation of styrene, with further kinetic and thermodynamic data for the reversible formation of (A) from hydrogen and  $[\text{RuCl}(\text{dppb})(\mu\text{-Cl})_2]$  corroborating this finding.

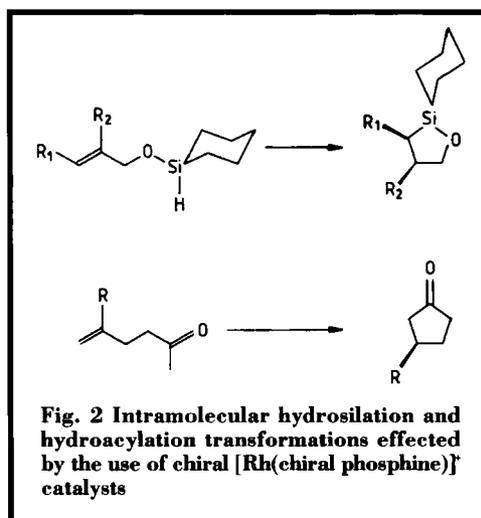
The co-ordination chemistry and C-F bond activation of fluoroarenes was discussed by R. N. Perutz, University of York, U.K. With an ionisation energy less than that of ethene and a high electron affinity, hexafluorobenzene is well placed to bond with transition metals. The reactivity of  $\text{C}_6\text{F}_6$  was succinctly summed up; notably, hexafluorobenzene may co-ordinate in  $\eta^2$ ,  $\eta^4$  or  $\eta^6$  modes to  $(\eta^5\text{-C}_5\text{R}_5)\text{M}$ , ( $\text{M} = \text{rhodium, iridium, rhenium; R} = \text{H, Me}$ ) fragments. C-F oxidative addition may be accompanied by HF elimination, thus providing a thermodynamic driving force for the reaction. C-H activation is preferred to C-F insertion with partially fluorinated arenes. C-H insertion may occur with  $\text{C}_6\text{F}_5\text{H}$  even in circumstances when benzene fails to react by oxidative addition.

The structure and reactivity of an ortho-metallated rhodium(I) complex, namely  $\text{Rh}\{\text{P}(\text{OPh})_3\}_3\{\text{P}(\text{OC}_6\text{H}_4)(\text{OPh})_2\}$ , in the isomerisation of allyl alcohols was the subject of a lecture by A. M. Trzeciak, University of Wroclaw, Poland. This complex was found to be a very active and selective catalyst for the isomerisation of allyl alcohols (such as 1-octen-3-ol, 3-buten-2-ol, 2-propen-1-ol) into aldehydes or ketones.

In a particularly stimulating talk, Professor B. L. Shaw, University of Leeds, discussed a new method of creating co-ordinative unsaturation in metal complexes and a new approach to selective and synthetically useful C-H metallation using azine diphosphines. The

azine diphosphine  $Z,Z$ - $\text{Ph}_2\text{PCH}_2\text{C}(\text{Bu})\text{-CCH}_2=\text{N-N}=(\text{Bu})\text{CCH}_2\text{PPh}_2$ , (C), reacts with  $[\text{IrCl}(\text{CO})_2(p\text{-toluidine})]$  to give the co-ordinatively saturated iridium(III) hydride  $[\text{IrHCl}(\text{CO})\{\text{Ph}_2\text{PCH}_2\text{C}(\text{Bu})\text{CCH}_2=\text{N-N}=(\text{Bu})\text{CCH}_2\text{PPh}_2\}]$  which isomerises rapidly and reversibly to the co-ordinatively unsaturated and reactive  $[\text{Ir}(\text{CO})\{\text{Ph}_2\text{PCH}_2\text{C}(\text{Bu})\text{CCH}_2=\text{N-N}=(\text{Bu})\text{CCH}_2\text{PPh}_2\}]\text{Cl}$ . The hydrazone  $Z$ - $\text{Ph}_2\text{PCH}_2\text{C}(\text{Bu})=\text{N-N}=(\text{Q})\text{CR}$ . This  $Z,E$ -configuration is exactly what is required to force the R-group against the metal. Professor Shaw and his co-workers found that on treatment of these mixed azines with  $[\text{IrCl}(\text{CO})_2(p\text{-toluidine})]$  or  $[\text{PtMe}_2(\text{COD})]$ , the R groups are metallated in every case under mild conditions (that is, at or a little above room temperature), to give a tridentate metal complex containing a carbon-metal bond. When R = a range of substituted phenyls, metallation occurs in the 2- or 6- positions; thiophene and furan are metallated in the 3-position; indole in the 2-position; the condensation products from  $\text{PhCH}=\text{CHCHO}$  or  $\text{MeCH}=\text{CMeCOMe}$  metallate readily at  $=\text{CH}$ ; and the condensation product from  $\text{MeCO}^t\text{Bu}$  iridates exclusively at Me but platinates exclusively at a  $^t\text{butyl C-H}$  – an “unactivated methyl”. This synthetic strategy may provide an alternative to the oxime-palladation reaction of “unactivated methyls” which is used in the synthesis of organic intermediates.

The main subject of the talk by Professor P. M. Maitlis, University of Sheffield, was the homogeneously catalysed process in which methyl iodide is carbonylated to acetyl iodide, which is part of the methanol to acetic acid carbonylation process, commonly known as the Monsanto process. While a cobalt catalyst, which costs \$ 0.3/g, requires high pressure and high temperature and gives a selectivity of 90 per cent, the rhodium catalyst  $[\text{RhI}_2(\text{CO})_2]^-$  which costs \$ 180/g and requires only low pressure and temperature, has an associated selectivity of greater than 90 per cent.



In his keynote lecture Professor B. Bosnich, University of Chicago, discussed asymmetric catalytic intramolecular hydrosilylation and hydroacylation. Catalysts of the type  $[\text{Rh}(\text{chiral diphosphine})]^+$  are very good at effecting these transformations, see Figure 2. With appropriate R-groups on the substrates, enantiomeric excesses of 90–99 per cent can be realised. Professor Bosnich discussed in great detail the mechanisms of the two enantioselective reactions.

M. Schröder, University of Edinburgh, reported on his continued studies on platinum metal complexes of aza and thioether macrocyclic ligands. In particular, he described the co-ordination chemistry of a range of these ligands, such as  $[9]\text{aneS}_3$ ,  $[10]\text{aneS}_3$ ,  $[9]\text{aneNS}_2$ ,  $[9]\text{aneN}_2\text{S}$  to palladium(II) and platinum(II). He noted the need for S-donor atoms in these and other similar ligands to provide for thermodynamically stable and kinetically inert platinum group metal complexes.

Accurate *ab initio* treatments of second-row transition-metal species have presented an enormous theoretical challenge. R. J. Deeth, University of Bath, introduced Density Functional Theory (DFT). This method promises to remedy the deficiencies of the more traditional Hartree-Fock and post-Hartree-Fock methods, which are too inaccurate or too expensive in terms of computer resources. After a

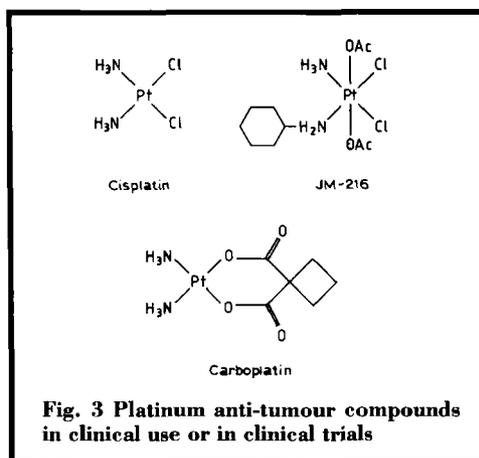
brief introduction of DFT and its capabilities, Dr Deeth presented the results of DFT geometry optimisations for a range of ruthenium-oxo and ruthenium-phosphine compounds, which were in good agreement with experimental data.

The synthesis and characterisation of a wide variety of arene-cluster derivatives based on  $Ru_3$ ,  $Ru_4$ ,  $Os_4$ ,  $Co_4$ ,  $Ru_5C$  and  $Ru_6C$  units were reported on by Professor B. F. G. Johnson, University of Edinburgh. These include compounds containing  $\eta^6$ -arenes, solely  $\mu^3$ - $\eta^2$ : $\eta^2$ -bonded arenes and compounds in which both modes are present. The solid-state structures of many of the *bis*-arene derivatives and their molecular organisation have been investigated. In all cases, graphitic-like interactions have been established in the lattice and the units have been observed to stack as ribbons or snakes.

### Electrochemistry

Another area of strong emphasis at the conference was electrochemistry. Ruthenium and osmium polypyridyl complexes are of interest because the photophysical and electrochemical properties of the compounds can be varied by judicious variations in their ligand composition. This polypyridyl chemistry was discussed by Professor T. J. Meyer, University of North Carolina. In particular, he concentrated on the extensive redox chemistry of these complexes. Polypyridyl complexes are known which can oxidise water to oxygen and can reduce carbon dioxide. There are also examples which demonstrate the  $5e^-$ , reversible, interconversion of nitrogen dioxide and ammonia. In polymeric films, these compounds may provide a basis for imaging and microstructure formation.

N. G. Connelly of the University of Bristol gave a lecture on the use of a combination of synthetic and electrochemical techniques to isolate a wide range of redox-active dirhodium complexes, derived from  $(CO)_2Rh(RN-NR)_2Rh(CO)_2$ , and containing a  $[Rh_2]^{z+}$  core ( $z = 2-4$ ). He discussed their substitution reactions and their intramolecular electron-transfer reactions with oxygen and *o*-quinones. The electrochemical theme was further pursued by G. A. Heath from the Australian National



**Fig. 3** Platinum anti-tumour compounds in clinical use or in clinical trials

University. In an in-depth study of the redox properties and spectro-electrochemistry of binuclear complexes, he highlighted a series of molecular architectures, from unsupported directly-bonded systems  $M_2X_8$  ( $Re_2Cl_8^{2-}$ ,  $Os_2Cl_8^{1-}$ ); to face-sharing  $M_2X_9$  ( $Os_2Cl_9^{1-}$ ,  $Ir_2Cl_9^{1-}$ ); and edge-sharing  $M_2X_{10}$  bi-octahedra, ( $Os_2Cl_{10}^{2-}$ ).

### Biological Aspects

One session of the conference was devoted to the biological aspects of platinum group metal compounds. Professor J. Reedijk, Leiden University, gave an illuminating lecture, in which he discussed the history and background behind the development of platinum amine compounds as anti-tumour agents, see Figure 3. Cisplatin, *cis*- $PtCl_2(NH_3)_2$ , is a very successful anti-tumour drug, especially in combination with other drugs such as vinblastine and bleomycin. It is used for the treatment of testicular and ovarian cancer, and is being increasingly used against cervical, bladder and head/neck tumours. Derivatives of this *cis*- $PtCl_2$ (amine)<sub>2</sub> structural class, see Figure 4, show equal and similar biological activity, although relatively few platinum compounds have been tested in preclinical tumour screens. Currently, new structural classes of platinum anti-tumour drugs that possess chemical and biological properties quite different from those of Cisplatin are being investigated. Professor Reedijk and co-workers are concentrating on the study of such platinum

co-ordination compounds; that is into their structural and spectroscopic characterisation, their biological activity and their specific interaction with cellular components, with special attention to nucleic acid binding. In all cases binding to a guanine-N7 site appears to occur. Different compounds, however, have different binding kinetics, and also the structures of the resulting DNA adducts appear to differ.

The kinetics of acid hydrolysis of Carboplatin was discussed by Professor R. W. Hay of the University of St. Andrews. Carboplatin is another platinum anti-tumour drug currently in clinical use. In acid solution, the kinetic data indicate that the Carboplatin irreversibly loses the cyclobutane-1,1-dicarboxylate ligand to form, first of all, the monocarboxylate bound species and then the *aqua* species  $[\text{Pt}(\text{NH}_3)_2(\text{OH}_2)_2]^{2+}$ . Using the acquired data it is then possible to monitor the degradation of Carboplatin in acid solution with time. Further experiments on this degradation in the presence of sulphur nucleophiles, such as cysteine and glutathione, will follow.

Using platinum group metal complexes as donors and acceptors which avidly bind DNA, Professor J. K. Barton and her co-workers from the California Institute of Technology have explored the possibility that the DNA helix can serve as an efficient " $\pi$ -way" through which electron transfer reactions could be promoted efficiently, that is can DNA act as a wire? A variety of tris-phenanthroline/bipy type complexes of rhodium, ruthenium and cobalt are able to enhance this electron transfer. There appear to be two modes of binding to the DNA. One phenanthroline ligand can partially insert into the DNA helix and become part of the stack (intercalative mode). Alternatively, the ligands may nest into the minor groove but not into the general stacking of the DNA. By varying the ancillary ligands of the complexes, the specificity of the complexes for binding with the DNA can be tuned.

Using this approach, the nature of the purported " $\pi$ -way" in DNA may be elucidated. Photoinduced electron transfer is found to occur very rapidly over distances of up to 40 Å through

a pathway consisting of  $\pi$ -stacked DNA base pairs.

Newly synthesised ruthenium(III) compounds such as *trans*-(HInd) $[\text{Ru}(\text{Ind})_2\text{Cl}_4]$  (where Ind = indole), and *trans*-(HImid) $[\text{Ru}(\text{Imid})_2\text{Cl}_4]$  (where Imid = imidazole), show some degree of tumour-inhibiting activity in various models such as autochthonous colorectal tumours in the rat. B. K. Keppler of the University of Heidelberg, discussed the possible advantages of ruthenium compounds as anti-tumour agents compared to the platinum based drugs. Both ruthenium(III) and ruthenium(II) have reaction kinetics broadly similar to those of platinum(II); these kinetics are considered to be the most appropriate with regard to therapeutic suitability. He also pointed out that the change in oxidation state in the case of ruthenium(II/III) does not include a significant change in the co-ordination number, as happens in the platinum(II/IV) case. He postulated a mode of action for the ruthenium complexes whereby the complex, after injection into the blood stream, is bound by transferrin and transported into the tumour cell. Once inside the cell, the ruthenium(III) could be reduced to ruthenium(II) and an aquated species formed, which would then bind to the DNA.

### Surface Chemistry and Materials

The development in recent years of scanning tunnelling microscopy (STM) has opened up a new, atomic scale opportunity to study materials and in particular the surfaces of solid materials. Professor N. V. Richardson from the University of Liverpool lectured on the catalytically significant clean-off reaction between carbon monoxide and preadsorbed oxygen on a single crystal rhodium surface, a reaction of relevance to the car-catalyst industry. Results show that reaction is initiated at steps on the rhodium(110) surface and then proceeds along the one-dimensional chains of oxygen atoms, lifting the oxygen induced reconstruction of the metal surface. Thermal desorption experiments, on metals such as rhodium and palladium, can give rise to extremely narrow features

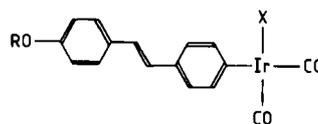
interpreted as autocatalytic decompositions. Professor Richardson reported on the characteristics of these "surface explosions". Co-adsorbed atoms, such as carbon, nitrogen and oxygen, are an essential requirement for these "explosions" to occur. However, they will only happen with specific metals and, in particular, specific planes, such as the rhodium(110) and rhodium(111) planes. These "explosions" have also been observed on "real catalysts".

The chemistry of nanoscale transition metal colloids was the theme of a talk by J. S. Bradley, Exxon Corporate Research, U.S.A. A series of crystalline palladium nanoclusters had been prepared with sizes of about 75 Å, 40 Å and 23 Å and with polydispersities of about 10 per cent. A size dependence is observed for the bonding mode of CO on the palladium particles, with the smallest particles giving the highest ratio of terminal CO to bridging CO, and the largest particles showing only bridging CO. This size dependence is ascribed to the increasing abundance of edge sites and the corresponding relative decrease in face sites as the particle size decreases. Dilution of these palladium lattices with copper is achieved in a series of colloidal bimetallic copper-palladium alloy nanoclusters with particle sizes of about 40 Å. Carbon monoxide adsorbs reversibly on the surface of the particles in solution, binding to both copper and palladium sites. The relative intensities of the Cu(CO) and Pd(CO) absorption bands, in saturated CO solutions of the bimetallic colloids is time dependent, suggesting a rearrangement of the surface layers with enrichment in palladium. R. Whyman from the University of Liverpool, described the preparation of sub-colloidal ruthenium, rhodium, platinum, gold and palladium particles in non-aqueous solutions, using vapour synthesis techniques. In the presence of suitable dispersing agents (about 0.1 weight per cent in co-condensates such as methylethylketone, acetone/water or toluene) the dimensions of these particles can be controlled within the 1–3 nm size range.

Professor H. D. Kaez, University of California, reported on the growth of thin plat-

inum(111) films on highly oriented pyrolytic graphite by organometallic chemical vapour deposition (OMCVD) and the results of scanning tunnelling electron microscopy. One such deposition was carried out on a substrate, such as pyrex or *n*-type silicon(110), held at 205°C and contacted with a stream of helium gas saturated with  $(\eta^5\text{-C}_5\text{H}_5\text{CH}_3)\text{Pt}(\text{CH}_3)_3$ , combined with a stream of hydrogen. This technique has found practical application in the manufacture of platinum electrodes found in heart pace-makers.

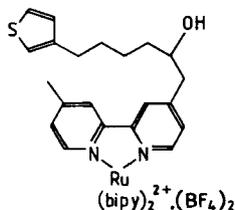
In a particularly entertaining and entrepreneurial talk which crossed interdisciplinary boundaries, D. W. Bruce of Sheffield University, discussed the stilbazole complexes of iridium(I) as liquid-crystalline materials, see below.



These materials have relatively low-temperature liquid crystal mesophases and non-linear optical properties. These complexes also form very high quality Y-type Langmuir-Blodgett films, with good pyroelectric responses compared to "Ru-bipy" materials. P. R. Raithby and his group from the University of Cambridge have prepared a whole series of rigid-rod polymers for the majority of the platinum group metals using the bis trimethylstannyl(acetylide) species  $\text{Me}_3\text{SnC}\equiv\text{C-R-C}\equiv\text{CSnMe}_3$  (R = aryl) in reactions with metal halides and their derivatives. The complexes formed have the general formula  $[-\text{M}(\text{PR}_3)_2\text{-C}\equiv\text{C-R}'\text{-C}\equiv\text{C-}]_n$ , M = nickel, palladium and platinum, and  $[-\text{MX}_4\text{-C}\equiv\text{C-R}'\text{-C}\equiv\text{C-}]_n$ , M = iron, ruthenium, osmium, cobalt and rhodium; X =  $\text{PR}_3$  or CO. The aim of the work is to produce a range of materials which have a range of solubilities and also have a capability for undergoing redox processes, neither of which are possible with organic polymers.

A new approach to incorporating redox-active ruthenium complexes into conducting polymer matrices, that may have useful electrocatalytic

and electroluminescent properties as modified electrodes, was reported by J. A. Crayston of the University of St. Andrews. He discussed the synthesis of a monomer containing the



$\text{Ru}(\text{bipy})_2^{2+}$  group, see above, in which one of the bipyridyl ligands is linked to a thiophene group. This monomer readily polymerises to

yield a modified electrode with both electroactive ruthenium(III) and ruthenium(II) attached to polythiophene chains.

The conference provided an in-depth insight into the current state of platinum group metal chemistry. Recent results from both academia and industry were very much in evidence both in the form of lectures and in the poster presentations. The academic research is clearly becoming more targeted towards commercial applications, which is much to be welcomed, although there is a need for a degree of fundamental research. The next conference in the series is scheduled to be held at the University of York in 1996.

## Iridium Coatings on Structural Carbon Materials

Carbon reacts rapidly with oxygen at temperatures as low as 800 K and therefore carbonaceous materials intended for high temperature structural applications have to be protected against oxidation. Silicon- or boron-based coatings can provide reasonable protection for limited times at temperatures up to about 1700 K, but above this other refractory coatings are required.

Iridium appears to be a favourable material for such coatings for the following reasons: it melts at 2713 K, it has a very low permeability to oxygen, it does not react with carbon below 2553 K and it forms an excellent barrier to carbon diffusion. The preparation of iridium coatings on carbon-based materials, their structure, and the effects of mismatch in the thermal expansions have not been widely reported. Now a group of researchers at Tohoku University, Sendai, Japan, have published the results of their investigations of the surface and growth morphology, and the structural changes of iridium coatings on carbon materials (K. Mumtaz, J. Echigoya, T. Hirai and Y. Shindo, "R.f. Magnetron Sputtered Iridium Coatings on Carbon Structural Materials", *Mater. Sci. Eng.*, 1993, **A167**, (1-2), 187-195).

Iridium was deposited by radio frequency magnetron sputtering onto isotropic graphites and carbon-carbon composite substrates held either at room temperature or 1073 K, and the coatings were examined in the as-deposited state and after heat treatment. Regardless of substrate temperature, columnar grained homogeneous coatings were obtained, with those deposited at room temperature having the finest grain size. However, coatings deposited onto substrates held at 1073 K were denser and less

strained. After heat treatment in nitrogen at 1973 K or 2173 K iridium coatings which had been deposited at 1073 K onto isotropic graphite having a coefficient of thermal expansion of approximately  $7.6 \times 10^{-6}/\text{K}$  were crack-free. Furthermore there was no outward diffusion of carbon, no dislocations were observed and porosity was either reduced or eliminated from the equiaxial grain structure.

## Palladium in Cholesterol Sensors

Since the first discovery of the connection between high cholesterol levels in human serum and various diseases, such as heart disease and arteriosclerosis, there has been a need to develop a fast, accurate method to measure its level.

Now, a team at Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, has developed a fast response cholesterol sensor based on an amperometric enzymatic technique, using a layer of palladium electrodeposited on a glassy carbon electrode (S. Dong, Q. Deng and G. Cheng, *Anal. Chim. Acta*, 1993, **279**, (2), 235-240).

The dispersed palladium particles electrocatalysed the oxidation of hydrogen peroxide giving a large decrease in overvoltage. Cholesterol oxidase was immobilised on the electrode by cross-linking with glutaraldehyde. A layer of poly(o-phenylenediamine) film was electropolymerised on the enzyme layer thus preventing interference from uric acid and ascorbic acid and increasing the thermal stability of the sensor. The sensor had a response of less than 20 seconds in a concentration range 0.05-4.5 mmol/l. The sensor can be used for 200 assays without any decrease in activity.