

The Chemistry of the Platinum Group Metals

A REVIEW OF THE INTERNATIONAL CONFERENCE

For the first time an international conference has been devoted solely to the chemistry of the platinum group of metals. Organised by the Dalton Division of the Royal Society of Chemistry and the School of Chemistry at the University of Bristol, this highly successful meeting attracted well over three hundred participants from twenty-seven countries, the proceedings including four main lectures, thirty invited papers and more than a hundred contributions in the form of posters.

The greatly increased and widespread interest now being taken in the biological potential of the platinum metals, in their usefulness in homogeneous catalysis and generally in their organometallic compounds prompted the organisation of this unique conference attended by representatives of the major oil, chemical and pharmaceutical companies as well as by academic chemists. It is possible to review only briefly the more important developments that were discussed during the five-day meeting held at Bristol in July. A comprehensive book containing abstracts of all the papers and posters is available from the School of Chemistry at the University of Bristol.

Platinum in Cancer Therapy

The opening lecture on the mechanism of action of platinum anti-cancer drugs was given by Professor Barnett Rosenberg of the Michigan State University, the discoverer in 1967 of this method of treatment. His original compound *cis*-dichlorodiammineplatinum(II), now known commercially as cisplatin or Neoplatin, is well established as a drug. It is particularly useful in the treatment of genitourinary tumours such as testicular, ovarian and bladder, especially when used in combination with other anti-tumour drugs. However, this is likely to be only the first of a new class of anti-tumour drugs based on platinum co-ordination complexes. Many structural variants have been screened and it is evident that a *cis* configura-

tion for two amine ligands is an essential prerequisite for an active complex. Five compounds of this type are currently undergoing phase I clinical trials.

Several papers dealing with aspects of the same subject and with the reaction of these compounds with DNA were presented by Professor Stephen Lippard of Columbia University, Dr. Bernhard Lippert of the Institut der Technischen Universität in Munich, Dr. J. P. Macquet and his colleagues from the Laboratoire de Pharmacologie et de Toxicologie Fondamentales du CNRS, Professor R. Bau of the University of Southern California and Professor W. M. Beck of the University of Munich. A paper from Professor Michael Cais and his colleagues at the Israel Institute of Technology in Haifa described some novel platinum complexes with potential anti-tumour activity based on the increased selectivity conferred by the antigenic properties of the ligands, while Professor R. D. Gillard of University College, Cardiff, reported on the effect on bacterial growth of some rhodium complexes.

Organometallic Chemistry

The main lecture on the sessions on co-ordination and organometallic chemistry was given by Professor Sei Otsuka of Osaka University under the intriguing title of "What can be achieved with bulky phosphines?" It was demonstrated that bulky trialkylphosphines

could effectively stabilise co-ordinatively unsaturated platinum and rhodium complexes which had high nucleophilic reactivity towards small molecules. A number of examples were presented including the production of hydrogen from water by a rhodium complex.

Professor M. A. Bennett of the Australian National University, Canberra, then discussed the chemistry of arene ruthenium(II) complexes which could be reduced under mild conditions in the presence of an olefin. Protonation of the resulting ruthenium(0) arene-olefin complexes gave monohydrido ruthenium(II) salts which, in solution, were fluxional with the hydrogen migrating between metal and olefin.

Ring systems formed by amine attack on olefins co-ordinated to platinum(II) formed the subject of a paper by Professor B. L. Shaw and three of his colleagues at the University of Leeds. Variation of the amine and olefin gave rise to either four or eight membered ring cyclic complexes or to binuclear platinum complexes with two *trans*-fused five-membered rings.

New compounds of ruthenium and osmium containing the dichlorocarbene ligand were reported on by Dr. W. R. Roper of the University of Auckland, New Zealand, while a paper from Professor M. F. Lappert and his colleagues in the School of Chemistry at Sussex University described a series of stable α -halogenoalkyls of platinum and amides of rhodium and iridium.

Homogeneous Catalysis

Professor P. M. Maitlis of the University of Sheffield contributed a paper on new types of homogeneous catalytic reactions with the half-sandwich complexes of the platinum metals. Reactions that had been investigated included olefin hydrogenation and carbonyl and arene hydrogenation, while hydrogen transfer reactions were found to be well promoted. Novel aldehyde disproportionation reactions offering a useful route to ethanol and acetic acid were described, using rhodium and ruthenium complexes, while some new rhodium and iridium complexes provide an insight into the mechanism of the Fisher-Tropsch reaction.

A remarkable performance by Professor B. M. Trost of the University of Wisconsin opened the discussions on organic synthesis and homogeneous catalysis. His main conference lecture, on organopalladium intermediates as chemical chameleons, had the underlying theme that olefins may be activated by formation of an intermediate palladium π -allyl complex which can subsequently be attacked by a variety of nucleophiles. The reactions discussed were highly regio- and stereoselective and were used to prepare a wide range of products of biological interest ranging from insect pheromones to precursors for macrolide antibiotics and prostaglandins. Professor Trost also described a novel approach to the synthesis of five-membered carbocyclic rings by reaction of an olefin with the palladium complex of trimethylenemethane.

The study of the mechanisms by which platinum metal complexes catalyse organic reactions and of the application of these processes in selective organic synthesis formed the subject of a paper by Dr. J. M. Brown of the Dyson Perrins Laboratory in the University of Oxford. These factors were illustrated by work on homogeneous hydrogenation employing cationic rhodium complexes in aprotic solvents. The mechanism of the industrially important rhodium complex catalysed hydroformylation process was studied and shown to be a highly complex system with many stable states accessible.

Professor W. Keim of the Institut für Technische Chemie, Aachen, discussed his recent work on the telomerisation of isoprene with water or ammonia using homogeneous palladium catalysts. This offers an attractive route to commercially important terpenoid compounds but is complicated by the large number of possible products, although the selectivity could be improved by variation of the phosphine ligand or addition of acid.

Professor B. R. James of the University of British Columbia described some aspects of the chemistry of ruthenium porphyrin complexes, including a system for the catalytic decarbonylation of aldehydes which was proposed to

occur through formation of ruthenium(III) species and free radicals.

The major change in industrial chemical processes towards homogeneous catalysis and the reasons for this were surveyed by Dr. D. Forster of the Monsanto Company, St. Louis, Missouri, in the last of the four main lectures. The catalysis of methanol carbonylation by a rhodium in place of a cobalt complex has the advantages of operation at lower temperatures and pressures with a higher selectivity and the use of a very much lower metal concentration in the catalyst. The water gas shift reaction and the fundamental chemistry involved in its catalysis by rhodium complexes in acidic media were also reviewed, as was the catalysis of olefin hydrocarboxylation by rhodium and iridium complexes.

Cluster Compounds of the Platinum Metals

The session on cluster compounds of the platinum metals was opened by Dr. G. Longoni of the University of Milan who described the synthesis and characterisation of high nuclearity carbonyl clusters of platinum and rhodium and suggested that these clusters may fill the gap between co-ordination and solid state chemistry. Professor J. Shapley of the University of Illinois then discussed the synthesis of a range of cluster compounds where a metal-hydride bond was used to couple two metal centres in inter- and intramolecular reactions. The synthesis of heterometallic cluster compounds containing rhodium was the subject of the lecture by Professor F. G. A. Stone of Bristol University who showed that tungsten carbyne complexes and compounds with metal-metal double bonds can react with simple co-ordination compounds to give a variety of cluster complexes.

Industrial Technology

As a source of background information on the platinum metals, their extraction, refining and applications, a further series of papers was presented. Operations at Rustenburg Platinum Mines, the largest source of the platinum metals

in the world, were outlined by Mr. Howard Bush who emphasised that the concentration of these metals in the ore amounts to only 3 parts per million and that therefore some ten tons of rock have to be mined and brought to the surface to yield one ounce of platinum.

The separation and refining of the six platinum group metals to the high degree of purity essential in many of their applications involves a complicated series of selective precipitation operations from solutions containing these metals. Even in favourable conditions repeated dissolution and reprecipitation are required, and in order to improve on this procedure separation techniques have been developed based upon solvent extraction. A joint paper by Dr. M. J. Cleare and Mr. R. A. Grant of the Johnson Matthey Research Centre and Mr. P. Charlesworth of Matthey Rustenburg Refiners outlined the new method and related its mechanism to the complex chemistry of the platinum metals. The advantages of this approach include a reduction in processing time, a lower lock-up of valuable metals, a higher yield at lower cost and the possibilities of automation.

The industrial relevance of the chemistry of the platinum metals was discussed by Dr. D. T. Thompson, also of the Johnson Matthey Research Centre at Sonning Common. Dealing briefly with the extensive use of palladium in liquid phase hydrogenation, with platinum on carbon in phosphoric acid electrolytes in fuel cells, the oxidation of ammonia to nitric acid over rhodium-platinum gauze catalysts and the hydrocracking and reforming of hydrocarbons over supported platinum metal catalysts, he turned to the relatively new subject of industrial homogeneous catalysis, first used for a major process in the early 1960s for the conversion of ethylene to acetaldehyde. Since that time homogeneous processes based upon soluble rhodium catalysts have been introduced for the hydroformylation of olefins and the carbonylation of methanol to acetic acid. The advantages of using platinum metal systems for the commercial development of a number of organic transformations were emphasised, such as the

conversion of ethylene to vinyl acetate, of propylene to acetone and to butyraldehyde. These one-phase systems offer economy in energy and a lower concentration of metal in the catalyst by comparison, for example, with cobalt.

Lastly, the development of rhodium hydroformylation technology for process licensing was described by Mr. N. Harris of Davy McKee. This process, developed by Union Carbide, Johnson Matthey and Davy McKee during the early 1970s for the hydroformylation of propylene, offers the advantages of high efficiency and low pressure operation, but a detailed knowledge had to be built up of the

effects of process variations such as rhodium concentration, temperature of operation, and carbon monoxide and hydrogen pressures, on both the efficiency of the process and on catalyst stability, while data had also to be accumulated on the effects of impurities in the feed stocks. All this information has been put to use as a basis for optimising the process design and for the formulation of guarantees for the licencees of the technique. Mr. Harris concluded his paper with the statement that an output of two million tons of the product, n-butyraldehyde, involved the use of less than one ton of rhodium.

L.B.H.

B.A.M.

A Detector for Formaldehyde Vapour

SUPPORTED PLATINUM ELECTRODES USED IN ELECTROCHEMICAL SENSOR

Formaldehyde is an important industrial chemical with a wide range of applications. In aqueous solution it is used as a disinfectant, as a preservative and as an auxiliary agent in the textile, leather, paper and wood industries. However most formaldehyde is used for making resins which are then used in the manufacture of many products including plywood, chipboard and cavity-wall foam. Only extremely low levels of free formaldehyde are evolved from such products if the correct resin is used under appropriate conditions, and even where the resin is made significant levels of atmospheric formaldehyde are rare. However the gas has a pungent odour and an irritating effect on the eyes, and all parts of the respiratory system, and in Great Britain the Threshold Limit Value-Ceiling set by the Health and Safety Executive is only 2ppm.

While a number of analytical techniques are available for determining formaldehyde in the atmosphere, all have their advantages and disadvantages. Now, as a result of a joint research and development programme between Lion Laboratories Limited, of Cardiff, and Ciba-Geigy Plastics and Additives Company of Duxford, Cambridgeshire, an accurate pocket-size electrochemical instrument for detecting and determining atmospheric formaldehyde vapour has been produced.

The development and evaluation of this "Formaldemeter" has recently been described by P. M. Williams, I. R. Whiteside and T. P. Jones (*International Environment & Safety*,

1981, Guide Issue, 15-20). The detector incorporates a fuel cell which, although based upon a sensor originally developed by Professor H. L. Gruber and H. Huck of Innsbruck University, has been modified extensively at the University of Wales. Used in conjunction with its unique aspirating sampling system and related electronic circuitry, it can respond to atmospheric formaldehyde and provide a measurement of the vapour concentration.

The fuel cell electrodes consist of platinum-black supported on porous plastic, and are initially subjected to an activation process to prepare them for subsequent formaldehyde oxidation; in use they are separated by an immobilised acid electrolyte and are connected to the measuring circuit by fine platinum wires. When a sample is drawn into the detector any formaldehyde is adsorbed on the anode and spontaneously oxidised, producing an electron flow across the electrolyte to the cathode. As a result the potential across an external load resistance is changed, and this potential change is amplified and displayed on a digital meter. Following initial calibration, and with periodic in-the-field checks and adjustments, the meter provides a direct reading in formaldehyde vapour concentration units.

The Formaldemeter has high, but not total, specificity to formaldehyde and in addition it requires a short time delay between successive samples. Work to increase specificity and to develop a continuous monitoring facility is proceeding at both Duxford and Cardiff.