

# Conferences Report Progress in Catalysis

## 11TH INTERNATIONAL SYMPOSIUM ON HOMOGENEOUS CATALYSIS

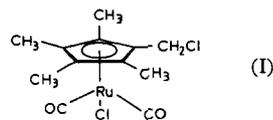
This series of meetings, which began in 1978, has regularly drawn around 400 researchers from around the world to discuss new developments in homogeneous catalysis. For this eleventh meeting, held from July 12th to 17th, the delegates gathered at St. Andrews University, Scotland, and enjoyed traditional Scottish hospitality and a very full programme of both oral and poster presentations.

### Professor Peter M. Maitlis

On this occasion, the opening day of the symposium was a celebration of the work of Professor Peter M. Maitlis, marking his 65th birthday and 45 years of chemical research. The organising committee had reflected the global reach of his influence by inviting speakers from Canada, Mexico, Japan, Russia and Israel, as well as Europe, including his own group at the University of Sheffield, U.K. The topics discussed covered a wide range of applications of homogeneous catalysis in organic synthesis (for example carbonylation, cycloaddition, addition to alkenes, oxidation chemistry and C-C coupling). The association of Professor Maitlis's research with current industrial developments was emphasised in the presentation by M. J. Howard (BP Chemicals, U.K.) on the iridium-catalysed *Cativa*<sup>TM</sup> process for the carbonylation of methanol to give acetic acid. This has replaced the rhodium (Monsanto) process in plants in the U.S.A. (from 1995) and more recently in Korea, increasing capacity there from 200 kt to 350 kt per annum. Retrofitting of the *Cativa*<sup>TM</sup> process in BP plants in the U.K. is underway and on completion the process will account for almost 20 per cent of worldwide acetic acid production. The first new plant using this technology is planned for operation in Malaysia in 2000.

The day concluded with a retrospective lecture by Professor Maitlis, reviewing some of his early collaborations. However, he did not deny himself the opportunity to describe some new results on the chemistry of complexes contain-

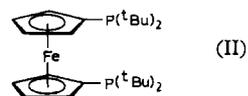
ing functionalised cyclopentadienyl ligands,  $\text{Me}_1\text{CpCH}_2\text{X}$ . The ruthenium complex  $[\text{RuCl}(\text{Me}_1\text{CpCH}_2\text{Cl})(\text{CO})_2]$  (I) is sufficiently



stable to allow the  $\text{CH}_2\text{Cl}$  functional group to undergo a wide range of organic transformations while leaving the parent complex intact. However, the carbonyl and chloride ligands are sufficiently reactive to undergo the expected reactions for such organometallic compounds, for example, substitution reactions. The complexes are active catalysts for the cyclopropanation of styrene with ethyldiazoacetate.

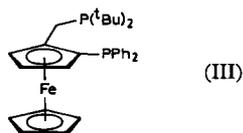
### Palladium-Catalysed Coupling Reactions

The considerable progress made recently in the area of palladium-catalysed coupling reactions was emphasised by several talks and many posters. J. F. Hartwig (Yale University, U.S.A.) discussed the use of 1,1'-*bis*(phosphino)ferrocene ligands for C-C and C-X (X = N or O) coupling. Mechanistic considerations suggested that the large bite angle of this ligand was effective in stabilising the reaction intermediate and that increasing the basicity of the phosphine would lead to rate enhancements. This was borne out by the comparison of 1,1'-*bis*(diphenylphosphino)ferrocene and 1,1'-*bis*(di-*t*-butylphosphino)ferrocene (II) ligands. The



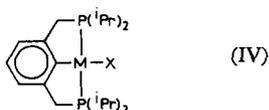
latter proved to be an effective ligand for the coupling of aryl chlorides which were otherwise unreactive. 1,2-Disubstituted ferrocenes are also suitable ligands for this reaction and provide a convenient route for varying the substituents on

each of the phosphorus atoms. A mixed di-*t*-butyl/diphenyl (III) was used for the selective



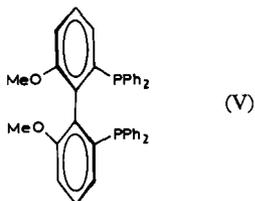
mono-arylation of primary amines.

J. M. Brown (University of Oxford, U.K.) described mechanistic studies employing low temperature heteronuclear NMR to characterise intermediate species in the catalytic cycle for the Heck reaction involving oxidative addition, alkene insertion and reductive elimination steps. Factors influencing the insertion of palladium and rhodium into C-X (X = C, H, O or halogen) bonds were discussed by D. Milstein (Weizmann Institute of Science, Israel) for complexes containing 1,3-disubstituted aryl ligands (IV)



(‘pincer’ ligands). The palladium complexes are highly stable catalysts for Heck reactions.

The application of MeO-Biphep ligands (V)

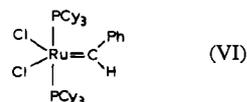


for enantioselective Heck reactions was described by P. S. Pregosin (ETH Zürich, Switzerland), while, by contrast, J. G. de Vries (DSM Research, The Netherlands) described the development of phosphine-free Heck chemistry for industrial applications. Through the use of a decarbonylative reaction with benzoic anhydride, the arylation of olefins is possible in good yield with easy reprocessing of the reaction by-products (CO and benzoic acid). This eliminates the environmental problems caused by the waste streams associated with an equivalent

Friedel-Crafts reaction. Evidence supporting both Pd(0)/Pd(II) and Pd(II)/Pd(IV) cycles as possible mechanisms for Heck reactions was presented during these many presentations and this topic provided some lively discussion.

## Polymerisation Catalysts

In the area of polymerisation catalysts, R. H. Grubbs (California Institute of Technology, U.S.A.) and others described the development and application of ruthenium-alkylidene complexes, such as  $[\text{RuCl}_2(\text{CHPh})\{\text{P}(c\text{-C}_6\text{H}_{11})_3\}_2]$  (VI), for olefin metathesis. Improvements in the

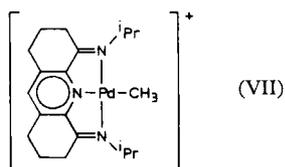


preparation of these catalysts have been made by several groups so that they can now be prepared in high yield, one-pot processes and are available commercially. The initial industrial application of these catalysts will be for the polymerisation of dicyclopentadiene, but due to the ability of the complexes to tolerate water and the presence of a wide variety of functional groups further applications will soon follow. The use of this type of catalyst for ring closing metathesis in synthetic organic chemistry was described by A. Fürstner (Max-Planck-Institut für Kohlenforschung, Germany). Using an allylidene complex (also described by P. H. Dixneuf, Université de Rennes, France, along with other metallacumulenes  $[\text{L}_n\text{Ru}(\text{C}=\text{C}=\text{CR}_2)]$ ) the synthesis of a number of large ring molecules from  $\alpha,\omega$ -dienes was achieved. Functional groups in the diene play an important role in the complexing of the olefin to the metal allowing ring closure to predominate over oligomerisation of the diene.

## Polyketone Synthesis

The use of palladium catalysts for polyketone synthesis by alternating copolymerisation of CO and olefins is being developed by Shell International. Modelling of the reaction intermediates was described by K. Vrieze (Universiteit van Amsterdam, The Netherlands).

The use of rigid, potentially terdentate nitrogen donor ligands (VII) gave very high rates for



CO insertion. The strain created by the rigid backbone leads to one nitrogen donor being easily displaced to create a site for CO or olefin binding. Development of a catalytic system for CO/styrene copolymerisation and CO/ethane/styrene terpolymerisation was described by B. Milani (University of Trieste, Italy). With  $[Pd(bipy)_2][PF_6]_2$  as catalyst, the use of trifluoroethanol instead of methanol as solvent resulted in significantly greater stability for the catalytic intermediate and hence high productivity from the catalyst, and high molecular weight ( $\sim 75,000$ ) for the polymer.

### Unusual Solvents

Presentations on catalysis in unusual media as solvents reflected the growing interest in this area. K. R. Seddon (Queen's University of Belfast, U.K.) discussed the potential of ionic liquids. These are good solvents for many organic, inorganic and polymeric compounds. They remain liquid over a much wider temperature range than conventional solvents and by selection of the constituents they may be

moisture sensitive or tolerant. The wide choice of quaternary ammonium and phosphonium salts as cations, combined with different anions, such as  $AlCl_4^-$ ,  $BF_4^-$  and organic carboxylates, allows the properties of the solvent to be tuned to suit the needs of a specific reaction, for instance to give easy product separation.

The potential of supercritical carbon dioxide,  $scCO_2$ , as a medium for catalysis was discussed in a number of posters and by a presentation by T. Sakakura (National Institute of Materials and Chemical Research, Japan). Arylphosphine complexes have inadequate solubility in  $scCO_2$  for satisfactory catalysis, so modification of the phosphine ligands with perfluoroalkyl substituents has been used to improve their solubility. These ligands are also applicable to catalysis in perfluorohydrocarbon solvents, as described by A. M. Stuart (University of Leicester, U.K.). Examples of rhodium-catalysed hydroformylation for higher olefins in each of these media were given in poster presentations, the main benefit being the easier separation of the product from the catalyst.

Many other excellent presentations were made on homogeneous catalysis using platinum group metals (pgms) and non-pgm transition metal catalysts. This high standard and the sustained interest of the many delegates will no doubt lead to continued success for these symposia. The 12th meeting is scheduled for Stockholm, from August 27th to September 1st, 2000.

C. F. J. BARNARD AND W. WESTON

## 9TH INTERNATIONAL SYMPOSIUM ON RELATIONS BETWEEN HOMOGENEOUS AND HETEROGENEOUS CATALYSIS

The 9th meeting in this series was held in Southampton from 20th to 24th July 1998 and attracted over 200 participants, the vast majority coming from overseas. As is often the case, the experience and knowledge gained from studying one type of system can often be applied to others, so this Symposium on homogeneous and heterogeneous catalysis, was aimed at helping the flow of ideas between these two very similar areas of catalysis.

The opening plenary talk, by Jean-Marie Basset

(University of Lyon-1, France) examined the field of immobilised homogeneous catalysis, a theme that was well represented in the remainder of the conference. Basset's remarks that synergy – as opposed to relations – between homogeneous and heterogeneous catalysis, should be what is considered, were thus rather prophetic.

A highlight of the first day was undoubtedly the presentation by Richard Lambert (University of Cambridge, U.K.) who has developed STM (scanning tunnelling microscopy) techniques to

the point where he is able to apply surface science techniques to fine chemical synthesis. Lambert described the palladium-catalysed trimerisation of acetylene to benzene. For the Pd(0) surface, under low coverage the benzene molecules lie flat, whereas at high coverage they are tilted to the palladium surface. Several isotopic studies have been conducted using C<sub>2</sub>D<sub>2</sub> to gain insight into the possible mechanism for this reaction. In conjunction with several surface techniques, the statistical distribution of products has indicated that the mechanism proceeds via a C<sub>4</sub>H<sub>2</sub> metallocycle intermediate. Lambert found that the desorption temperature for the flat benzene coverage is higher than for the tilted configuration.

Using pseudo-real time STM he was able to identify the likely active site for alkyne coupling reactions on various Au/Pd surfaces. Extensive mixing of the two metals occurred around 500°C and palladium was found to deposit onto the gold particles in an orderly fashion. The activity of these particles towards alkyne coupling increased as the palladium coverage approached a monolayer. At a coverage above one monolayer the activity began to fall, as the palladium surface became rough (with steps and terraces, and so on) and was no longer the regular Pd(111) surface.

## Enantioselective Hydrogenation

The second day was dominated by enantioselective hydrogenation. A. Baiker (ETH Zürich, Switzerland) gave a broad review of the work performed on the asymmetric hydrogenation of  $\alpha$ -ketoesters over chirally modified supported platinum metals catalysts during the last decade. His more recent work on the application of the technology to new reactants, including ketopan-tolactones, (the hydrogenated product of which is useful in the manufacture of vitamins) was also presented.

John Bradley (Max-Planck-Institut für Kohlenforschung, Mülheim, Germany) and Robin Whyman (University of Liverpool, U.K.) reported their respective studies into the use of colloids as model catalysts for the study of enantioselective hydrogenation. As always, the

use of model catalysts to try to explain catalytic behaviour under real reaction conditions generated controversy. However, Whyman's observation that minute quantities of water were essential to attain a rate enhancement, although not yet understood, must be relevant to the rate enhancements seen under normal operating conditions.

Peter Wells (University of Hull, U.K.) presented molecular modelling which supported the generally accepted mechanism for the asymmetric reaction. The same ideas were also used to explain the mechanism for the functioning of oxycodone as a modifier, the major difference being that a step-site on the metal surface is required to enable the enantioselective site to form.

Martin Wills (University of Warwick, U.K.) spoke on two aspects of the asymmetric reduction of ketones to secondary alcohols. Firstly using chiral phosphinamide catalysts in the presence of a borane Lewis acid. The catalysts are air- and moisture-stable, with the reactions proceeding in good yield. However, the reactions require 10 mol per cent of catalyst and high temperature conditions (110°C).

The second part of his talk involved ruthenium(II) catalysed hydrogenation reactions. These systems have the advantage of running at room temperature which is advantageous for less stable ketones. The active species is derived from [RuCl<sub>2</sub>(*p*-cymene)]<sub>2</sub> and a hydroxylamine ligand, such as 1-amino-2-indanol. The rigidity of the indanol ligand structure is necessary for achieving the desired high stereoselective control, see Figure 1. Enantiomeric excesses (e.e.) of up to 98 per cent have been obtained using just 1 mol per cent of ligand and 0.5 mol per

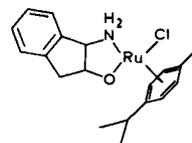


Fig. 1 Ruthenium catalyst giving optimal results for ketone hydrogenation

cent of ruthenium. Both yield and e.e. were shown to decrease with different, less rigid hydroxylamine ligands.

## Polymer Synthesis

A series of ruthenium catalysts for ring opening metathesis polymerisation (ROMP) and ring closure metathesis reactions (RCM) have been developed by R. H. Grubbs (California Institute of Technology, U.S.A.), who talked at length about his work. Some of the ruthenium carbene catalysts (VI) have been commercialised and are now being sold in kg quantities.

He stated that the activity of the catalyst depends on the phosphine ligand. Bulkier groups tend to give higher activity catalysts such that  $P(\text{Cy})_3 > P^i\text{Pr}_3 > P\text{Ph}_3$ .

Heterogeneous analogues to these systems have been attempted by attaching the ruthenium to a phosphine polymer support. Unfortunately the supported phosphine is typically labile and undergoes ligand exchange reactions. This leads to the ruthenium becoming detached from the support and consequently leaching from the catalyst. Grubbs has also incorporated functionalised phosphine ligands into the catalysts to obtain water soluble metathesis catalysts, see Figure 2. Such catalysts require the presence of HCl to give acceptable rates and yields but do offer a great benefit for carrying out aqueous phase reactions.

L. Delaude (University of Liège, Belgium) continued with the subject of ROMP catalysts in a paper on the polymerisation of 2,3-dicarboalkoxy-norbornadienes. The active catalytic species was similar to Grubbs' Ru(II) carbene, but without co-ordinated phosphine ligands. The catalyst was derived from  $[\text{RuCl}_2(p\text{-cymene})]_2$

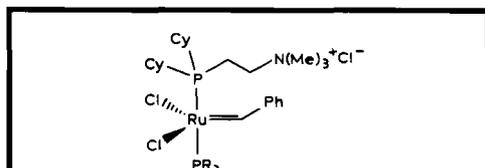


Fig. 2 Water soluble ruthenium catalyst with functionalised quaternary amine

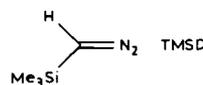


Fig. 3 Trimethylsilyldiazomethane (TMSD)

and was activated by the carbene precursor, trimethylsilyldiazomethane see Figure 3. The polymers produced from this reaction have high stereo-regularity reaching 99 per cent *trans* configuration. Even in the absence of stabilising phosphines the catalysts are still quite stable. The activities of these catalysts were not significantly different to those produced by Grubbs. Interestingly, the addition of a phosphine (tricyclohexylphosphine) to the reaction actually leads to a decrease in both yield and selectivity.

## Clusters in Catalysis

G. Schmid (Universität GH Essen, Germany) spoke of recent developments in the field of metallic cluster catalysis. Cluster molecules can be thought of as being somewhere between discrete molecules and bulk metal. Schmid explained how the absorbance relaxation of gold clusters changed with size.  $\text{Au}_{13}$  clusters exhibited molecular optical behaviour whereas  $\text{Au}_{55}$  clusters acted like a bulk metal.

The transition from molecular to bulk properties occurs somewhere between the two cluster sizes. The different clusters should exhibit properties relating to homogeneous and heterogeneous catalysis, respectively. Recently Schmid has put clusters into nanoporous alumina membranes. These membranes are formed by the anodisation of aluminium and contain small channels running perpendicular to the surface. The pore walls can be functionalised with alkoxysilanes and used to trap catalytically active (cluster) species. These systems are still under development and show good potential for gas phase catalysts.

## Ionic Liquids

H. Olivier (Institut Français du Pétrole, France) gave a lecture on the use of ionic liquids and how they can be used in reactions that involve

complexes or ligands that are either poorly soluble in water or unstable in water. Ionic liquids have been explored as solvents for transition metal catalysts for over 20 years, and used in hydrogenation and hydroformylation reactions (DuPont, Texaco, Unilever). A new range of room temperature non-aqueous ionic liquids (NAILs) were presented by Olivier based on organic cations (such as quaternary phosphonium or ammonium ions) and inorganic anions (such as  $\text{AlCl}_4^-$ ,  $\text{Al}_2\text{Cl}_7^-$ ,  $\text{BF}_4^-$ ,  $\text{PF}_6^-$ ). The transition metal catalysts remain in the ionic liquid, giving the benefits of reduced catalyst consumption and disposal. By changing the combinations of anions and cations the ionic liquids can be tailored to industrial reactions, thus providing new solvents for hard or soft metal catalysts.

Other novel ideas were presented in the two poster sessions and some of these will undoubtedly mature in time for the next conference in this series, which is to be held in Lyon, France in 2001.

One poster, which won a poster prize was by R. L. Augustine (Seton Hall University, U.S.A.), who described the immobilisation of homogeneous catalysts on high surface area supports such as carbon, silica and alumina. It will be interesting to see whether his work will justify the opening remarks on synergy made by Professor Basset.

The proceedings of this conference will be published in a special issue of the *Journal of Molecular Catalysis*.

K. E. SIMONS AND A. F. CHIFFEY

## Combinatorial Chemistry Identifies Fuel Cell Catalyst

The combinatorial chemical screening of large numbers of samples has received much attention in recent years, particularly due to its use in drug discovery for the identification of new leads, although the approach has been used for about twenty years to find new inorganic materials. The technique is now being adapted and applied to finding new materials (1).

Direct methanol fuel cells (DMFCs) have an advantage over other fuel cells in converting methanol directly at the anode to electricity, but poor performance has limited their commercialisation, the major limitations being anode and membrane performances (2). Combinatorial screening can be used to find more active electrochemical catalysts, but presently-used current-voltage methods are time-consuming and cumbersome for such large numbers of samples. In other combinatorial screenings, a fluorescent indicator has been used to detect the presence of ions (such as  $\text{H}^+$ ), the intensity of the fluorescence being an indication of activity.

Now, fluorescent detection and combinatorial chemistry have been used by scientists at Pennsylvania State University, Illinois Institute of Technology and ICET in Massachusetts to identify a combination of platinum group metals with improved properties, which they say may be used as the anode in a DMFC (3).

Platinum, ruthenium, osmium, iridium and rhodium were combined in a 645-electrode array, deposited onto carbon paper and screened in a methanol/fluorescent indicator medium. The most active components were selected; bulk

samples were characterised by various techniques and tested as anode catalysts in DMFCs. The best combination was Pt(44)/Ru(41)/Os(10)/Ir(5), which had a current density 40 per cent higher than presently used Pt-Ru at 400 mV and more than double the value under short circuit conditions.

With this method a wide range of compositions was searched rapidly and thoroughly, allowing areas of apparent inactivity to be investigated. In fact, the activity of this particular combination does not lie in the expected active regions. Such optical screening may be useful to identify other electrochemical materials.

### References

- 1 *Chem. Week*, Aug. 12, 1998, 501, p. 18
- 2 M. P. Hogarth and G. A. Hards, *Platinum Metals Rev.*, 1996, 40, (4), 150
- 3 E. Reddington, A. Sapienza, B. Gurau, R. Viswanathan, S. Sarangapani, E. S. Smotkin and T. E. Mallouk, *Science*, 1998, 280, (5370), 1735

### The Development of the Platino-Calixarenes

In the January 1998 issue of *Platinum Metals Review*, on page 15, right hand column, the seventh line should read "obtained by reacting complex 3 with 4,4'-bipyridine, see Scheme V." In the legend of Scheme V  $\text{L}^+$  must be replaced by 3.

### Polymers of Platinum Metals Complexes Immobilised on Electrodes

In the April 1998 issue of *Platinum Metals Review*, on page 61, right hand column, the thirteenth line should read "[Rh(bpy)(PPh<sub>2</sub>Et)<sub>2</sub>(Cl)(H)]<sup>+</sup>".