

Organometallic Chemistry and Applied Catalysis

A REVIEW OF THE THIRD ANGLO-DUTCH SYMPOSIUM

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The latest Anglo-Dutch Symposium on organometallic chemistry and applied catalysis was held at the University of Sheffield from 29th to 30th March 1999. It was the third symposium of these highly successful meetings between the Dutch and British communities involved in organometallic chemistry and catalysis. Previous meetings have been held in Amsterdam (1997) and in Sheffield (1996) following an initiative by P. M. Maitlis, K. Vrieze and G. van Koten (Universities of Sheffield, Amsterdam and Utrecht, respectively).

A total of 120 participants attended this symposium which covered a wide range of subjects in catalysis. In addition to lectures by a large number of well-known researchers, a poster session displaying more preliminary results also formed part of the programme. Below, highlights relevant to catalysis using platinum group metals are described, as well as some generally interesting developments in catalysis which were discussed during this meeting.

General Developments in Catalysis

A promising new development using micro-reactors in catalysis was presented by R.W. K. Allen (University of Sheffield). The favourable heat and mass transfer properties in these reactors can lead, in some cases, to better selectivity (reactor control). These reactors appear to be especially promising for fuel cells but may be even more so for rapid parallel screening of catalyst libraries.

An overview on recent developments in combinatorial synthesis, especially in the area of catalysis, was given by M. L. Turner (University of Sheffield). Although the so-called "split and mix technique" is very effective for creating large

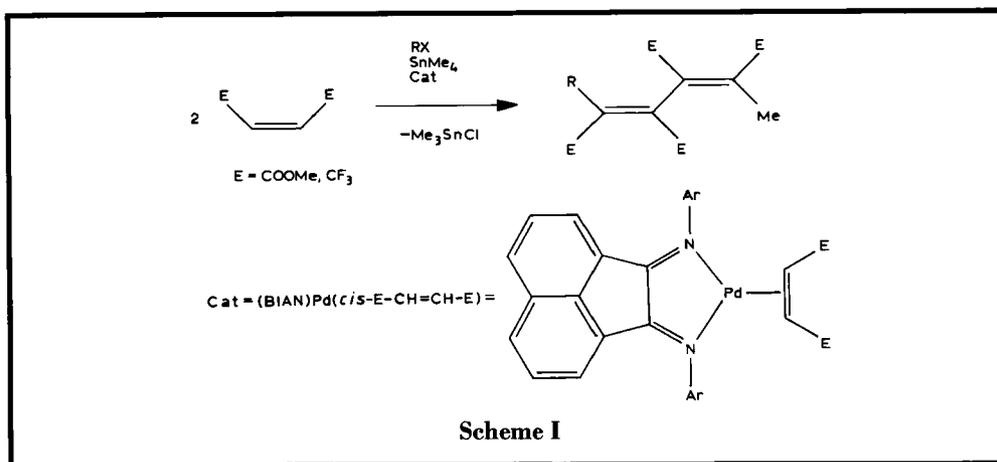
libraries, containing over 10,000 members, there is a practical problem with identifying and keeping track of the many individual ligands or catalysts that are synthesised.

This problem does not occur in parallel syntheses, but the technique appears to be best suited for smaller libraries, typically with less than 1000 members, although equipment for the generation of larger libraries is being developed.

Current applications and developments in "combinatorial catalysis" are therefore mainly carried out using the parallel approach. It is clear that another very relevant issue, although not addressed by Turner, concerns how a ligand/metal complex library with sufficient diversity of ligands should be constructed, and how the feedback from the screening results should be incorporated into the library, so as to help focus the screening process.

Platinum group metal based homogeneous catalysts and the use of rapid screening techniques for finding catalysts for specific catalytic reactions is also of interest to Johnson Matthey, as reported by A. K. Keep. Often, each specific combination of substrate and desired catalytic reaction requires a particular catalyst and consequently a dedicated screening process. This observation explains the intense current interest in rapid parallel screening techniques for catalysis.

Workers at the University of Liverpool have developed a new high pressure gas flow cell for NMR spectroscopy. This has been developed for *in situ* spectroscopy and B. T. Heaton described the cell and its uses. It can, for example, be used to study intermediates in rhodium catalysed hydroformylation. The technique



allows NMR measurements to be made under catalytic conditions while gas is bubbling through the sample.

New and Improved Catalysis

R. A. van Santen (Technical University of Eindhoven, The Netherlands) described the oxidation of ammonia to dinitrogen and water, achieved using alumina-supported platinum, iridium or copper catalysts. The catalysts developed have a high tolerance to water and use oxygen as the promoter.

Interestingly, the detailed thermodynamics of every step of the catalytic cycle as well as those of deactivation pathways and side reactions ((NO)_x formation) are well understood, based on high level molecular orbital (MO) calculations on low molecular weight model compounds. Pt(NH₃)₄ supported on HZSM-5 zeolite also proved to be an active ammonia reduction catalyst at low temperatures (473 K), with increased activity and selectivity when water is present in the feed. The group at Eindhoven is now developing catalysts for the electrochemical oxidation of ammonia.

Detailed accounts of recent improvements and better understanding of the BP/Amoco Ir/I⁻ catalysed methanol carbonylation process were given by R. Watt (BP/Amoco) and A. Haynes (University of Sheffield). From a technical and process economics viewpoint, the iridium system has some major advantages over the older

rhodium-based process. For instance, it has been found that deactivation of the catalyst takes place by the build-up of HI which enters the water-gas shift reaction to form inactive [Ir(CO)₂I₂]⁻. This can now be successfully suppressed using ruthenium carbonyls (such as [Ru(CO)₂I₂]) and other Lewis acidic I⁻ acceptors (such as InI₃ or GaI₃) as promoters. It was demonstrated by model reactions that the role of the promoters is to abstract I⁻ from the electronically unsaturated [Ir(CO)(Me)I₃] intermediate, which accelerates the migratory insertion of CO to form the iridium acyl complex, by ~ 800 times.

The selective hydroformylation of *internal* olefins to *linear* aldehydes was described by P. C. J. Kamer (University of Amsterdam). This was achieved using rhodium-xantphos and closely related complexes as catalysts under low carbon monoxide pressures. The catalyst first isomerises the alkene to the terminal olefin and then starts to hydroformylate it.

An elegant 3-component coupling of two equivalents of an electron-poor alkene, an alkyl halide and an alkyltin compound, using a Pd⁰ complex of the BIAN ligand (BIAN = bis(imino)acenaphthene), was described by C. J. Elsevier (University of Amsterdam), see Scheme I.

The selective partial hydrogenation of *internal* alkynes was also accomplished using (BIAN)Pd⁰(*cis*-E-CH=CH-E) (E = CF₃, C(O)OMe) (87 per cent selectivity for stilbene).

Compared to the well-known Lindlar catalyst, less E-alkene was synthesised, but sometimes more alkane is formed.

Asymmetric Homogeneous Catalysis

In an enthusiastic presentation, V. K. Aggarwal (University of Sheffield) explained that his group has developed a catalytic process for the direct synthesis of chiral epoxides from aldehyde and diazoalkane derivatives, see Scheme II. The catalytic process is believed to consist of two cycles, one involving a rhodium alkylidene and one involving a chiral sulfur ylide. In some cases, $[\text{Cu}(\text{acac})_2]$ was found to be more beneficial than $[\text{Rh}_2(\text{OAc})_4]$, although it is not clear which copper species are formed. Enantiomeric excesses (ee) were generally better than 90 per cent. Using a similar approach, chiral aziridines were also accessible, starting from a functionalised imine as reactant instead of the usual aldehyde.

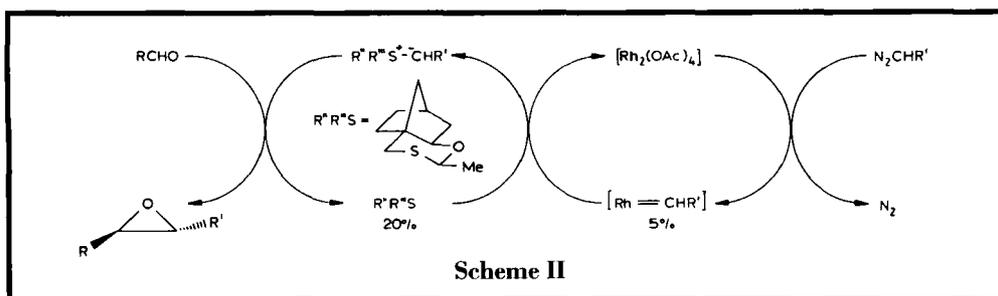
Chiral cyclopentadienyl ligands with pendant $-\text{C}_6\text{H}_4-2-\text{C}^*(\text{H})\text{MeNMe}_2$ arms were reported by C. White (University of Sheffield) to be reasonably effective (ee > 71 per cent, using $[\text{C}_3\text{Me}_5-\text{C}_6\text{H}_4-2-\text{C}^*(\text{H})\text{MeNMe}_2\text{RhCl}_2]$ as catalyst and a 10-fold excess of free ligand) for the asymmetric hydrogenation of non-functionalised 1-alkenes, a reaction which is known to be notoriously difficult.

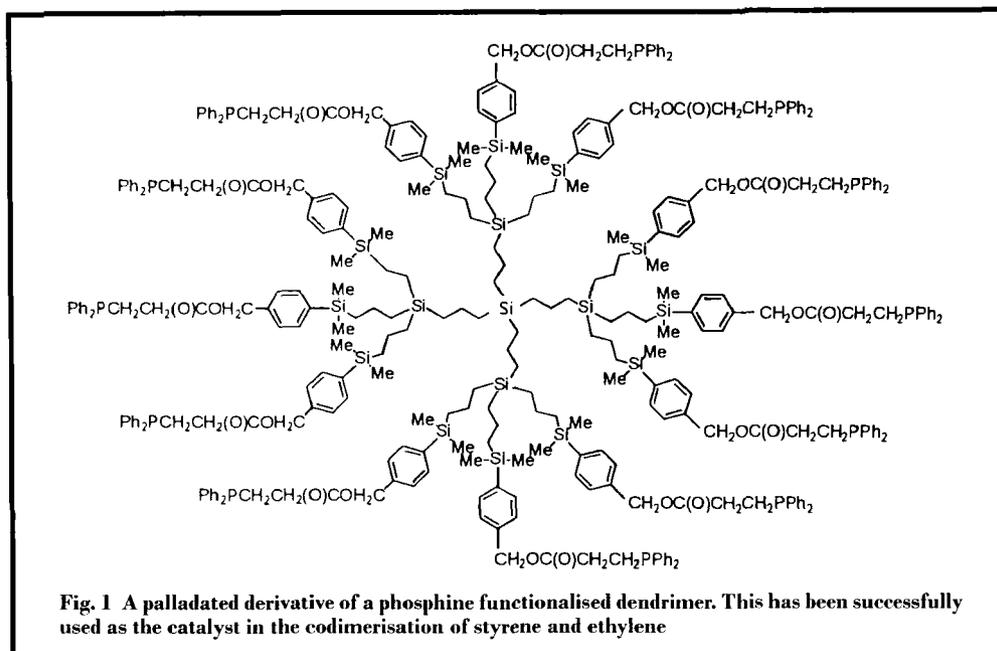
Supported Catalysts and Catalyst Recycling

A number of presentations dealt with catalyst deactivation and methods for recycling. As explained by the symposium host, Professor P. M. Maitlis, catalyst deactivation in homo-

geneous catalysis is largely an undiscovered territory. Deactivation is understood for only a few well-known catalysts. The question remains why this is so. It may be that deactivation is not usually investigated because of the higher ratio of product:catalyst value, compared with heterogeneous catalysts which are often used in bulk applications. If this is the case, then homogeneous catalyst recycling may be less economically interesting. Nevertheless, there may be other reasons (environmental issues or optimising the use of noble metals) to explain the efforts going into developing methods for recycling homogeneous catalysts.

One such approach is the development of fluororous catalysts (fluororous refers to being soluble in a fluorinated solvent) which can be recovered by selective extraction with fluororous solvents. Some methods for rendering conventional noble metal catalysts fluororous, by the use of $4-\text{C}_6\text{H}_4\text{C}_n\text{F}_{2n+1}$ units to prepare triaryl phosphines and bis(diarylphosphino)ethane ligands, were presented by E. G. Hope, University of Leicester. In most cases the fluororous domain of the catalyst has a negative effect on catalytic activity, but at the same time preferential fluororous phase affinity requires the catalyst to have substantial fluororous character (> 60 weight per cent F). The "trick" in this branch of catalysis appears to be to design an ideal electronically insulating spacer to separate the large fluororous domain from the active metal centre. While better results were obtained using $\text{P}(\text{O}-\text{C}_6\text{H}_4-4-\text{C}_n\text{F}_{2n+1})_3$ (for rhodium catalysed hydroformylation) and $\text{P}(\text{C}_6\text{H}_4-4-\text{OC}_n\text{F}_{2n+1})_3$ (for rhodium catalysed hydrogenation), the retention of the fluor phase by the catalysts and ligands, and





consequently their efficient recycling, remain to be investigated.

Another approach to catalyst recovery is to anchor the catalyst to a well defined macromolecular support, which will keep the catalyst on one side of the microporous membrane in a membrane reactor. If the large support is soluble and indeed well defined, then fast single site homogeneous catalysis can take place. Professor G. van Koten, Utrecht University, described this technique and noted that carbosilane dendrimers may be the ideal support for this. In his group nickel- and palladium-functionalised dendrimers have already been prepared. The palladated derivative of a phosphine functionalised dendrimer has been successfully used as the catalyst in the codimerisation of styrene and ethylene, see Figure 1. Catalyst retention in a membrane reactor is already rather good for relatively low molecular weight dendrimers but catalyst deactivation is still a problem. Investigations into the origin of this deactivation, whether membrane or dendrimer-related, are now being performed.

Other interesting contributions, not concerned with the platinum group metals, were presented

at the Symposium, but are not reviewed here.

In conclusion, the quality of the work undertaken in the U.K. and in The Netherlands and described at the Symposium should ensure that these Symposia will play an increasing role in the exchange of ideas on catalysis.

The fourth Anglo-Dutch Symposium is expected to take place in The Netherlands in the autumn of 2000, probably at the University of Utrecht.

Sonochemical Platinum Reduction

Platinum nanoparticle, of interest because of their high catalytic activity, were prepared in an aqueous system using high density ultrasound (200 kHz and 6 W cm⁻²). The nanoparticles were found by researchers from Osaka Prefecture University (Y. Mizukoshi, R. Oshima, Y. Maeda and Y. Nagata, *Langmuir*, 1999, 15, (8), 2733–2737) to be smaller and more regular than those made radiochemically. Stable, homogeneously spherical, monodispersed Pt nanoparticles, of average diameter 2.6 nm, were formed at the rate of 26.7 μM min⁻¹ in a Pt(II)-sodium dodecyl sulfate system. Three kinds of reducing species are proposed to be formed in the sonicated system, near and/or in the hot bubbles, and these then react with the PtCl₄²⁻ complexes to form the platinum nanoparticles.