

Catalysts Play a Major Role in Development

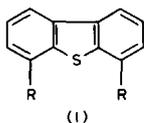
By A. F. Chiffey

Chemicals Development, Precious Metals Division, Johnson Matthey, Royston

The second Anglo-Dutch Symposium on Catalysis and Organometallic Chemistry was held on the 26th September 1997, in Amsterdam, The Netherlands. The symposium was attended by more than 80 participants from industry and universities in Britain and The Netherlands. A series of lectures was given on catalysis and its applications, and there were more than thirty poster presentations. This report highlights some aspects involving the platinum group metals.

Towards Cleaner Fuels

Sulfur compounds, which occur naturally in crude oil, give the pollutant sulfur dioxide when burnt. Legislation, particularly in the U.S.A., is forcing the maximum sulfur limits in fuels to become progressively lower. This requirement, to produce more environmentally acceptable fuels, has led Professor P. M. Maitlis of the University of Sheffield to investigate metal catalysed hydrodesulfurisation reactions. Conventional methods of hydrodesulfurisation involve passing hydrogen with the fuel over Co/Mo/S or Ni/W/S catalysts at 300°C. However, in crude oil, alkyl substituted sulfur heterocycles, such as dimethyl dibenzothiophene (I), below, are, for steric reasons, more resistant to attack in these systems.



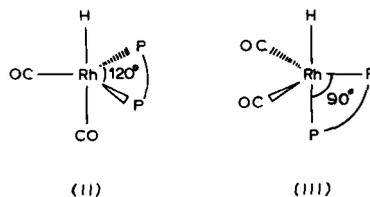
Dibenzothiophene (DBT)
R = Me

Professor Maitlis has shown that certain platinum catalysts have significant activity for removing dibenzothiophenes from crude oils. These catalysts, containing triethylphosphine or diphenylphosphinoethane, are involved in

the key reaction stages of oxidative insertion, hydrogen activation and the breaking of two carbon-sulfur bonds. The reactions have so far been performed under hydrogen pressures of 20 atmospheres and at a temperature of 100°C for 24 hours. While results from these systems have been encouraging and should help in the development of the next generation of hydrodesulfurisation catalysts, scaling these reactions to tonnage quantities is as yet impractical.

Catalysts with Bite

In chelate complexes with bidentate ligands the angle between the two donor atoms of the bidentate ligand and the metal centre is termed the 'bite angle'. The importance of the bite angle in a series of complexes, was reported by Professor P. W. N. M. van Leeuwen of the University of Amsterdam, see II and III.

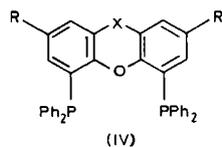


Distortions of this angle can affect reaction products, as was shown for the rhodium catalysed hydroformylation of alkenes. In this reaction, catalyst (II) with the phosphine ligand in the trigonal plane, gives a higher ratio of linear:branched products than isomer (III).

The size of the bite angle can be tailored by altering the length of the backbone between the donor atoms. Longer backbones tend to give larger angles, which reduce the strain in the chelate ring. Unfortunately, backbones which are longer than [C5] tend to give ligand bridged bimetallic compounds or (Rh-C) bound

organometallics. Ligands can be designed with rigid backbones resulting in greater control in the chelate structure.

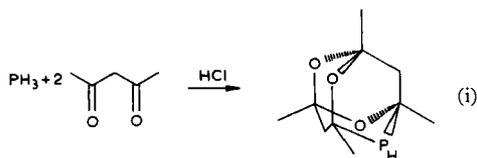
A range of diphosphines of the type (IV) has been studied to investigate the effect of the bite angle on product selectivity.



Rhodium complexes containing these ligands have bite angles between 102° and 112° . When these are used in hydroformylation reactions the linear:branched product ratio varies, the optimum performance being at a bite angle of 109° . Deviations in the angle on either side of 109° gave both poorer yields and selectivities for the linear product. There are also secondary effects which should be considered with these ligands. Different substituents at X can contribute electron donating or withdrawing properties, which are known to modify the *n:iso* product ratio. However, the overall effect of changing the bite angle is only small, giving just percentage changes in product yields, but for commercial processes the impact could be dramatic.

Ligands Designed for Catalysis

The discussion of the relationship between structure and activity of catalyst was continued by P. Pringle of the University of Bristol, who described the design of ligands which would put metals into unusual environments.



Such ligands can modify the catalytic properties of a complex by, for example, introducing large steric bulk. Cage phosphine ligands have been prepared for this purpose from the simple

phosphine, PH_3 , see Equation (i). Palladium complexes containing cage phosphine ligands have shown good activity for catalysing hydrocarboxylation reactions.

Similar ligands have been designed to give enhanced performance, by changing the groups bound to the phosphorus. Rhodium phosphite catalysts, $[\text{Rh}]\text{-P}(\text{OR})_3$, have been shown to be 200 times faster than the corresponding rhodium phosphine catalysts, $[\text{Rh}]\text{-PR}_3$, in certain hydroformylation reactions. Unfortunately the (P-OR) bond in phosphites is susceptible to hydrolysis. Hence the search for more robust ligands has become an active area, and ligands such as biaryl diphosphites may be the answer. Binaphthite for example, shows good hydrolytic stability in tests when heated in acetone under reflux conditions. Once co-ordinated with metals, it has a greatly extended half-life (the half-life being the time when the catalyst decomposes (hydrolyses) to leave only half the active species). The same can be said of a range of novel water soluble phosphites.

Putting the phosphorus donor in a crowded cage environment offers stabilisation and greater protection against hydrolysis. These phosphite containing materials have a combination of steric protection and exposure of the active sites that is necessary for successful catalysis. Research is continuing to improve the synthesis of these ligands and to extend the range of structures that are available.

Looking Ahead

A little of the interesting work being carried out by both British and Dutch research groups has been highlighted here. Some of this work may well contribute to the development of industrial processes. With the close collaboration that is taking place between institutions on both sides of the North Sea the third Anglo-Dutch symposium, for which the date is yet to be confirmed, should certainly have much to look forward to. The third symposium is expected to take place in the U.K. in September 1998 and the organising chairman from whom information may be obtained will be Professor Peter Maitlis of Sheffield University, Fax: +44-(0)141-273-8673.