

Platinum Metals in Catalysis

Homogeneous Transition Metal Catalysed Reactions: Advances in Chemistry Series 230
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This volume developed from a meeting of the American Chemical Society held at Boston in April 1990. It was published to reflect the growing importance of homogeneous catalysis and updates earlier works published by the New York Academy of Sciences. It was intended that this book would prove valuable to both practitioners and educators. It comprises 41 chapters with 116 contributing authors and is divided into five sections. The relative importance of the platinum group metals can be gauged by the fact that 28 chapters deal with the use of platinum group metals and the majority of these deal exclusively with precious metal catalysts.

In the section on spectroscopy and mechanism, W. R. Moser discusses the development of cylindrical internal reflectance reactors for monitoring high pressure reactions by infrared spectroscopy with reference to rhodium catalysed hydroformylation and the palladium catalysed carbonylation of aryl halides. The theme of infrared spectroscopy is continued by R. Whyman who describes high pressure *in situ* studies involving the identification of unstable species such as $[\text{Rh}_2(\text{CO})_8]$ and $[\text{HRh}(\text{CO})_4]$ and the conversion of synthesis gas to ethylene glycol type esters using rhodium/ruthenium clusters. D. C. Roe describes his seminal work on the development of sapphire nuclear magnetic resonance tubes which has enabled this technique to be used at pressures of 1000–2000 psi. Other novel techniques discussed in this section include a paper from R. Eisenberg and colleagues on the use of parahydrogen induced polarisation as a mechanistic probe in rhodium and ruthenium catalysed hydrogenation reactions and work by P. C. Ford and S. T. Belt on flash photolysis studies on reactive rhodium and ruthenium species relevant to carbon-hydrogen activation.

The development of ruthenium(II) Binap compounds and their effectiveness as asym-

metric hydrogenation catalysts for a wide range of applications including isoquinolines, benzomorphans, naproxen, citronellol, amine alcohols and the synthesis of new phosphine ligands is discussed by H. Takaya and coworkers. Asymmetric induction is further considered by H. Brunner with reference to rhodium catalysed hydrosilation and hydrogenation and by K. Burgess and M. J. Ohlmeyer who discuss stereocontrol in rhodium catalysed hydroborations. In these latter cases the enantiomeric excesses obtained were moderate.

The next theme to be studied is the problematic one of carbon-hydrogen activation. M. Tanaka and T. Sakakura discuss the use of $[\text{RhCl}(\text{CO})(\text{PMe}_3)_2]$ for the functionalisation of alkanes in the presence of ultraviolet irradiation. Examples include the insertion of carbon monoxide, isocyanides and alkynes into alkanes and dehydrogenation reactions in which alkenes, biaryls, silanes and alcohols may be formed. R. G. Bergman describes systems based on $[\text{C}_3\text{Me}_3\text{Rh}(\text{PMe}_3)_2\text{H}_2]$ and the corresponding rhodium compound which activate carbon-hydrogen bonds in cycloalkanes to give R-M-H. Subsequent functionalisation of the alkane has proved difficult because all hydrocarbon solvents are reactive. Systems incorporating indenyl instead of C_3Me_3 and liquid xenon or krypton as solvents are showing more promise.

Carbonylation and synthesis gas conversion provide the largest topic in this book where thirteen chapters are devoted to it. J. F. Knifton and J. J. Lin describe the industrial applications of amidocarbonylations using cobalt/rhodium catalysts including the preparation of surface active agents, speciality surfactants, intermediates for artificial sweeteners, food additives and chelating agents. F. Petit and A. Mortreux discuss the merits of electrochemistry as a means of synthesis of catalytic moieties, in particular the platinum catalysed hydroformylation of alkenes.

The use of this technique can result in obtaining specifically different oxidation states and as there are no chemical reagents present in excess, side reactions involving them are minimised. The rhodium-diphosphine catalysed reductive carbonylation of methanol is described by R. W. Wegman and K. G. Moloy where these systems give comparable rates and selectivity to the best cobalt systems, albeit at significantly lower temperatures and pressures. Moreover the addition of ruthenium results in *in situ* hydrogenation and the formation of ethanol. G. G. Stanley and S. A. Laneman demonstrate that homobimetallic rhodium catalysts incorporating an electron rich binucleating tetrateritary phosphine ligand (eLTTP) are surprisingly active and selective hydroformylation catalysts, unlike the mononuclear analogues with basic phosphines, and this behaviour is rationalised in terms of an intramolecular hydride transfer which facilitates the removal of the product aldehyde. Platinum complexes incorporating phosphinite ligands are shown by P. W. N. M. van Leeuwen and C. F. Roobeek to be moderately active hydroformylation catalysts, giving high product aldehyde linearities for both terminal and internal alkenes and modest quantities of byproduct alkanes.

J. R. Zoeller and colleagues describe the rhodium catalysed carbonylation of methylacetate to give acetic anhydride, which has been operated by Eastman Kodak since 1983. Other papers on carbonylation include one from B. B. Wayland and coworkers on the use of rhodium (II) porphyrin radicals to activate carbon monoxide; the hydroformylation of allylamides by rhodium complexes by I. Ojima and coworkers; the effect of heterogeneous oxides on ruthenium catalysed hydrocarbonylation (G. Braca and coworkers); electronic effects of phosphines on the activity and selectivity of rhodium hydroformylation catalysts by D. E. Hendrikson and coworkers, and the influence of organophosphines on alkenes which are hydroformylated by anionic ruthenium clusters by G. Süss-Fink.

The section on general functionalisation includes contributions by J. A. Marsella on selectivity control in the amination of ethylene gly-

col using ruthenium catalysts where amine alcohols and diamines can be formed in high yields and by M. P. Doyle on catalytic intramolecular insertion reactions of diazocompounds. In the latter case selectivities can be enhanced by the use of rhodium (II) carboxamide compounds and these systems offer significant potential for highly enantioselective catalysis. B. M. Trost describes the successful use of palladium catalysts to form carbon ring systems where the use of a polymer supported catalyst can avoid problems of high dilution in the synthesis of 10–27 carbon membered ring systems, and new strategies using terminal alkynes as donors and acetylenes or allenes as receptors in condensation or cycloaddition reactions have permitted the synthesis of antibiotics and polyene macrolides. The theme of allyl palladium compounds is continued by P. B. Mackenzie and coworkers in discussing high velocity palladium compounds and C. P. Kubiak and J. Ni describe the stoichiometric deoxygenation of phenols by carbon monoxide using $[\text{Pt}(\text{dppe})_2(\text{OR})_2]$. L. N. Lewis, N. Lewis and R. J. Uriarte review platinum catalysed hydrosilylation and provide evidence that the catalysts are not homogeneous but in a more reduced form than the precursor.

Model systems for various carbon-carbon coupling are described by P. M. Maitlis and coworkers in the section on oligomerisation and polymerisation. These are based on labelling studies on the thermal or oxidative decomposition of $[\text{C}_5\text{Me}_5\text{Rh}(\mu\text{-CH}_2\text{R})_2]$ and $[\text{C}_5\text{Me}_5\text{Rh}(\mu\text{-CH}_2)_2\text{R}(\text{L})]$. A new mechanism for promoted Fischer-Tropsch is proposed in which the chain carriers are alkenyl rather than alkyl groups.

This book is clearly organised with good illustrations. It includes original research from many workers at the forefront of their field. Refreshingly, over a quarter of the contributions are from industrialists. The topic of hydrogenation is not dominant and this is probably a reflection that the formation of functional groups is of more relevance to the chemist. Homogeneous catalysis will be of increasing importance and platinum group chemicals will continue to play a prominent role. M.J.H.R.