

Catalysis by Metal Complexes

Homogeneous Catalysis with Compounds of Rhodium and Iridium

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Rhodium, and to a lesser extent iridium, systems are particularly effective at fulfilling the necessary requirements for homogeneous catalysis; reactions such as co-ordinative addition, oxidative addition, reductive elimination and cis-migration all take place readily at these metal centres. Although these metals are intrinsically valuable, the high activity and specificity often obtained make them cost effective and attractive for use in a number of commercial syntheses. This monograph provides information useful to organic and organometallic preparative chemists in both industrial and academic research laboratories. Most of the reactions considered are homogeneous but the relationship of these to heterogeneous systems supported on both inorganic and polymeric materials is also described.

The activation of C-H and C-C bonds, including both saturated and unsaturated systems, is described in detail, and this is followed by a chapter on the many hydrogenation reactions used to form C-H bonds. $\text{RhCl}(\text{PPh}_3)_3$, Wilkinson's catalyst, is probably the most extensively studied of all the known homogeneous hydrogenation systems and can be used at room temperature and atmospheric pressure. The rate of hydrogenation is increased by the presence of polar co-solvents, and the reaction often occurs with high stereoselectivity. Thus in the hydrogenation of steroids, selective reduction of the least hindered double bond in the presence of other double bonds can be achieved more cleanly than when using heterogeneous catalysts.

Asymmetric homogeneous hydrogenation has been achieved using chiral rhodium complexes as catalysts. A synthesis of L-dopa (3,4-dihydroxyphenylalanine), which is used for treating Parkinson's disease, has been developed by Monsanto. Up to 90 per cent optical purity has been achieved in this synthesis using a rhodium catalyst. Many soluble

rhodium and iridium species also catalyse the hydrosilylation reaction, and the asymmetric reduction of prochiral ketones can be achieved via hydrosilylation in the presence of prochiral rhodium complexes.

In the chapter on carbonylation and hydroformylation, there is discussion of the many reactions catalysed by soluble and supported rhodium and iridium species. These include the water-gas shift reaction, the hydrogenation of carbon monoxide, and the catalytic reduction of nitric oxide by carbon monoxide, as well as the large variety of methods available for incorporating carbon monoxide into organic molecules via carbonylation or hydroformylation. Some of these reactions have already achieved considerable commercial significance, notably the hydroformylation of propylene (Johnson Matthey/Davy McKee/Union Carbide), and the carbonylation of methanol (Monsanto). Both of these reactions achieve high selectivities for the desired products, n-butyraldehyde and acetic acid, respectively. However, the most significant application of all for rhodium catalysts is their use to control emissions of nitrogen oxides from car exhausts. Mixtures of platinum metals adsorbed on ceramic supports, either monoliths or pellets, are used and one function of the rhodium is to catalyse the decomposition of nitric oxide. The high pressure reaction between hydrogen and carbon monoxide to give ethylene glycol and methanol is promoted by soluble rhodium carbonyl catalysts.

The book thus provides a very readable and useful review of the present state of knowledge on catalysis involving rhodium and iridium species. Literature up to 1982 is comprehensively covered and very clear mechanistic schemes are provided, while in addition a helpful tabulation of homogeneous catalysts and their applications is presented as an Appendix.

D.T.T.