Palladium Catalysts in Organic Synthesis

Palladium Reagents and Catalysts – Innovations in Organic Synthesis
BY JIRO TSUJI, John Wiley & Sons, Chichester, 1995, 574 pages, ISBN 0-471-95483-7, £125.00

The main catalysts which are traditionally used for the hydrogenation of organic compounds are supported platinum group metals, and while these heterogeneous catalysts are generally not effective in carbon-carbon bond forming reactions, there has been a growing interest in recent years in soluble complexes of the platinum group metals for use as catalysts in organic synthesis. Rhodium catalysed alkene hydroformylation and carbonylation of methanol to acetic acid are two particularly notable industrial successes in this area, and there have also been many dramatic advances in laboratory-scale carbon-carbon bond forming reactions.

A tremendous amount of research has shown that palladium is one of the most versatile centres in this context, and many otherwise difficult-to-achieve organic transformations can be accomplished in convenient practical procedures, when mediated by soluble palladium species. This is illustrated by two important reaction types: coupling processes – of the kinds developed by R. F. Heck and reviewed in his book "Palladium Reagents in Organic Synthesis", Academic Press, 1985; and direct incorporation of carbon monoxide into certain organic compounds to give a variety of carbonyl derivatives (aldehydes, carboxylic acids, amides, esters, etc.) – often under conditions as mild as room temperature and atmospheric pressure, which palladium compounds have the ability to promote. A book on these reactions by the present reviewer and his colleagues appeared more recently ("Carbonylation – Direct Synthesis of Carbonyl Compounds", by H. M. Colquhoun, D. J. Thompson and M. V. Twigg, Plenum Press, 1991 (1)).

The present book is to be welcomed, since it not only gives an update of progress in the two areas mentioned, but also embraces the entire field of palladium reagents and catalysts in organic synthesis. In his authoritative book Professor Tsuji provides more than 2400 original literature references, as well as information about relevant monographs and other texts. It comprises three short and two long chapters. The first chapter, of only ten pages, describes characteristic features of palladium catalysed reactions, and fundamental concepts in palladium organometallic chemistry. The second, even shorter, chapter (six pages) describes how reactions are classified in the book, while the third chapter, of over one hundred pages, deals with oxidation reactions involving palladium(II), such as Wacker chemistry (alkenes to aldehydes, etc.). The fourth chapter is very long, some four hundred pages, and is concerned with carbon-carbon bond forming reactions. The fifth and final chapter, of twenty pages, brings together various catalysed reactions, which have unclear mechanisms, or which, for other reasons, do not fit into any of the categories of the two main chapters.

The index is useful, although not exhaustive. References are collected at the end of chapters and also at the end of some main sections in the largest chapter; this could cause confusion for readers wishing to pursue the original papers. The two other previously mentioned books give practical details for those wanting to make use of palladium-based procedures in their own work. In contrast, the present book does not provide such information, but as the discussion is detailed, and there are copious references, there should be no major problems translating theory into practical applications.

As suggested by the layout of the chapters, material is organised according to the involvement of the metal, while in the two main chapters it is organised according to the organic transformations. This could make it rather difficult for a reader who wants to establish how palladium catalysis might help with a particular transformation. However, by using the contents list and the index, specific information can be tracked down. Due to the wealth of information it contains, browsing through this book will always be a rewarding experience. It is nicely produced, and is an important addition to books about modern applications of palladium chemistry to organic synthesis. It is comprehensive in the literature coverage to early 1994, and it is recommended for purchase by research libraries associated with palladium chemistry or synthetic organic chemistry. M.V.T.

Reference

1 *Platinum Metals Rev.*, 1992, **36**, (1), 39

Platinum Complexes Used in DNA Binding Studies

DNA binding studies need unsaturated complexes with emissions sensitive to environmental changes to bind to DNA. Some ruthenium and platinum complexes have photoluminescence changes upon intercalation into calf-thymus (ct) DNA. Scientists at the University of Hong Kong, (H.-Q. Liu, T.-C. Cheung and C.-M. Che, *Chem. Commun.*, 1996, (9), 1039–1040) have now found two platinum complexes with dramatically enhanced photoluminescence on binding. $[Pt^{II}(dpp\text{-}C,N,N')(MeCN)]^+$ had a 271-fold increase in emission and $[Pt^{II}_2(pby\text{-}C,N,N')_2(\mu\text{-}dppm)]^{2+}$ had a 117-fold increase; dpp-*C,N,N'* = C-deprotonated 2,9-diphenyl-1,10-phenanthroline; pby-*C,N,N'* = C-deprotonated 6-phenyl-2,2′-bipyridine and dppm = diphenylphosphinomethane. This is attributed to intercalation into ct DNA, and may be used as luminescent switches for DNA.

Platinum 1996

For more than a decade Johnson Matthey has conducted an annual survey of commercial aspects of the platinum metals, and presented the findings in a comprehensive yet readable fifty-two page review.

The recently launched "Platinum 1996" records that during 1995 a recovery in South African production and increased Russian shipments lifted platinum supplies by 10 per cent to 4.98 million oz, while platinum demand improved by 5 per cent to a new peak of 4.79 million oz. Despite a fall of 20,000 oz, at 1.85 million oz autocatalyst manufacture still formed the major requirement for platinum, followed by jewellery with an increased demand of 1.81 million oz.

It is interesting to note that usage by the automotive industry is not confined to emission control catalyst manufacture. Platinum-tipped spark plugs continue to replace base metal plugs on new vehicles, the oxygen sensors used in engine management systems employ platinum, and the lightweight plastics increasingly used in body parts and engine components are reinforced with glass fibre formed using platinum bushings. In addition, the petroleum industry uses platinum catalysts in the production of gasoline and cleaner-burning diesel fuels, while for the future, proton exchange membrane fuel cells could be used to power zero emission vehicles.

During 1995 industrial demand for platinum increased by 21 per cent to 990,000 oz, the highest level for sixteen years. At the same time sales of palladium for electronics applications rose by 19 per cent to 2.65 million oz, while high demand from the chemical and glass industries boosted industrial off-take for rhodium by 12 per cent to 48,000 oz. Despite a 12 per cent increase in demand for ruthenium from the electronics industry, a decline in purchases by electrochemical companies contributed to an overall fall in demand of almost 5 per cent, compared with 1994. Iridium demand increased from 42,000 oz in 1994 to 52,000 oz in 1995; although the electrochemical sector accounts for about half of the demand for iridium, smaller applications including crucibles, biomedical and spark plug tips for aerospace applications all increased.

Readers of *Platinum Metals Review* who wish to have access to this authoritative source of information on the many factors that influence the supply and demand of the platinum metals are invited to direct their request for a free copy of "Platinum 1996" to the author: Alison Cowley, Johnson Matthey PLC, 78 Hatton Garden, London EC1N8JP, England; Fax: +44-171-269-8389.