

# Aspects of Co-ordination Chemistry

**Synthetic Coordination Chemistry: Principles and Practice**

BY J. A. DAVIES, C. M. HOCKENSMITH, V. YU. KUKUSHKIN AND YU. N. KUKUSHKIN,

World Scientific Publishing Co. Pte. Ltd., Singapore, 1996, 452 pages,

ISBN 981-02-2084-7, £77.00

This book comprehensively covers all aspects of synthetic co-ordination chemistry, drawing together the rich wealth of research undertaken, but little known, from the former Soviet Union, and work performed in the West. It contains several very interesting chapters covering the more esoteric synthetic procedures, which are not normally readily accessible from the chemical literature, but are of great value. For example, Chapters 8 and 9 describe non-traditional oxidants and reductants in preparative co-ordination chemistry and constitute a fascinating review of the diverse synthetic techniques employed to produce novel co-ordination compounds. With such a broad scope, the book will prove valuable to most synthetic co-ordination chemists and be particularly useful when the synthesis of a specific metal complex is required and existing preparative methods either prove inadequate, non cost-effective or perhaps even impossible for the project concerned. Probably the greatest strength of the book lies in its being a 'idea provider' for those working in research.

Theoretical considerations for the synthesis of co-ordination compounds are described in Chapter 1, and the platinum group metals, especially platinum, are extensively featured. Although the majority of the material is available in currently established texts, it nevertheless provides a very helpful summary and reminder of the theory behind co-ordination chemistry. The style of writing together with extra material and examples covered, make this chapter an interesting read and a very useful teaching aid.

The solubility of co-ordination compounds and the relationship of solubility to composition and structure are investigated in Chapter 2. This is an ambitious and helpful contribution to the book, as no rigorous theory exists of the solubility of chemical compounds. The addi-

tion of hydrophilic counterion effects for ionic complexes and macrocyclic compounds are all described. Tabulated data and examples are also provided by the Authors.

## Solvento-Complexes

Chapters 3 and 4 relate to the generation and subsequent use of solvento-complexes (a compound containing co-ordinated solvent molecules as well as other co-ordinated ligands) as starting materials for preparative co-ordination chemistry. Chapter 3 has an informative introduction on such complexes. Halide abstraction reactions of platinum complexes and the synthesis of homoleptic solvento-complexes of palladium, platinum and ruthenium are all described. The synthesis of bridged hetero- and homopolynuclear complexes of gold, indium and ruthenium are included. Chapter 4 features an extensive Table concerning the synthesis of a wide variety of solvento-complexes, which is well referenced and describes all the platinum group metals.

Methods available for ion exchange and their implications for synthetic co-ordination chemistry are outlined in Chapter 5. Palladium complexes containing 'non-co-ordinating' anions as ligands and the generation of platinum-main group metal bonds are discussed.

The synthesis of bridged complexes and ring closures is considered in Chapter 6. The principal methods centre around the removal of an anionic ligand from a metal cluster to fuse two unsaturated fragments. The chapter, although short, is interesting and is almost solely concerned with the platinum group metals, especially palladium and platinum.

An overview of the electrosynthesis of co-ordination compounds is provided in Chapter 7. While this topic has received a fair amount of attention previously, this Chapter, in contrast

to many other reviews, focuses on the use of electrosynthesis for preparative chemistry and is therefore very useful. The use of inert electrodes, as well as sacrificial anodes and cathodes is considered, as is the solvent employed. Electrochemical synthesis of platinum and ruthenium complexes are described.

### Novel Oxidants and Reductants

The use of non-traditional oxidising and reducing agents in synthetic co-ordination chemistry is described in Chapters 8 and 9. These two chapters constitute a significant proportion of the book and are fascinating to read. Although some of the reagents may be familiar to synthetic co-ordination chemists, many may not be, and the use of such reagents offers valuable possibilities for the synthesis of novel materials as well as facile synthesis of established metal complexes. Oxidising agents, such as aryl-diazonium salts, tropylium salts, metal salts, non-metal halides and aminoxides are all considered in detail. The modification of such reagents for utilisation in aqueous media is also described. An extensive collection of novel reducing agents is also provided. The range of unusual products obtained, described by the use of the reagents employed, make these chapters of interest both to academic and industrial chemists. This information is not readily available, except by a lengthy and detailed search of the chemical literature. While more metals

are considered here than in other chapters, the platinum group metals still receive much attention.

The use of boron and aluminium hydrides in preparative chemistry is reviewed in Chapter 10, while the book concludes with features on molecular rearrangements of co-ordination compounds (Chapter 11) and some interesting possibilities for the solid state thermal synthesis of co-ordination compounds (Chapter 12). Many of these reactions are concerned with the expulsion of water or hydrogen halide from metal complexes to produce new species. The platinum metals again feature extensively.

Overall, the book is a welcome addition to the chemical literature and has much to recommend it. The platinum group metals receive excellent and thorough consideration, with roughly over 50 per cent of the book concentrating on them, the remainder being principally concerned with the 3d transition metals. The style, clarity and readability of the book are excellent and the book is well referenced and has sensibly constructed indexes. Most of the chapters deal with interesting research matters informatively, which is particularly important since many of the topics covered in the book are not covered in existing texts. I, therefore, consider this book to be a useful purchase for anyone seeking novel synthetic methodologies for academic or industrial application and I recommend it highly.

S. M. GODFREY

## Monodispersed Nanostructured Ultrafine Platinum

Nanostructured metal particles with interesting properties due to their quantum size effects, and with uses as advanced materials, have mostly been studied as isolated particles; while platinum monolayers have been little examined because of the difficult preparation of monodispersed ultrafine platinum particles.

However, a method has now been developed to control the size of polymer-protected ultrafine platinum particles (T. Teranishi, M. Hosoe and M. Miyake, *Adv. Mater.*, 1997, 9, (1), 65–67). Ultrafine platinum particles, of different diameters, protected by poly(*N*-vinyl-2-pyrrolidone) (PVP), were prepared by heating  $H_2PtCl_6$  under reflux in aqueous alcohol with PVP, and varying the reaction conditions.

Higher alcohol concentrations gave smaller particles of narrower size distribution; particle size reduced as: methanol > ethanol > 1-propanol. Thus nucleation rate is the principal factor in determining particle size and distribution. Electrophoresis produced monolayers dependant on platinum concentrations, voltages and times.

### Industrial Platinum Metals Chemistry

Please note that the following change should be made in "Industrial Platinum Metals Chemistry Towards the Year 2000", which appeared in *Platinum Metals Rev.*, 1997, 41, (1) 8–11.

On page 10, in Figure 4, the molecule involved in the palladium-catalysed Heck reaction should have been dihydrofuran and not furan.