

Inorganic and Co-ordination Chemistry

Chemistry of Precious Metals

BY S. A. COTTON, Blackie Academic & Professional, London, 1997, 374 pages,
ISBN 0-7514-0413-6, £99.00

This book covers the fundamental chemistry of the six platinum metals as well as silver and gold. The binary chemistry of these elements and their fundamental co-ordination chemistry is thoroughly reviewed, and any trends in reactivity are highlighted. However, the organometallic chemistry receives less attention and is largely restricted to σ -bonded complexes.

I was particularly impressed by the large quantity of physical data supplied by the author concerning bond lengths and vibrational spectroscopy. Such data is of great value to lecturers and can be surprisingly hard to access, particularly in a concise, compiled form. The explanation of trends in such data, provided by the author, is also very welcome.

The book is aimed at post-graduate students seeking a thorough grounding in the chemistry of the platinum group metals, as well as lecturers who are required to teach either an introduction to the chemistry of these elements or more advanced courses, particularly any involving the co-ordination chemistry of the platinum group metals. I would again highlight the value of the tabulated physical data by the author for this purpose. Although the book is probably of less utility to researchers involved in specialised topics concerned with these elements, they may still find it of use as a reference text.

A consideration of the chemistries of ruthenium and osmium constitutes Chapter 1 and logically moves from discussing the metals themselves, through the halides (which are very well covered, including many structural illustrations) to the oxides, ending in an examination of the aqueous chemistry of these elements. The chapter then proceeds with a step-by-step documentation of the chemistry of the co-ordination chemistry of ruthenium, broken down into subsections by oxidation state. Osmium then receives the same coverage. The breadth of the material is certainly impressive, with good use

of schematic reaction schemes to clarify the vast amount of study these elements have received. The frequent inclusion of structural illustrations throughout the chapter is very helpful, especially since important bond lengths and angles are included on the diagrams. The co-ordination chemistry of ruthenium and osmium in a variety of oxidation states is reviewed for complexes containing amine, tertiary phosphine, carboxylate, sulfide, sulfoxide, nitrosyl and EDTA donor ligands. Other topics investigated include complexes which contain polydentate ligands and porphyrin complexes. The simple aryl and alkyl species formed by the metals are also described.

Chapter 2 describes the chemistries of rhodium and iridium, both of which receive the same thorough coverage as ruthenium and osmium. The book continues with the same logical approach (beginning with binary chemistry and subsequently proceeding to co-ordination chemistry), maintaining an informative but very readable style. Good use is made of schematic reaction diagrams and I was particularly interested in the illustrated NMR diagrams which are very useful. Again the text is well supported by a variety of structural illustrations, all clearly labelled and discussed. Several molecular orbital (MO) schemes are included in the chapter and provide interesting theoretical support to some of the experimental observations concerning the chemistry of these elements. As in Chapter 1, the co-ordination chemistry of rhodium and iridium with all the common donor ligands is included. Vaska's compound, $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$, receives special attention and this chapter contains an impressive review of addition complexes, both 5- and 6-co-ordinate. Tabulated infrared data and important bond lengths are also described and discussed, as is the mechanism of addition to Vaska's compound. Additionally, dioxygen complexes of iridium are reviewed and

all such relevant compounds are tabulated, with the oxygen-oxygen bond lengths being quoted. A very informative and detailed section on complexes of these metals containing the ligand dimethylphenyl-phosphine is included in this chapter. Aspects of isomerism and variations in geometry and structure are critically discussed, with particular reference to NMR data. All reported crystal structures of such complexes are included. The last section of this chapter examines the simple σ -bonded alkyl and aryl compounds of rhodium and iridium.

Chapter 3 continues in the same concise style, reviewing the chemistries of palladium and platinum. Considering the huge amount of research material available on these metals, Dr Cotton is to be congratulated on producing a thorough, concise and readable review which discusses all the known complexes with common donor ligands. Again, excellent use of physical data provides the reader with all the information required for a detailed understanding of the chemistry involved. A very good section describes the *trans*-effect, related to rates of reaction of various metal complexes. Theoretical explanation of the *trans*-effect (and *trans*-influence) is also included and critically reviewed. A series of Tables show spectroscopic evidence for the *trans*-influence and helps to illustrate the importance of this effect to the reader. The concluding section in this

chapter concerns the anti-tumour activity of certain platinum complexes. This section is both interesting and informative, describing the complexes which exhibit anti-tumour properties and discussing their utilisation and toxicity. A section on how Cisplatin works (that is how it forms an adduct with DNA) is also of great value.

The concluding chapter concerns the chemistry of silver and gold. While this chapter (which constitutes just under a quarter of the book) was just as interesting and valuable as the preceding chapters, it is not reviewed here.

In conclusion, although I am well acquainted with review articles written by this author (which are always of a high standard), Dr Cotton is to be particularly congratulated on writing an excellent readable text, which contains a large quantity of valuable physical data. I would highly recommend this book to those requiring a sound knowledge of the binary and co-ordination chemistry of these elements. Anyone involved in teaching this chemistry should also seriously consider purchasing the book. This book will additionally serve as a very useful reference text for researchers concerned with any aspect of the co-ordination chemistry of the precious metals and I would recommend that research supervisors involved with the precious metals make this book available to their research students.

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Highly Active and Enantioselective Rhodium Catalyst

The development of platinum group metals complexes with chiral ligands, and their potential uses have been discussed here recently, with enantioselective catalysis being singled out (1). Adding chiral bisphosphine ligands – BINAP being one of the best known – to catalysts has provided a range of enantioselective catalysts capable of a variety of asymmetric transformations.

Now, scientists at the Merck Research Laboratories in New Jersey have used the planar chiral bisphosphine ligand, [2.2]PHANEPHOS, (4,12-bis(diphenylphosphino)-[2.2]-paracyclophane) with the rhodium complex, bis(1,5-cyclooctadiene)rhodium(I) triflate to produce an active and highly enantioselective catalyst, [[2.2]-PHANEPHOS Rh]⁺OTf⁻ which can hydrogenate dehydroamino acid methyl esters under very mild conditions (2). Formation of the catalyst before

substrate addition enabled complete conversions to be achieved in under 60 minutes, by bubbling hydrogen through the reaction mixture, at temperatures as low as -45°C.

Further activity of this catalyst was demonstrated by its reduction of tetrahydropyrazine to produce the HIV protease inhibitor Crixivan intermediate precursor, at -40°C and 1.5 bar in 6 hours with 100 per cent conversion and 86 per cent ee. Until now this reduction had incomplete conversions, with only moderate enantioselectivity, and thus required forcing conditions.

References

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