

Applications of Coordination Complexes

COMPREHENSIVE COORDINATION CHEMISTRY II. FROM BIOLOGY TO NANOTECHNOLOGY

Volume 9 APPLICATIONS OF COORDINATION CHEMISTRY

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This 9th volume in the set of books: "Comprehensive Coordination Chemistry II", covers applications of coordination chemistry and has an ambitious remit: to survey the developments in the applications of coordination chemistry since 1982. It follows on from the review of Volume 6, published in our April issue (1).

Coordination Complexes as Catalysts

The first half of the book focuses on the use of coordination complexes as catalysts for a diverse range of organic reactions. Chapters on supported metal complexes and combinatorial catalysis are also included in this half of the book.

Chapter 1, covering catalysts for polymerisation, is not an area where platinum group metal (pgm) complexes would be expected to dominate. There is, however, an interesting section on the re-emergence of Ru initiators for polymerisation. The use of Ru complexes (some now commercially available) for ring opening metathesis polymerisation (ROMP) of cyclic alkenes is discussed.

Chapter 2 by C. Pettinari, F. Marchetti and D. Martini covers metal complexes as hydrogenation catalysts with, naturally, a heavy emphasis on enantioselective reactions. I liked this chapter with its focus on mechanism and careful choice of example to demonstrate each point. Work which has become of industrial importance is covered together with proper discussion of Noyori's ground breaking design and synthesis of RuCl₂(diphosphine)(1,2-diamine) catalysts. The second half of the chapter concentrates on new developments and covers hydrogenation and enantioselective hydrogenation in aqueous systems and in supercritical CO₂, and biphasic catalysis amongst other topics. Additionally hydrogenation by Os and Ru cluster complexes is also discussed.

Metal complexes as catalysts for the addition of carbon monoxide is the focus of Chapter 3. This is

obviously a huge area and the authors (P. W. N. M. van Leeuwen and C. Claver) have concentrated on work which explicitly uses coordination complexes rather than materials prepared *in situ*. Additionally they cite a large number of review articles. The chapter begins by discussing the BP Cativa™ process (2) where Ir has found advantage over Rh for the carbonylation of methanol. A large section on hydroformylation covers Pt^{II}SnCl₂/phosphines as well as the extensive Rh chemistry dominated by phosphine or phosphite ligand systems. Drent's work with Pd is also included. Asymmetric hydroformylation with these types of systems is dealt with in separate sections. The development of thermoplastics has required the copolymerisation of alkenes and carbon monoxide; and the use of Pd complexes with chelating bidentate phosphine ligands, amongst others, is surveyed. The chapter concludes with sections on reductive carbonylation of nitro groups and the use of Pd complexes for hydroxy- and methoxycarbonylation.

In Chapter 4, T. Katsuki discusses metal complexes as catalysts for oxygen-, nitrogen- and carbon-atom transfer to alkenes. Ru metalloporphyrin and metallocene complexes feature as catalysts for chiral epoxidation and mention is made of work where molecular oxygen is the oxidant. Ru^{II} salen complexes have been found to be efficient catalysts for aziridination. Os chemistry dominates the section on dihydroxylation. In particular complexes with diamine and bis-cinchona ligands have excellent enantioselectivity. The Sharpless and Carey mechanistic models are thoroughly covered. There is a large section on the use of Rh and Ru catalysts for inter- and intramolecular cyclopropanation.

The addition of H-X (X = B, CN, Si, N and P) to carbon-carbon multiple bonds is reviewed by M. K. Whittlesey in Chapter 5. The comprehensive section on hydroboration covers a lot of work with

Rh catalysts – largely with phosphine ligands. Pd catalysts find favour for the addition of HB to alkynes and enynes. The section on hydrosilylation covers both Rh and Pt with a variety of chiral ligands and Pd with ferrocenyl phosphine ligands for the hydrosilylation of styrene. Rh and Ir are largely used for hydroamination, with some Pd phosphine systems suitable for activated alkenes.

Chapter 6 (metal complexes as catalysts for C-C cross-coupling reactions) by I. P. Beletskaya and A. V. Cheprakov, is possibly the best of all; a good introduction describes the various methods of cross-coupling. It is clearly laid out with discussion on leaving groups, activation of reagents and catalysts. There is a pleasing emphasis on the rationale behind the design of catalysts. Most of the work focuses on Pd although Ni is not neglected.

In Chapter 7, J. F. Hartwig describes metal complexes as catalysts for carbon heteroatom cross-coupling reactions, and not surprisingly reveals a huge emphasis on Pd in every type of reaction. The majority of the reactions discussed are aminations, but C-O, C-S, C-P and C-Se reactions are also included. The discussion of reaction intermediates at the end of the chapter is particularly interesting and it was a shame that more detailed discussions on individual reactions is beyond the scope of the chapter.

S. Kobayashi, Y. Mori and Y. Yamashita in Chapter 8 cover the use of metal complexes as Lewis acid catalysts in organic synthesis. In general, pgm coordination complexes do not play an important role in this area. However, it was interesting to learn that a Ag^+BINAP complex has been found to activate aldehydes and imines effectively allowing asymmetric allylations, aldol reactions and Mannich-type reactions to proceed in high yield with high selectivity. Additionally both Ag(I) and Au (I) ferrocenylphosphine complexes promote asymmetric aldol reactions of α -isocyanocarboxylates to form chiral oxazolines.

Although some of the preceding chapters briefly mention immobilisation, Chapter 9 by F. Quignard and A. Choplin reviews supported metal complexes. Most of the supports covered are conventional but new advances including dendrimers and meso-structured materials are mentioned. I

felt that the newer approaches could have been covered in a little more detail but I liked the conclusion and perspective section at the end of the chapter.

In Chapter 10, entitled ‘Electrochemical Reactions Catalyzed by Transition Metal Complexes’, A. Deronzier and J.-C. Moutet review 20 years of literature of mainly electroreduction reactions with target molecules such as CO_2 , organic halides and oxides of nitrogen. Surprisingly, given the importance of electroreduction to, for example, fuel cells, the description of the catalysis of oxygen reduction using coordination compounds is comparatively brief. Rh complexes, especially with P-containing ligand systems, are popular choices for reduction reactions, including hydride transfer in, for example, NADH catalysis. Ru complexes appear to be better suited for heavy-duty oxidation work such as oxygen evolution.

Chapter 11 by M. T. Reetz, discusses combinatorial methods in catalysis by metal complexes. Methods of catalyst screening are discussed with the calorimetric assay developed to screen the hydroamination of 1,3-dienes by various phosphines with Pd, Rh, Ir, Ni and Ru precursors being one of the examples. Capillary electrophoresis is also mentioned with the optimisation of the Pd-catalysed annulation reaction of an indole derivative as a prime example. The evaluation of Pd 1,2-diimine complexes for ethylene polymerisation by a combinatorial approach is also included. The bulk of this chapter focuses on the use of combinatorial methods for enantioselective processes and reviews new methods for high throughput ee-assays as well as the modular synthesis of chiral ligands. This is an excellent résumé of an exciting field of work.

Optical Properties of Coordination Compounds

Five chapters (Chapters 12 to 16) deal with optical properties of coordination compounds as a central theme, and the predominance of Ru-N ligand species as systems for academic study will come as no surprise. The sweep of the field is vast, both in terms of the science and the history, and

the reader does get a *comprehensive* review of the literature. However, in Chapter 12, by P. Gregory, on metal complexes as speciality dyes and pigments, pgms feature very little: most of the metal complexes described are from the early transition elements. Nevertheless, the history of dyes and pigments is well accounted for. Key advances through the ages include the discovery of mordanting (typically using alum) and the synthesis of artificial dyes, which paved the way for the modern colours and coatings industry. Increasingly, coordination compounds are being used to provide functionality, as well as decorative effect in coatings and surface finishes. The role of metal complexes in photography, electrophotography and ink-jet printing are concisely described.

The pgms reappear in Chapter 13 (R. J. Mortimer and N. M. Rowley) entitled 'Metal complexes as dyes for optical data storage and electrochromic materials'. In contrast to the technology described in the previous chapter, electrochromic devices have yet to achieve widespread application, mainly due to poor durability and slow response times. The lack of stability is initially surprising given that the ubiquitous phthalocyanine, porphyrin and polypyridyl complexes of transition metals, which confer such stability in other applications, fail to do so here, until one considers the stresses and strains induced in thin films by rapid ion movement. Optical data storage on the other hand, has flourished despite many practical constraints. Here the phthalocyanines have reigned supreme although azo-type dyes are presently the system of choice for DVDs.

In Chapter 14 entitled 'Nonlinear optical properties of metal complexes' by B. J. Coe, the investigation of molecular complexes exhibiting both quadratic and cubic (non-linear) optical (NLO) responses is described. The list of candidate ligand systems again includes phthalocyanines, porphyrins, and polypyridyl complexes, as well as a diverse range of less-common conjugated ligands. The importance of inter-system-crossing (ISC) of spin-states in NLO means that complexes with heavy metal ions such as Pt, Os, Ir and Ru, are popular choices for many of these studies.

Many of the precursors of inorganic phosphors

are coordination compounds, as described by J. Silver in Chapter 15, 'Metal compounds as phosphors'. Phosphor materials usually rely heavily on Group 10 and the rare earths for the key properties required. However, the ISC properties of complexes with the pgms are usefully applied in several types of organo-electroluminescent devices described in this Chapter.

In Chapter 16, by Md. K. Nazeeruddin and M. Grätzel, the conversion and storage of solar energy using dye-sensitised nanocrystalline TiO₂ cells is discussed. Since the pioneering work of Grätzel some 15 years ago, Ru-based polypyridyl ligands have remained the first choice due in part to good absorption characteristics and remarkably efficient charge injection (into the inorganic semiconductor). Although other metal-based dye systems are also active, the stability of the Ru (and also Os) complexes is a major advantage in their use. More recently, advantage has been taken of the axial coordination sites on the Ru ion to fine-tune the molecular environment of the charge injection site for both solar cell and photoelectrocatalysis applications.

Hydrometallurgy and Extraction

Chapter 17 relates to 'Metal complexes in hydrometallurgy and extraction', especially, mineral processing, leaching, separation and concentration. This covers both base metals and precious metals: Pt(IV), Pt(II), Pd(II), Au(I), Au(III), and Ag(I).

Coordination Compounds for Medicine and Biology

The interaction of transition metal ions with biological molecules provides one of the most fascinating areas of coordination chemistry. The application of this field to biomedical uses is dealt with in 5 chapters. Chapter 18 by N. Farrell, deals with the use of metal complexes as drugs and chemotherapeutic agents. Farrell concentrates on Pt anticancer drugs and, in particular, the differing interactions of mono-, di- and trinuclear complexes with DNA and the differing antitumour effects this may produce. Chapter 19, by É. Tóth, L. Helm and A. E. Merbach, describes the application of transition metal ions and in particular

Gd(III) as MRI contrast agents. The spectacular growth in use of MRI as a diagnostic tool would not have occurred without the use of contrast agents. Radioactive nuclei, for example, Rh, described in Chapter 20, by S. Z. Lever, J. D. Lydon, C. S. Cutler and S. S. Jurisson, have been a vital part of medicine for a much longer period but developments are still being made through coordination chemistry in modifying the distribution of the elements. Chapter 21, by S. Faulkner and J. L. Matthews, describes the use of fluorescent compounds in diagnosis. A different method of cancer treatment is discussed in Chapter 22 on Ru, Pd and Pt complexes for photodynamic therapy. This area is dominated by porphyrin complexes.

Conclusions

In summary this book certainly is a comprehensive overview of the applications of coordination chemistry, and in particular the use of pgms in catalysis, in dyes for optical applications,

and in medicinal and biomedical applications. It is an informative read and the individual chapters offer good introductions to the various areas.

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References

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The Reviewers

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Sonochemical Asymmetric Hydrogenation with Palladium

Enantioselective hydrogenation is one of the most versatile methods of asymmetric synthesis, with heterogeneous catalysis, using chiral modifiers, rapidly becoming an alternative to the “traditional” homogeneous methods. The role of modifiers in asymmetric hydrogenations is to enhance catalysis, with the bonding mode and geometry of adsorption being important, as well as the modifier concentration and the type and position of the substituent groups in the aromatic ring.

Ultrasonic irradiation (sonication) is known to be beneficial in catalytic asymmetric hydrogenations. Sonication removes catalyst surface impurities, and gives enhanced adsorption to the chiral modifiers.

Now a team from Michigan Technological University, Houghton, U.S.A. (S. C. Mhadgut, I. Bucsi, M. Török and B. Török, *Chem. Commun.*, 2004, (8), 984–985; DOI: 10.1039/b315244h) has revisited the Pd-catalysed, proline-modified, asymmetric hydrogenation of isophorone (3,3,5-trimethyl-2-cyclohexen-1-one (with a C=C bond)). They examined the catalyst, the modifier and the effects of sonication.

Pd/Al₂O₃ was found to give a better, though low, enantiomeric excess (ee) than Pd/C. Proline

and its derivatives (isomeric hydroxyl-prolines, prolinols and proline esters) were tested as chiral modifiers for Pd/Al₂O₃. Proline was the best modifier, and both enantiomers gave ee ≤ 35%.

Presonication was found to enhance the enantioselectivity when both the Pd/Al₂O₃ catalyst and the proline modifier were present. “Modifier-free” presonication and the presence of substrate during pretreatment decreased the enantioselectivity.

The reaction was performed at 50 bar pressure and 25°C. Presonication for 20 minutes gave the highest optical yields, and increased optical yields across all the H₂ pressure range. Maximum ee occurred at a 1:2 isophorone:proline ratio, and with optimised conditions and presonication, the ee for the Pd/Al₂O₃-(S)-proline catalytic system was ≤ 85%.

Ultrasonic cleaning of the catalyst enhanced both the adsorption of the modifier and the modifier-induced surface restructuring of the Pd. The high ee was due to proline adsorption on the Pd surface. New catalysts that can strongly adsorb proline could thus become important in heterogeneous catalysis for C=C double bond hydrogenation of α,β -unsaturated carbonyl compounds.