

## Book reviews

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### Modern amination methods

Alfredo Ricci (ed.)

Wiley-VCH, Weinheim, 2000

xvii + 267 pages. £75 (hardcover)

ISBN 3-527-29976-9

This book aims to provide an overview of a number of areas of research where amination methods play an important role, covering some of the more recent methods used to construct C—N bonds. With the current impetus to prepare enantioomerically pure compounds there is a significant emphasis on asymmetric approaches, making this a very useful read.

Internationally recognized experts in their particular fields have provided contributions. The book is presented in seven chapters, starting with modern allylic amination methods (K. A. Jørgensen). This initially considers the use of the allylic C—X functionality, and then covers enantioselective reactions, but moves on to review the formation of allyl amines using alkenes possessing allylic C—H bonds, a comparatively new field. Chapter 2 describes electrophilic amination routes from alkenes and their potential (E. Fernandez and J. M. Brown) and progress on the indirect amination of organometallic species. An overview of the stereoselective electrophilic amination of chiral carbon nucleophiles to construct  $\alpha$ - and  $\beta$ -amino acids is then discussed in Chapter 3 (J.-P. Genet, C. Greck and D. Lavergne) covering the literature up to 1998. Syntheses of the same synthetic targets in high optical purity are then described in Chapter 4 (H. Kunz, H. Tietgen and M. Schultz-Kukula) but using a carbohydrate-derived prochiral imine strategy. The synthesis of metal hydride complexes is covered in Chapter 5 (E. Carreira, C. S. Tomooka and H. Iikura), and Chapter 6 (M. Komatsu and S. Minakata) reviews the transfer of a nitrogen atom from a nitrido complex with applications in enantioselective aziridation reactions. Finally, the use of the palladium-catalysed amination of aryl halides is reviewed (J. F. Hartwig), highlighting catalyst design and the remaining challenges to chemists working in this area.

Overall, the work is well presented and comprehensively referenced and gives the reader a large variety of stoichiometric and catalytic synthetic strategies that could be considered. There is a significant amount of published material on amination methods, and bringing recent C—N construction strategies together within this work is extremely useful.

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### Rhodium catalyzed hydroformylation

P. W. N. M. van Leeuwen and C. Claver (eds)

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xii + 286 pages. £78

ISBN 0-7923-6551-8

This book is the latest (volume 22) in the well-known series, *Catalysis by Metal Complexes*, published by Kluwer, and maintains the standards set in previous volumes. *Rhodium Catalyzed Hydroformylation* covers the principal developments during the last decade in this specific aspect of the broader topic of hydroformylation. It is written by authors who are authorities in different aspects of the field and the subject matter is presented in ten chapters. After a brief introductory chapter, the coverage can be summarized under three main themes: the basic background chemistry associated with the use of unmodified rhodium, phosphite and (mono- and di-) phosphine-containing rhodium catalysts (Chapters 2–4); specific applications of hydroformylation in both asymmetric and general organic synthesis, and the use of aqueous biphasic media (Chapters 5–7); and process aspects and catalyst preparation/decomposition (Chapters 8 and 9). A concluding chapter provides a perspective towards the future by a consideration of recent developments relevant to hydroformylation.

A somewhat disappointing feature of the background chemistry described in Chapters 2–4 concerns the fact that no attempt has been made to provide a general perspective on the impact of rhodium catalysts on hydroformylation processing. Notwithstanding the extensive developments in rhodium catalysis, it is a sobering fact that, in the hydroformylation of olefins of chain length higher than C<sub>3</sub> to aldehyde/alcohol products, for applications as commodity solvents, plasticizers and detergents, cobalt-based processes currently outnumber their rhodium counterparts by a factor of *ca* 9:1. There are a number of features common to both cobalt and rhodium hydroformylation catalysts that could have been addressed to advantage, particularly those relating to the discussion of kinetics and mechanism. These include both the role of phosphorus-containing ligands as selective poisons of catalytic activity (whilst enhancing selectivity to the desired straight-chain products) and the competition between acyl hydrogenolysis *versus* insertion of alkene into M—H bonds as 'rate-determining' steps under industrial operating conditions. The latter are highly dependent upon such factors as the nature of the olefin, the presence of phosphorus-containing modifiers, and overall reaction conditions. With cobalt catalysts a broad rationalization is as follows. Acyl hydrogenolysis is only rate determining in the

hydroformylation of simple terminal olefins with unmodified catalysts; alkene addition to the metal hydride ' $\text{HCo}(\text{CO})_2\text{L}$ ' is rate determining when more sterically hindered internal/branched olefins are used as substrates ( $\text{L} = \text{CO}$ ), and with all alkenes when  $\text{L}$  is phosphine or phosphite.

Although Chapter 5 is entitled 'Asymmetric Hydroformylation', the coverage is limited to vinylaromatic substrates, principally styrene. Some of the general problems inherent in this area are outlined in detail, together with a discussion of chiral bidentate phosphine- and phosphite-modified rhodium catalysts that exhibit high enantiomeric excesses in such transformations. The section on uses of rhodium-catalyzed hydroformylation in organic synthesis (Chapter 6) covers a broader perspective; a particularly useful aspect, for the synthetic organic chemist, concerns consecutive processes that may proceed under hydroformylation reaction conditions. These include acetalization, amination, hydroamination, aldol and Wittig reaction chemistry. Aqueous biphasic hydroformylation (Chapter 7) has been topical for the past 20 years since its commercial application in the hydroformylation of propylene to *n*-butyraldehyde. In spite of intensive research effort, however, it has not proved to be generally applicable to higher olefins because of sluggish reaction rates arising from their limited solubility in the aqueous phase. The discussions of process and catalyst preparation/decomposition aspects (Chapters 8 and 9) are welcome inclusions (frequently omitted in other texts), which are of particular importance to industrial chemists and chemical engineers. These topics represent essential reading for any chemist embarking on research involving catalysis

by rhodium complexes, and particularly so in the case of hydroformylation. Chapter 10 provides a view of future options, with particular emphasis on the bane of the lives of the practitioners of homogeneous catalysis, namely catalyst separation. New(ish) developments include micellar catalysis, supported aqueous-phase catalysis, supercritical fluids, fluorous biphasic catalysis, and dendrimer-supported catalysts; only time will tell if any of these can ultimately provide realistic and cost-effective options in hydroformylation processing.

Overall, this work is certainly timely, and it complements rather than duplicates other recent detailed treatments of aspects of hydroformylation (e.g. Cornils and Herrmann, Beller and Bolm). The subject matter has been researched thoroughly and the book is well written. However, some duplication of coverage is evident, and there are a number of typographical errors, possibly the consequence of both the writing and production 'taking only a few months'. As I have commented previously, in monographs of this type the index should be considerably more comprehensive. The above reservations apart, however, the book provides a very good perspective on recent developments in rhodium-catalyzed hydroformylation and should appeal to a wide readership, including both synthetic organic and organometallic chemists, together with chemists and chemical engineers in both academic and industrial environments.

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