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## Book Review

***Transition Metals for Organic Synthesis, volumes 1 and 2, Building Blocks and Fine Chemicals, Edited by M. Beller, C. Bolm, Wiley-VCH, Weinheim, 1998, pp. 1066. DM 798 (hbk), ISBN-3-521-29501-1***

More than 100 authors (about one third from Germany) from 15 countries have contributed to this 1066 page, two-volume publication. Many of the chapters are from practitioners in the field and the stated aim of the editors is 'to provide the reader with the basic possibilities of organometallic chemistry for organic synthesis', to justify their claim that 'really new discoveries' will result from this rapidly developing area. This book comes hard on the heels of the similarly priced, excellent two-volume 'Applied Homogeneous Catalysis with Organometallic Compounds: A Comprehensive Handbook' edited by B. Cornils and W.A. Herrmann, (1996) from the same publishers and inevitably there are several areas of overlap. Likewise, the Wiley publication 'Palladium Reagents and Catalysts, Innovations in Organic Synthesis' by J. Tsuji (1996) gives a much more in-depth account of organopalladium chemistry than is attempted in the present publication.

A comprehensive coverage of the vast area of endeavour suggested by the title 'Transition Metals for Organic Synthesis' is clearly out of the question, but the editors, Beller and Bolm, have selected what they feel are the most important transition-metal-catalysed (or -mediated) reactions and the resulting contributions cover the literature up to 1997. The organisation of the book into two volumes enables Volume 1 to deal largely with methods of making carbon-carbon bonds, whereas Volume 2 concentrates mainly on oxidation and reduction reactions but also briefly mentions some further specialised topics. The subject matter in the two volumes is dealt with by the individual authors in widely varying degrees of detail and it seems likely that the readership will dip into the book for the specific information they require rather than read it from cover to cover.

The general standard of production is very high, with clearly printed text, figures, tables and schemes. However, the use of multidigit section numbering occasionally gets out of hand. For example, in Chapter 2.13 of Volume 2 the introduction labelled 2.13.2. in the list of

contents has no subsequent entries although the text contains additional sections up to 2.13.2.5. etc. The use of the same numbering system for the chapters in both Volumes 1 and 2 also leads to unnecessary additional confusion.

The first chapter of Volume 1, entitled 'Basic aspects of organic synthesis with transition metals', is a personal view by one of the leading experts in the field (Trost), who sets out the ground-rules that are encountered throughout the two-volume series. This is an exemplary, albeit short, introduction which highlights the importance of chemoselectivity, regioselectivity, diastereoselectivity, enantioselectivity, and atom economy. The second introductory chapter (by Keim) succinctly summarises the concepts for the use of transition metals in the industrial syntheses of fine chemicals, touching on both economic and environmental concerns. The remainder of Volume 1 details the more specific transition-metal-catalysed (section 2) or metal-mediated (section 3) reactions as outlined below.

In section 2, Botteghi, Marchetti, and Paganelli discuss hydroformylation reactions, particularly in the context of synthesising pharmaceuticals, natural products and agrochemicals, while El Ali and Alper cover hydrocarboxylation and hydroesterification reactions. The uses of Pd and/or Pd-Co catalysts for the carbonylation of allylic and propargylic compounds and amidocarbonylations are discussed by (i) Tsuji and Kiji and (ii) Kühlein and Geissler, respectively. Mechanistic details figure prominently and the reader is provided with further information in the reviews cited in the references. Transition-metal-catalysed alkene and alkyne hydrocyanation (including asymmetric hydrocyanation) is covered by Casalnuovo and RajanBabu; likewise the field of cyclopropanation is well described by Pfaltz, although the treatment of the Simmons-Smith reaction is rather brief.

Bönnemann and Brijoux give an authoritative account of the very important area of cyclomerisation of alkynes, and focus in particular on the formation of six-membered carbocycles, and extensions to the synthesis of the related nitrogen containing heterocycles. Crowe describes synthetic routes to the construction of cyclopentane ring systems by intramolecular hydroacylation and reductive cyclisation, and a fairly brief

overview of alkene isomerisation reactions is presented by Otsuka and Tani, two very active pioneers in this area.

Geissler's coverage of palladium- and nickel-catalysed cross-coupling reactions includes not only organoboron (Suzuki reactions) and organotin (Stille reactions), but also organo-copper, -aluminium, -zirconium, -magnesium, -lithium and -silicon compounds. Both C–N and C–O bond-formation reactions are detailed by Beller and Riermeier. The use of chiral *ansa*-bridged metallocenes for the enantioselective alkylation of alkenes is very briefly discussed by Hoveyda, who also provides information on the kinetic resolution of unsaturated heterocycles and cyclic allyl ethers.

Recent developments in the versatile Heck reaction, first discovered in the late 1960s, are described by Beller, Riermeier, and Stark, mechanistically and with an emphasis on the use of chiral Pd catalysts. There is an interesting coverage of applications for the synthesis of natural products, pharmaceuticals and a variety of complex organic building blocks, together with a useful bibliography. Related coupling reactions involving C–H activation represent a recently developing field and are reviewed by Dyker. Palladium-catalysed allylic substitution reactions are discussed by Heumann, who cites more than 100 references, while Takahashi, Doi, and Yamamoto review the Pd-catalysed cyclisation of allylic acetates with alkenes and allenes.

I had expected a rather more in-depth coverage in the chapter on the applications of olefin metathesis (Schuster and Blechert) than the fairly brief summary provided, although the article does contain several important references up to 1997. Some further information is contained in the chapter in section 3 by Petasis, mainly concerned with titanium–carbene-mediated reactions, and both these chapters describe briefly ring-opening metathesis polymerisation (ROMP). The final chapters in section 2 are devoted to quite an extensive coverage of the synthetic use of both homo- and heterometallic lanthanide compounds (Kobayashi, Shibasaki and Sasai) and a very short account by Oguni of the metal-catalysed addition of cyanides to aldehydes.

The third section of Volume 1 is concerned with stoichiometric systems and begins with articles by Doetz and Pfeiffer on the reactivity of Fischer-type carbenes, followed by titanium–carbene-mediated systems (Petasis), featuring the Tebbe reagent. The coverage includes aldol and Michael addition reactions, cyclo-additions, cyclopropanation and metathesis reactions and carbene–CO coupling. Reactions of titanocenes with alkynes and nitriles are considered, but no mention is made of the rapidly developing related field of phospho-alkyne chemistry.

The McMurray reaction, involving low-oxidation-state titanium-promoted coupling of aldehydes or ketones to alkenes, is covered by Fürstner who includes a

short selection of different applications. Vanadium-mediated couplings are described by Jendralla, who also alludes very briefly to related niobium systems, and this is followed by useful discussions of chromium(II)-, (Hodgson and Comina) and samarium II-mediated coupling reactions (Gu and Curran). This last chapter also refers briefly to radical and cascade reactions. The oxidative radical cyclisation reactions based on manganese(III) (Snider) is followed by a chapter by Duthaler and Hafner concerned with chiral, titanium-mediated reactions involving addition of nucleophiles to aldehydes, and cycloaddition reactions.

Zinc-mediated reactions are covered in some detail by Knochel in a chapter containing over 200 references, and applications range from asymmetric synthesis to combinatorial chemistry. The role of zinc is also dealt with in the short chapter by Marek and Normant covering carbometalation reactions. Enantioselective conjugate addition reactions are the main theme of the very short chapter by Alexakis and the volume ends with the chemistry of iron–acyl complexes, (Rück–Braun), iron–diene compounds (Knölker), chromium–arene complexes (Schmalz and Siegel), and Pauson–Khand chemistry (Jeong). Here the treatment of the iron systems is fairly brief and predictable, the emphasis in the iron–acyl chapter being largely on derivatives chiral at iron. The iron–diene chapter focuses on cyclopentadienone synthesis, applications of butadiene and cyclohexadiene systems, alkaloid synthesis, and diastereoselective spiroannulations. Nucleophilic additions, ring lithiation and side-chain activation form the main topics in the very short description of the chemistry of arene–chromium complexes. The coverage of Pauson–Khand chemistry includes both stoichiometric and catalytic aspects. Topics presented include regioselectivity and promoter-assisted reactions as well as synthetic strategies in which the Pauson–Khand reaction figures prominently.

Section 1 of Volume 2, which also contains many chapters by experienced researchers, begins by addressing the vast area of organic reduction reactions. This is subdivided into chapters on homogeneous and heterogeneous hydrogenation reactions, transfer hydrogenations, hydrosilylations, metal-catalysed hydroboration, and transition-metal hydride reduction of imines and enamines. Following a very brief outline by Börner and Holz of mono- and poly-olefin hydrogenation, including diastereoselective and asymmetric hydrogenation, Burk and Bienewald consider unnatural  $\alpha$ -amino acid formation via asymmetric hydrogenation of enamides. Ohkuma and Noyori give an informative account of the very important area of hydrogenation of carbonyl compounds, with 160 references cited. Useful tables of data on hydrogenation of ketones, aldehydes, CO<sub>2</sub> and carboxylic acids are presented. The following section by Spindler and Blaser addresses the enantioselective re-

duction by dihydrogen of C=N bonds and gives an assessment of Rh, Ir, and Ru catalysts.

The section devoted to heterogeneous hydrogenation begins with a useful overview by Blaser, Steiner, and Studer of catalytic suppliers, catalyst choice, reaction media and conditions, details of apparatus and procedures, before a consideration of selected reactions. Transfer hydrogenations are dealt with by Gladiali and Mestroni in a 20-page review, covering mechanisms and relative merits of metals and promoters, before a discussion of substrates for which H-transfers are assessed as being particularly useful. The important area of hydrosilylation is described by Yamamoto and Hayashi, augmented by a short contribution from Brunner dealing with carbonyl compounds. Fu gives a very brief treatment of metal-catalysed hydroborations and the final aspect of this topic, by Singaram and Goralski, concentrates on the reduction of imines and enamines. Curiously, although the title of the chapter refers only to transition-metal hydrides, the subject matter concerns hydrides of boron, aluminium, silicon, tin, and tellurium.

Section 2 of Volume 2 is devoted to oxidation, and following Jorgensen's description of the basics, there are important contributions by Meunier on C–H bond oxidations (including discussions of mono-oxygenases and cytochrome P-450 models) and allylic oxidations by Schlingloff, Bolm, Grennberg and Bäckvall. A very short account of metal-catalysed Baeyer–Villiger reactions (Bolm, Beckmann, and Khanh Luong) is followed by authoritative discussions on both asymmetric dihydroxylation and aminohydroxylation reactions by Kolb and Sharpless.

Various aspects of epoxidations involving titanium, manganese, rhenium, and other transition metals, as well as metalloporphyrins, are considered in some detail by a number of authors in Chapter 2.7 (Katsuki, Muniz–Fernandez, Bolm, Herrmann, Fischer, Weskamp, Thiel, and Halterman) but for some reason a further

treatment of rhenium-catalysed epoxidations by Fischer and Herrmann appears in Chapter 2.11 following the discussions of Wacker oxidation (Feringa), hydroamination of alkenes and alkynes (Müller and Beller) and a brief discourse on heteropolyanions (Neumann). The remaining chapters of section 2 concern aerobic, metal-catalysed oxidation of alcohols, (Marko, Giles, Tsukazaki, Brown, and Urch), the oxidation of heteroatoms (Kagan and Luukas) and amine oxidation (Murahashi and Imada). Section 3 of Volume 2 is devoted to six special topics treated roughly equally, namely, supported metal catalysts (Basset, Candy, and Santini), two-phase catalysis (Sinou), photocatalysis (Hennig), applications of ultrasound (Peters), microwaves (Herwig and Trainor), and high pressure (Reiser).

In a compendium of this complexity, with such a wealth of information, there is obviously something for everyone, but I suspect that the more active researchers may find the sections they are already familiar with to be too brief to be of real use. However, newcomers to the field, and students, will find the two volumes extremely useful in drawing their attention to the vast armoury that organic chemists now have at their disposal in the pursuit of synthetic objectives. This new two-volume production should certainly join the comprehensive handbook edited by Cornils and Herrmann mentioned above on the shelves of all industrial and academic libraries. Regrettably the high price will almost certainly limit the number of individually owned copies.

John F. Nixon  
*School of Chemistry,  
Physics and Environmental Science,  
University of Sussex,  
Brighton BN1 9QJ,  
UK*