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Book Review

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Transition Metals for Organic Synthesis: Building Blocks and Fine Chemicals

Wiley-VCH, 2004; 2nd edition,
two-volume set, hardcover,
1314 pp; price 389 Euro,
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This two-volume series represents an update to the first edition published in 1998, which contains contributions from 116 authors. The key question is whether there was really a need for a second edition to this very popular *must-have* book describing the use of transition metals in organic synthesis? The editors immediately address this point in the preface. It is obvious in the last six years that the application of transition metals in organic synthesis has expanded significantly. It has matured into an area that is a mainstay in the synthetic chemist's armoury or tool-box, providing a myriad of broadly applicable and versatile transformations in ways that facilitate exquisite control in the manipulation of simple starting materials into targets of varying complexity. Selectivity is a key facet of transition-metal-mediated synthesis, e.g. in chemo-, regio- and stereoselective processes, that allows one to access some of the most difficult synthetic targets not affable by traditional methods. When was the last time you perused a synthetic journal that did not report a new application of a given transition-metal-mediated process? Importantly, it is often the unusual observations that drive the expansion of this field, in terms of both development and mechanistic understanding.

Arguably the book would be better titled as 'Transition Metals in Synthesis', particularly given that the barrier between inorganic and organic synthesis has all but disappeared and the fact that transition-metal-mediated synthesis is used in so many applied fields, e.g. in materials and pharmaceutical chemistry. For example, it is hard to imagine how the field would cope without palladium catalysis. Cross-coupling reactions such as those named after Kumada, Negishi, Hiyama, Sonogashira, Stille and Suzuki are key to those working in applied synthesis.

So, what is different about the new edition? First of all, authors of the first edition were asked to update their original chapters. A comparison with the first edition also shows that most chapters have been constructively modernized. In some cases, the first contribution by the author was updated with an additional section. The chapters are written, in the main, by world-leading experts. Importantly, opportunities have been given to younger active colleagues in the field, which provides a good balance to the overall feel of the book. All chapters have information listed in tables and helpful schemes. Chapters are appropriately sectioned and referenced extremely well, so that the reader will be completely up-to-date for the next five to ten years. Chapters are referenced up to the end of 2003. The subject index section contains significant keywords, which is very useful, and most topics of interest can be found in a few seconds.

The main topics in the book are reviewed here, which assumes that some readers may not possess a first edition. Volume one starts with a general overview of the basic aspects of the area (Trost), and then describes the concepts used in the application of transition metals in industrial fine chemical synthesis (Kein).

The second chapter concentrates on transition-metal-catalysed reactions. This begins with hydroformylation and focuses on its application in pharmaceutical and fine chemical synthesis (Beller/Kumar). Tandem and multiple carbon–carbon bond-forming reactions using hydroformylation are discussed by Elibracht and Schmidt. Hydrocarboxylation and hydroesterification alkenes, allenes, dienes and simple hydroxyalkynes are described by Ali and Alper. Amidocarbonylation of aldehydes (Beller), alkene and alkyne hydrocyanation processes (Rajan Babu) and cyclopropanation (Pfaltz) are presented clearly, providing new directions for these interesting applications. We then move onto alkene reactions, which begins with isomerization processes and their related transformations (Otsuka/Tani). This covers a plethora of functional alkene systems, but also provides mechanistic insight and examples of asymmetric skeletal rearrangements. Perhaps the most applied reaction in academic laboratories, and increasingly so in an industrial setting, is Suzuki cross-coupling. This topic is reviewed by a promising young scientist and covers all the important features of the reactions, namely the mechanism and aromatic halide substrate scope (Zapf). One of the main problems in this type of chemistry is knowing which ligand to use. In this respect, the author has sectioned separately the use of phosphine and carbene ligands, which is clear and concise. Important developments in the area, e.g. the coupling of alkyl halides and tosylates, are discussed and a clear summary and outlook are provided. Aryl amines and ethers are important structural units in many natural products, pharmaceuticals and agrochemicals. One may argue that metal-catalysed processes in which aryl halides are coupled with amines and alcohols has revolutionized this area. Since the mid-1990s there has been increasing interest in the development of catalytic C–N and C–O coupling processes. The Pd, Ni and Cu-catalysed arylation of amines are discussed (Zapf, Beller and Riermeier). A separate section deals with C–O formation. Hoveyda describes the catalytic enantioselective alkylation of alkenes by chiral metallocenes (this has not changed from the first edition). The Pd-catalysed alkenylation of aryl halides (Heck reaction) has been focused upon in some detail (Zapf, Beller and Riermeier). General mechanism, specific catalysts, asymmetric processes and the mechanistic implications and the application of the Heck reaction, particularly the intramolecular variant, are discussed. Allylic substitution reactions mediated by Pd are described by Heumann. The important emerging area of alkene and alkyne metathesis is discussed by Thiel. This provides a general introduction and overview to this ever-expanding area, which is followed by the mechanisms involved in alkene metathesis, the types of catalysts available and potential applications. Enyne metathesis is then introduced as a variant, which leads logically onto an examination of alkyne metathesis and its application in target-directed synthesis. Homometallic lanthanoids, particularly lanthanide triflate-catalysed synthetic reactions, are comprehensively introduced by Kobayashi. Asymmetric applications of lanthanide complexes are reviewed by Shibasaki, Sasai and Yoshikawa. This part of the first volume culminates with a critical analysis of bismuth reagents and catalysis, applied generally in synthesis.

The final section of the book deals with transition-metal-mediated reactions. This is a somewhat confusing split into either reaction type or the type of transition metal used. It is conceded that it is difficult to know how best to do this differently, however the section presents some very interesting and important applied transformations. Dötz and Minatti introduce Fischer-type carbene complexes, explaining the origin of their synthesis and reactivity. Both carbene-centred and metal-centred reactions are discussed, including applications in $[3+2+1]$ benzannulation, cyclopropanation and photo-induced processes. Titanium–carbene-mediated reactions (Petasis), McMurry reactions (Fürstner), chromium(II)-mediated carbon–carbon bond-forming processes (Hodgson/Comina), manganese(III)-mediated oxidative free-radical cyclizations (Snider), conjugate addition reactions (Alexakis) and carbametallation reactions of zinc enolates (Banon-Tenne/Marek) are examined. The application of iron–acyl complexes (Rück-Braun), iron–η^4-diene complexes (Knölker), chromium–η^6-arene complexes (Schmalz/Dehmel) and Pauson–Khand processes (Strübing/Beller) are further described.

The second volume is more traditionally split into three sections: reduction, oxidation and special topics. The first section thus deals with the vast field of homogeneous hydrogenation processes. The addition of hydrogen to alkenes, carbonyls, imines and enamines is discussed in detail, with a particular emphasis on asymmetric hydrogenation processes. New developments driven by recent mechanistic studies shed more light on the transmission of chirality from chiral ligands such as Phanephos. This highlights the important contributions made by Bargon and Brown, who detected agostic hydride interactions prior to the formation of a key alkyl hydride species in the Rh-catalysed hydrogenation of enamides. One essential inclusion in this section is the separation of the bibliography into individual subsections, which allows the reader effortless access to references. Various applications of asymmetric hydrogenations in natural products and pharmaceutical lead compounds are described. Blaser introduces heterogeneous hydrogenation processes, which traditionally have been used in industry. Some special features of this type of catalysis are noted. The review is focused on the more practical issues involved in producing high-yielding hydrogenation protocols. Transfer hydrogenation, e.g. transfer of hydrogen from a donor, DH_2, to a hydrogen acceptor, A or A–X, by the action of a transition-metal catalyst, has become very important. It is a field that has notably developed over the past six years, an area reviewed by Gladiali and Alberico. The obvious advantage of transfer hydrogenation over catalytic hydrogenation by molecular hydrogen is the elimination of safety restrictions associated with the use of high-pressure vessels. It is conceded that transfer hydrogenation can be a more complex system to control. The authors have highlighted the pros and cons in a balanced manner. Asymmetric processes and mechanistic insights are detailed. The hydrosilylation of alkenes, alkynes, dienes, carbonyls and imines is described by Yamamoto and Hayashi. This review highlights the seminal contributions of Widenhoefer, who was able to create an intramolecular cycloisomerization/hydrosilylation process, from various dienes mediated by palladium, to give highly functionalized cyclic compounds. Fu provides a concise overview on the transition-metal-catalysed hydroboration of alkenes, which covers specifically the period 1999–2002. Catalytic asymmetric alkene hydroboration, general applications of hydroboration mediated by transition metals in synthesis and its use in supercritical CO_2 are described.

The fundamental principles underpinning transition-metal-mediated oxidation processes are described by Sheldon and Arends in the second chapter. This is a rather unassuming and realistic overview of catalytic oxidation processes. The side-reactions that occur are examined in depth, e.g. free-radical pathways. This is a *must-read* section for novices and experts alike. The selective and efficient oxidative functionalization of C–H bonds is well covered by Shul'pin. It is, however, disappointing to find that this section concludes somewhat abruptly without a conclusion and outlook. Allylic oxidation mediated by Pd (Grennberg/Bäckvall) and Cu (Bolm and others) is described. The general principles and mechanistic implications are of interest. Metal-catalysed Baeyer–Villiger reactions are discussed again by Bolm and others. Emphasis has been placed on the development of asymmetric Baeyer–Villiger oxidations of racemic and prochiral ketones. Although it is conceded that the scope of the reaction is still limited (selectivity is the main issue), very high enantioselectivities can be accomplished. Developments in asymmetric dihydroxylation of simple alkenes is described by Kolb and Sharpless. This review is almost written in the style of an instruction manual, which is very useful. Recent developments are tagged onto the end of this review (Muñiz), which provides the majority of key papers. Asymmetric aminohydroxylation is described by Kolb and Sharpless, and again updated by Muñiz. Epoxidation reactions, including those catalysed by Ti (Katsuki), Mn (Muñiz/Bolm) and Re (Herrmann and others), are discussed. Thiel describes the use of miscellaneous transition metals in alkene epoxidation, including the lanthanides. The oxidative functionalization of alkenes by means of Pd-catalysed reactions, known as the Wacker process, has been important in industry and research-scale synthetic chemistry for many years. Hintermann introduces the general principles and mechanism to the process, and describes many applications. Unfortunately, some duplication of the section written by Bäckvall is noticeable, which was probably unavoidable given the size of this two-volume book. Asymmetric aziridination (Bolm), amination of alkenes and alkynes (Beller), oxidative cleavage of alkenes (Herrmann), aerobic oxidation of alcohols (Markó), asymmetric sulfide oxidation (Kagan) and amine oxidation (Murahashi/Imada) are covered in depth.

The last chapter in the book is very interesting indeed, covering a range of special topics on two-phase catalysis (Sinou), transition-metal-based fluorous catalysts (Gladysz), transition-metal-mediated reactions in compressed CO_2 (Leitner), in ionic liquids (Wasserscheid), in photocatalysis (Hennig), in applications of ultrasound (Cintas) and microwaves (Lee) and reactions under high pressure in the liquid phase (Reiser). To pick out one section, microwavable reactions have experienced a dramatic rise to fame, particularly those mediated by transition metals. Indeed, this section illustrates just how versatile microwave technology is in cross-coupling processes mediated by Pd, alkene metathesis, the Pauson–Khand reaction, reduction processes and heterocyclic ring synthesis, particularly in academic problems (small-scale reactions).

Overall, as a holder of the first edition of the book, I have no reservation in recommending this second edition. It is a *must-have* book for every research laboratory, and importantly it is a page-turner. It is generally very well structured and the majority of key references are included—it is quite extraordinary that so many areas have been covered in ~1300 pages—which at the very least provides an excellent starting point for this ever-expanding branch of synthetic chemistry.

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