Synthetic Methods of Organometallic and Inorganic Chemistry, Volume 9. Transition Metals Part 3. Edited by W. A. Herrmann, Thieme: Stuttgart, 2000, 221 pp, DM 135, hardcover. ISBN 3 13 115141 2.

This is the penultimate Volume of a series that began in 1996 as a modernized, English language version of a classic German language compendium, Georg Brauer's "Handbuch der Präparativen Anorganischen Chemie". The objective is to collect a broad range of detailed synthetic procedures of general interest and utility for the entire community that makes use of inorganic and organometallic compounds. Volumes 1-8 systematically treated each segment of the periodic table, and were reviewed earlier, normally with high enthusiasm [p 1402, 1996; p 372, 736, 981, and 1352, 1997, and p 1838, 1999]. Volume 9 is the third to focus on transition metals. The previous two covered the traditional starting materials, and selected newer developments. The new Volume highlights very recent developments, reflecting the Editor's insightful predictions for the classic educts of the future. As such, it is the most engrossing in the series to date.

A variety of themes are emphasized. One grouping involves the family of unsaturated hydrocarbon ligands represented by alkenyl, η^3-allyl, and η^5-pentadienyl (52 pages). The procedures span the range of transition metals, and also include some main group element building blocks. Another grouping features π complexes of five-membered heterocyclic ligands (31 pages). Generous coverage is accorded to η^5-pyrrole, pyrrolyl, phospholyl, and stibole systems. Some diheterocycles are also presented.

One especially forward-looking theme involves complexes of N-heterocyclic carbene ligands (28 pages). This is a very active area of catalyst development that most readers of this journal are well aware of. The nickel, palladium, iridium, and ruthenium complexes described, or close relatives thereof, may prove to be catalysts of choice for a number of common laboratory transformations, such as the Heck reaction and olefin metathesis. A section on oxo- and alkoxy- complexes extends the representation of $RReO_3$ compounds and their Lewis base adducts (27 pages), some of which were introduced in earlier Volumes. These versatile catalysts may soon see large-scale commercial application in olefin expoxidation. A number of molybdenum and tungsten oxo complexes are also featured.

Metal carbonyl complexes were an integral part of the earliest incarnations of the Brauer series. This Volume continues this tradition, but in the context of modern, highly reduced tantalum carbonyls that are valuable precursors for many types of tantalum complexes (10 pages). This is followed by a treatment of sulfonated phosphine ligands and water-soluble metal complexes thereof (18 pages). Such compounds are being used in large-scale industrial aqueous catalytic processes, which receive special attention as examples of "green chemistry". In view of their limited solubilities in organic solvents, non-traditional workups involving gel permeation chromatography are often required. Detailed descriptions are thoughtfully provided.

A concluding section covers miscellaneous compounds, most of which are connected to a current area of catalyst development (24 pages). These include ruthenium and tungsten alkylidene complexes, several ruthenium $=C=C=CR_2$ and 1,3-diynyl complexes, and a variety of group 8-10 chelating di(imine) complexes. The latter represent an exciting new class of olefin polymerization or copolymerization catalysts.

In summary, this Volume attempts to anticipate the future of preparative inorganic and organometallic transition metal chemistry. This reviewer strongly endorses the vision presented, and wholeheartedly recommends the entire series for all scientific libraries. This Volume would also be a useful desk reference for anyone engaged in developing transition metal catalysts or water soluble complexes.

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The Chemical Synthesis of Natural Products. Edited by K. J. Hale. Sheffield Academic: Sheffield, 2000, 429 pp, £ 99 hardback. ISBN 1-84127-039-3.

The chemical synthesis of natural products continues to occupy a central position in organic chemistry research and books on the subject are bound to inspire and enlighten their readers. This volume is no exception. It is divided into twelve chapters and largely focuses on total syntheses of complex molecules that were completed in the last decade. A broad range of subject areas are covered including alkaloids; complex carbohydrates; enediynes and dienediynes; amino acids and peptides; terpenes and terpenoids; naturally occurring aromatics and heteroaromatics; macrolides and polyethers. In all some twenty authors contributed to the work under the stewardship of Professor Hale. The highlight for me was a chapter entitled "Total synthesis of macrolides" by Bode and Carreira. Acknowledging that comprehensive coverage was impossible within the allocated space, they nonetheless attempted "to provide a wide perspective of the field". They accomplished this brilliantly by focusing on the syntheses of four natural products - oleandolide, Sch 38516 (fluvirucin B1), macrolactin A and lankacidin C. Their choice was inspired as each of these targets presents a different challenge to the synthetic organic chemist and each has been addressed using a variety of strategies. Most authors, though less bold in their approach, were equally successful in presenting a broad perspective. Several chapters warrant a special mention. "The chemical synthesis of naturally occurring cyclodepsipeptides" by Hale, Bhatia and Frigerio is an excellent monograph - concise yet detailed, incisive and informative. Similar sentiments are justified

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for the review of enediyne and dienediyne synthesis by Caddick, Shanmugathasan and Smith which was undoubtedly the most comprehensive in the book. The chapter entitled "Important developments in the total synthesis of alkaloids" dovetailed beautifully with the following contribution on naturally occurring aromatic heterocycles. Likewise, the back to back chapters on linear and cyclic peptide synthesis. In common with most multiple author works, the style of each review varied greatly from chapter to chapter. This was seldom a distraction - though I was disappointed by three contributions. One because it was presented in an uninformative and unimaginative way; another because the author appeared to forget that the book was concerned with the synthesis of natural products half way through his article; and finally by a chapter that included an excessive number of synthetic approaches ahead of completed total syntheses. [I presume that the failure to provide references in full for Chapter 7 was an oversight.] These gripes aside, "The Chemical Synthesis of Natural Products" is easy to read from cover to cover and well worth flicking through when seeking inspiration. As you read it you are bound to wonder why a particular synthesis was included ahead of a “better” one. In truth our views are subjective and any selection will attract criticism. That the book succeeds in showing how total synthesis has inspired developments in contemporary organic chemistry is more important than the omission of this or that natural product. As a consequence, the book is sure to grace chemical libraries for years to come and will be loaned out on a regular basis. A reasonably priced paperback would doubtless attract a wider audience.

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Transition Metal Reagents and Catalysts. By J. Tsuji. Wiley: Chichester, 1999, 478 pp, £ 125, hardback. ISBN 0-471-63498-0.

Over the last three decades, explosive growth in the chemistry of transition metals, both catalytic and stoichiometric, has been made and transitions metals contribute to the asymmetric synthesis of natural products and apply to industry and pharmaceuticals. Thus it should be a challenging task for organic chemists to publish a comprehensive book about transition metals reagents and catalysts. Professor Jiro Tsuji did publish a concise and excellent book. This book appears to be an updated version of Professor Tsuji’s previous book written in Japanese, Transition Metals Exploitation for Organic Synthesis in 1997. Alternatively, this book is a counterpart of the book edited by Professor Tsuji, Palladium Reagents and Catalyst. Innovations in Organic Synthesis published in 1995. This book is particularly useful for organic research chemists and graduate students and even novices. He tried to stress the mechanisms as well as the applications of transition metals in the synthesis of natural products and industrial applications.

This book begins with a brief history of the pioneering applications of transition metals in Chapter 1. In Chapter 2 the author provides an excellent overview of the formation of transition metal complexes and brief mechanistic considerations. I would recommend that those who are new to this area also look at the book “Transition Metals in the Synthesis of Complex Organic Molecules” by Louis S. Hegedus, University Science Books, 1994 for the detailed explanations and especially the electronic configurations of early transition metals. The characteristic feature in this book is based on the functional substrates, organic halides and pseudohalides, allylic compounds, dienes, propargylic compounds, alkenes, alkynes, and then carbene complexes, activation by transition metals, catalytic hydrogenation, and Pd(II)-catalyzed reactions.

In Chapter 3 many useful transition metal catalyzed cross-couplings are summarized: Heck, Suzuki, Stille, Sonogashira, and Buchwald-Hartwig aminations as well as carbonylative coupling, which seem to be the most useful couplings in organic synthesis. The schematic diagrams could be very useful to overview the reactions. In Chapter 4 the catalytic reactions of allylic substrates for the allylation with nucleophiles was chiefly treated together with allylic rearrangement. In Chapter 5, the transition metal catalyzed cycloaddition reaction of the conjugated dienes was described with halides and main group metal components. In Chapter 6, the reaction of propargylic derivatives was described based on the review by Tsuji (*Angew. Chem. Int. Ed. Engl*. 1995, *34*, 2589). In Chapter 7 the reaction with alkenes and alkynes via π-alkene and π-alkyne complexes, for example carbonylation, hydroformation, and cycloaddition to form rings with Rh, Co, Pd along with early transition metals are described. In Chapter 8 transition metal carbene complexes are introduced and explained systematically with alkene metathesis as a pioneer in this area. Particularly the application of ruthenium is emphasized for ring closure metathesis (RCM) in the synthesis of natural products. For more information about Ru, it is recommended to see *Chem. Rev*. 1998, *98*, 2599 written by Murahashi. In Chapter 9 deals with the advantages of coordination of Fe, Co, Cr, for activations. Chapter 10 describes asymmetric catalytic hydrogenation and transfer hydrogenation of alkenes and ketones as asymmetric version, which are the successes of transition metal catalysts and important reactions for industrial applications. The last chapter of this book deals with various transformations with Pd(II) species other than Pd(0) species in the organic synthesis.

In conclusion this book is an excellent and valuable resource for organic and other synthetic chemists.

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Modern Amination Methods. Edited by Alfredo Ricci, Wiley-VCH:Weinheim, 2000, 267pp, hard cover. ISBN 3-527-29976-9.

The central role of the amino group in biology has long been recognised and the preparation of amines is enormously important for the synthesis of natural products, pharmaceuticals, dyestuffs, materials and ligands for use in catalysis. Traditional methods of forming amines have served the chemical community well, but they have tended to be rather indirect, involving for example, nitration or the manipulation of oxygen- or halogen- containing functional groups. Many of the early achievements of asymmetric synthesis were concerned with alcohols, epoxides and carbonyl compounds but there is now a growing interest in stereoselective ways to form the C-N bond.

Professor Ricci has assembled a group of leading researchers to describe, in seven chapters, the development of some newer methods for introducing the amino group. Extensive references to the primary literature are included, mainly from the decade up to August 1999. Some previously unpublished work is included. Recurring themes are asymmetric synthesis and the use of transition metal catalysts to facilitate the manipulation of unsaturated systems.

Discussion of nucleophilic aminating agents starts with reactions at allylic positions using, for example, the Mitsunobu reaction, the Overman rearrangement of allylic trichloroacetimidates and palladium-catalysed displacements on allylic esters. A later chapter on palladium-catalysed amination of aryl halides and sulfonates provides an excellent account of how mechanistic understanding of this versatile and useful reaction has been gained. With an appropriate ligand for palladium, such as tri-*tert*-butylphosphine, even the formation of diphenylamine from aniline and chlorobenzene becomes feasible at room temperature.

Several authors deal with electrophilic aminating agents. Manganese nitrido complexes have a chapter to themselves: when used in stoichiometric amounts some of these species can effect the enantioselective transformation of styrenes into aziridines. The preparation of transition metal nitrido complexes is surveyed in an adjacent chapter, although reactions with organic substrates are not discussed apart from those of the aforementioned manganese complexes.

C-N bond forming reactions of chiral enolates with electrophiles such as azodicarboxylates and *O*-sulfonylhydroxylamine derivatives show proven synthetic utility and are well covered. Examples of direct aminations of simple alkenes are included: this topic is still in its infancy and the scope of the reaction is still extremely limited, consequently a very elegant account of the indirect electrophilic amination of alkenes via organoborane intermediates is also provided. Rather confusingly the half chapter on electrophilic amination at allylic positions has inadvertently been included as a subsection of the one on nucleophilic allylic amination: it includes ene-type reactions of chalcogen diimido compounds along with some transition metal (Mo, Fe, Ru) catalysed processes.

There is also a chapter on the use of glycosylamines as chiral auxiliaries in, for example, the Strecker, Passerini and Ugi reactions. The editor acknowledges that the book is not comprehensive and does not discuss the important topic of asymmetric aminohydroxylation. The hetero Diels-Alder reaction and other reactions of imines appear only in the context of the glycosylamine chiral auxiliaries.

The organisation and subdivision of material within the chapters is generally very clear and helpful. There are plenty of tables indicating reaction conditions, yields and levels of stereoselectivity and the chemical structures are well presented. Occasional slips have escaped detection: for example on p13 Wilkinson's catalyst appears as $Rh(PPh_3)_3$ and there is a mix up between phenanthrene and anthracene on p132. On the whole the authors write with evident authority.

This book will be inspiring and useful to all who prepare nitrogen-containing organic compounds or teach organic synthesis at an advanced level.

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