Book Review

Catalytic Antibodies Edited by Ehud Keinan (Technion-Israel Institute of Technology). Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany. 2005. xxx + 586 pp. $215.00. ISBN 3-527-30688-9.

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BOOK REVIEWS

Metallocenes in Regio- and Stereoselective Synthesis. Topics in Organometallic Chemistry, 8. Edited by Tamotsu Takahashi (Hokkaido University). Springer-Verlag: Berlin, Heidelberg. 2005. x + 244 pp. $229.00. ISBN 3-540-01606-6.

This monograph, whose editor is a well-known international authority, consists of a series of chapters on several very important applications of metallocenes to organic synthesis and the polymerization of alkenes. The impact of metallocene chemistry has been a huge factor in the systematic development of new catalysts for polymerization and has resulted in an already extensive number of reviews and books. The use of metallocenes for organic synthesis, on the other hand, is still very much in its infancy, with some applications relatively well developed and others still in the nascent stage. It is in the area of organic synthesis that this monograph should have the most impact.

The book has six chapters. The first, "Hydrozirconation and its Applications" by Wipf and Kendall, concentrates on developments reported in the field from 1996 to 2002. This contribution is somewhat unusual in that it includes very useful descriptions of the synthetic procedures involved in the synthesis of the best known hydrozirconation reagent, Cp_2ZrHCl, as well as of some applications. The authors also discuss at length functional group compatibility, halogenation, hydrogenation, and reduction of the organometallic products of hydrozirconation, and C−C bond formation via transmetalation of hydrozirconation products using, for example, nickel, palladium, copper, and zinc compounds. Approximately 60% of the 127 references are post-1996, many post-2000.

In the second chapter, "Construction of Carbocycles via Zirconacycles and Titanacycles", Xi and Li discuss preparative methods for three-, four-, five-, and six-membered metal-containing rings—saturated and unsaturated—and their use for the syntheses of carbocyclic compounds, including aromatics. While this review is useful, it includes only a handful of post-2000 references from the primary literature, omitting discussion of Stryker's work on the synthesis of titanacyclobutanes, for example.

The next chapter, "Metallocene-Catalyzed Selective Reactions" by Kotora, is much longer than the first two, as befits such a broad subject. Included are an assortment of topics, under the rubric of additions to multiple bonds, which includes group 4 metallocene halide-catalyzed additions of metal alkyls to C−C double and triple bonds. Departing from the heretofore pronounced emphasis on group 4 metal-induced reactions, the author also discusses at some length a variety of processes (conjugate addition, hydroacylation, hydroboration, etc.) involving monocyclopentadienyl compounds of metals such as ruthenium, rhodium, and iridium. The other major theme is the coupling of two or more multiple bonds. While there is some overlap with the review of Xi and Li, Kotora extends the discussion to late transition metal chemistry. This review finishes with a series of relatively minor topics and includes many post-2000 references. It will undoubtedly be widely read, especially by chemists wishing to compare group 4 and late transition metal metallocene-based catalysts.

Negishi and Tan cover a variety of reactions of alkenes and alkynes in Chapter 4, entitled "Diastereoselective, Enantioselective, and Regioselective Carboalumination Reactions Catalyzed by Zirconocene Derivatives", and include a long, very useful list of successful applications to natural products. Given the decided focus on their topic, the authors are rather more successful than others in this monograph in providing detailed, critical insights. The review will be much read, both because of the eminence in the field of the senior author and because it includes many post-2000 references and is thus very up-to-date.

The succeeding chapter, "Stereospecific Olefin Polymerization Catalyzed by Metallocene Complexes", stands apart from the others because its author, Suzuki, addresses applications to fields other than organic synthesis. As mentioned above, metallocene-promoted catalysis of polymerization is a huge, well-developed field that is reasonably well covered by reviews and books, although it does continue to evolve. Any attempt to deliver the essence and breadth of such a field in only 33 pages is bound to be found somewhat wanting, and in this case, also misleading. For instance, the classical coordination polymerization (Ziegler−Natta) is presented in order to give the newcomer to the field some key mechanistic information, but then it is implied that this mechanism is relevant to the polymerization of methyl methacrylate, which is not true. Nonmetallocene catalysts are also mentioned briefly, to no real benefit and counter to the theme of the monograph, and at least one interpretation published earlier but now discounted is mentioned uncritically.

Takahishi and Kanno wrote the sixth chapter, entitled "Carbon−Carbon Bond Cleavage Reaction Using Metallocenes". This rather slim article covers a variety of transition metal-induced rearrangements, such as β-methyl elimination from neopentyl compounds, reversible formation of metallacycles, and oxidative addition of nitriles to low-valent metal complexes. While some of the reactions are important in the field of alkene polymerization and hence are reasonably well understood, others are as yet little known or understood and have not found applications to organic synthesis.

Overall, this monograph is attractive and very well produced, with generally quite well drawn figures, although the subject index is rather brief. The target audience will be organic and organometallic chemists with interests in synthetic applications rather than in applications to homogeneous polymerization. All academic research libraries will want a copy, but at $229.00 this will be a bit rich for many individuals.

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Catalytic Antibodies. Edited by Ehud Keinan (Technion-Israel Institute of Technology). Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany. 2005. xxx + 586 pp. $215.00. ISBN 3-527-30688-9.

The field of catalytic antibodies makes one glad to have chosen a career in science. It is the perfect lean-back-in-your-chair-and-dream type of research that actually comes true. The intellectual challenges are limitless, enabling (or forcing) one to be knowledgeable in the fields of immunology, enzymology, biochemistry, and organic chemistry. Ever since Jencks stated that antibodies that are raised against transition state analogues should show catalytic properties, these research fields have come together to develop this idea and as a result have grown immensely from the endeavor. As with all novel research, successes in the early days seem unbounded, but with time, begin to confront barriers. At such later times, a critical review of the research is necessary to determine why the barriers exist and whether and how they can be overcome. This timely, well-written text provides such a review. It also offers a unique perspective of enzymes, i.e., why antibodies are inferior catalysts, and current screening techniques that are applicable to both antibodies and enzymes.

Although the editor states that these 19 chapters do not fully cover the science of catalytic antibodies in its entirety, reading the whole text will provide one with a strong foundation in catalytic antibodies and catalysts in general. Readers, such as myself, who are very familiar with catalytic antibodies will still grab a pen and jot down notes as they read about new discoveries and questions about the conclusions drawn by the authors. This stimulation is the beauty of the catalytic antibody field. For readers who are less familiar with the subject, I suggest starting with Chapter 16. It provides a general overview of catalytic antibodies and the thermodynamic equations that are used to describe their properties and, in my opinion, should have begun the book. The overall organization of the book in terms of the order of the chapters is, in fact, my only complaint with the text. Keinan, however, provides a short description of each chapter in the preface, which aids greatly for finding the information desired.

The major topics are the successes and failures of catalytic antibodies, the computational methods used to investigate them, the catalytic abilities of antibodies compared to enzymes, screening methods for catalysts, and natural catalytic antibodies. There are many color graphics that show key protein−ligand interactions, tables that contain kinetic parameters, several enlightening graphs that convincingly contrast antibodies to enzymes, and many figures that detail the newest screening methods. Although most of the studies of catalytic antibodies have appeared in various review articles, this text goes further by combining all aspects of this field within a single source and by providing an invaluable comparison of antibodies to enzymes. Readers will also find a unique chapter written by a science historian, where I was not surprised to read that the first proposals on enzyme antibodies were rejected in the early days because they lacked plausibility. I was surprised, however, to read that researchers in the catalytic antibody field are akin to the Cree hunters of caribou in that both had to develop the skills needed to succeed in their goals: hunting skills for the Cree and innovative means to tap the immune system for the scientists.

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