

Book Review

EDITED BY PAUL KNOCHEL

Handbook of functionalized organometallics: applications in synthesis

Wiley VCK, 2005,

2 volumes, 690 pp; price £175

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This two-volume handbook sets out to provide summaries of the developments in functionalized organometallics that have taken place mainly over the last twenty or so years. Many of the generalizations that were taught as rules at one time have simply been swept away by more subtle techniques, and the simple refusal of pioneering researchers to accept these rules. Thus the generalization that, for example, a Grignard reagent must be prepared from a simple unfunctionalized organo-halide, as otherwise self-reaction will render the reagent useless, is comprehensively demolished in Chapter 4, one of the many chapters co-authored by Knochel, with examples of Grignard reagents bearing diverse functional groups. What is also clearly demonstrated throughout the handbook is that modern work has gone beyond merely developing the techniques necessary for generating organometallics in the presence of reactive functional groups, now being at a stage that allows the design of synthetic routes and selectivities based on the functionalization in the organometallic reagent. Indeed, it is only when one sees all this work presented together in this collected form that the strides forward that have been achieved in this area are truly apparent. I have been guilty over the years of failing to notice as successive papers on the use of organometallics with particular substituents were published that the total body of work amounted to such a dramatic change in the way we should think about organometallic reagents, but this book drives the message home forcefully. Incidentally, the

contribution of Knochel to those strides is apparent upon flicking through the (comprehensive and well compiled) reference sections at the end of many of the chapters.

The handbook is arranged in a roughly periodic order of chapters, with most of the main-group chemistry described in the first volume, with the second volume concentrating on the transition elements and oddities (carbenes, etc.). After a general introduction, the first volume then contains chapters on the functionalized organics derived from lithium, boron, magnesium, silicon, tin and zinc. The second volume presents chapters on geminal organodimetallics [e.g. the $\text{CH}_2(\text{ZnX})_2$ reagents], the polyfunctional versions of organocoppers, organonickels, carbenes, zirconium and titanium (combined in one chapter) manganese, 'polyfunctional electrophilic multihapto-organometallics' (coordinated polyenes to those from a more 'inorganic' background) and finally electrosynthesis of polyfunctionalized organometallics. The style is reasonably consistent throughout, the diagrams well laid out and the text easy to follow. Generally, the authors of each chapter have hit the right balance of covering the present state of the published literature while also giving more detail of the areas in which they specialize, which makes for an interesting read.

The work presented in the first volume represents a real shift in the way we think about the applications of organometallic reagents, in terms of the tolerance of and application of complex functionality in organometallics derived from 'hard' metals. While tolerance of function groups is more expected with 'soft' metals, the second volume presents a clear summary of the great recent advances in synthetic applications of such species, and particularly in the use of functionality in control of reactions. The polyfunctional electrophilic multihapto-organometallics is particularly impressive in the way

it demonstrates the use of functionality in directing nucleophilic attack, although possibly more of a nod to the Davis–Green–Mingos rules by way of background in unfunctionalized cases would have been appropriate, and even would have helped to emphasize how far the area has developed.

My only real criticism of this handbook is that it would have dramatically increased the usefulness if each chapter had included a few sample procedures for the reactions covered. It is true that the reference sections give leads to full experimental procedures, and that the optimized procedure will vary from case to case. However, in the event that I was designing a synthesis including a step relying upon a functionalized organometallic of a type in which I have no previous background, a sample procedure for such a reaction selected by the author of the chapter (i.e. an expert in the area) as representative of typical conditions and likely to be suitable for a range of substrates would be a better starting point than a procedure selected after my own inexperienced literature work.

Overall, this is an impressive and useful handbook that would be a welcome addition to the bookshelves of any practicing organometallic chemist, but would really be of most use to those applying organometallics in synthesis. It may even convert some of those organic chemists who never stray beyond the use of commercially available organometallics, by demonstrating the staggering scope and range of functionalities that have been successfully incorporated into organometallics in more recent years.

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