Christoph Elschenbroich
Organometallics
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Organometallics

Translated by
José Oliveira
and
Christoph Elschenbroich

Third, Completely Revised and Extended Edition
From the disordered liquid or gaseous phase a methane molecule approaches a coordinatively unsaturated highly reactive metal atom and is about to form an M...CH₄ σ complex. Oxidative addition to yield a hydrido–metal–methyl unit eventually follows. The low-valent metal atom may either be stabilized by coordination to an allyl or pentadienyl ligand (the red ribbon) or may be part of a metal surface (the maroon/blue band pattern). If the northwestern C–H bond is replaced by a C–C bond that is connected to the ligand, the intermolecular C–H activation described in the scenario above becomes instead intramolecular C–H activation as encountered in agostic interactions.
Preface to the Third Edition

Whereas the Second Edition of this book followed only three years after the first, the Third Edition had to wait 14 years to go into print. In a field as flourishing as that of organometallic chemistry this time span borders to infinity. Since the former coauthor Albrecht Salzer reconsidered his priorities, Organometallics, 3rd Ed. has become a single author book, a fact that did not speed up the process of preparing it. If the Third Edition does not look completely alien to the reader this must be traced to the invaluable contributions Albrecht made to previous editions and which have kept their place in the most recent version.

Another obvious change is the considerably increased volume of the Third Edition, which appears simultaneously with the Fifth Edition of the German version. This growth reflects the impressive advances made in the field to which, among others, Nobel prizes awarded to six leading organometallic chemists during the last decade attest. Spectacular new achievements include synthetic masterpieces of fundamental importance, particularly in main-group organoelement chemistry, increased attention to the f-block elements as bonding partners to carbon, and the elaborate use of organotransition-metal complexes in homogeneous catalysis, serving laboratory-scale preparations as well as industrial processes. Bioorganometallic chemistry has emerged recently as a fascinating new discipline; the complexity of this topic often likens it to searching for a needle in a haystack. These highly disparate endeavors are now aided by access to sophisticated, yet routine, methods of structural analysis in solution and in the solid state as well as by the rapidly expanding use of computational quantum chemistry. Attempts to convey to the reader a little bit of all of this without a significant page increase would have been doomed to failure. Admittedly, the often cited excuse put forward by Blaise Pascal more than three centuries ago also applies in the present case: “I have made this a rather long letter because I haven’t had time to make it shorter.”

Organometallics 3rd Edition is thought to contain sufficient material for a one-year course meeting twice a week. Compared to previous editions only Chapter 16, which deals with metal-metal bonds and metal-atom clusters, has remained virtually unchanged as no principally new perspectives have turned up and a systematic approach to cluster synthesis does not appear to be in sight.

The selection of citations in the running text is based more on utility considerations than on historical fidelity. Often a full paper or a review article is more useful.
for the reader than the earlier short communication that protects priority interests. For “milestones” of pivotal importance, however, the appropriate primary references are generally given. In view of the vast amount of published work, the choice of articles for further reading collected in Appendix A-4 to some extent reflects “careful arbitrariness”. Notwithstanding, the literature accessible through the author index should be fairly representative of modern organometallic chemistry.

I am grateful to numerous colleagues who offered valuable hints. Taking the risk of incompleteness I would like to name A. Ashe III, A. Berndt, M. Bickelhaupt, G. Boche, M. Brookhart, K.H. Dötz, J. Ellis, R.D. Ernst, H. Fischer, G. Frenking, A. Hafner, J. Heck, G. Herberich, R.W. Hoffmann, P. Jutzi, W. v. Philipsborn, K. Pörschke, Ch. Reichardt, P. Roesky, H. Schwarz, W. Siebert, J. Sundermeyer, R. Thauer, W. Uhl, M. Weidenbruch, H. Werner, and N. Wiberg. To ex-coauthor Albrecht Salzer I am indebted for the splendid cooperation in the past. New formulae and schemes were drawn with insight and proficiency by Andrea Nagel; the author and subject indexes were converted for the English Edition by José Oliveira. More importantly, it is a pleasure to acknowledge the linguistic contributions of José Oliveira, who translated the new sections from the German Fifth Edition and who commented on those parts which I had translated myself. Cooperation with Project Editor Bettina Bems was both efficient and pleasant. Production Manager Hans-Jochen Schmitt must be commended for creating an attractive layout and for tolerating several last-minute corrections.

Last but not least I thank those colleagues and students who pointed out errors in previous editions and made suggestions for improvements. Hopefully, this practice will continue in future.

Marburg, December 2005

Christoph Elschenbroich
Preface to the First Edition

The present volume is the translation of the Second Edition (1988) of our text “Organometallchemie – Eine kurze Einführung”; corrections and a few results of very recent origin were included but otherwise the body was left unchanged.

Can a 500 page treatise on a branch of chemistry still be called “concise”? On the other hand, a section of only 20 pages covering transition-metal olefin complexes certainly must be regarded as short. This contrast illustrates the dilemma encountered if one sets out to portray the whole of organometallic chemistry in a single volume of tolerable size. The book developed from an introductory course (one semester, about 30 lectures) on organometallic chemistry for students confronted with the field for the first time. The material covered is a mixture of indispensible basic facts and selected results of most recent vintage. Attempts to systematize organometallic chemistry by relating molecular structures to the number and nature of the valence electrons are presented as are applications of organometallics in organic synthesis and in industrial processes based on homogeneous catalysis.

An apparent omission is the absence of a chapter specifically dealing with organometallic reaction mechanisms. It is our contention, however, that mechanistic organometallic chemistry has not yet reached the stage which would warrant a short overview from which useful generalizations could be drawn by the beginner. Note, for example, that even reactions as fundamental as metal carbonyl substitution are currently under active investigation, the intermediacy of 17 or 19 valence electron species opening up new possible pathways. Interspersed within the text, however, the reader finds several comments and mechanistic proposals ranging from well established kinetic studies to catalysis loops which at times have more the character of mnemotechnic devices than of kinetic schemes based on experimental evidence. Detailed mechanistic considerations should be deferred to the second act of the study of organometallic chemistry and several textbooks, mainly concentrating on organo-transition metal compounds, offer a wealth of material with which to pursue this goal.

We have structured the text in the traditional way – following the periodic table for main-group element organometallics and according to the nature of the ligand for transition-metal complexes – which we find most suitable for an introduction. Apart from the Chapters 16 and 17 (Metal-metal bonds, clusters, catalysis) somewhat more specialized material is presented in sections called “Excursions”. Rigor-
ous scientific referencing would be inappropriate in a text of the present scope. At the end, a literature survey (300 odd entries) is given which leads the reader to important review articles and key papers, including several classics in the field. Furthermore, in the running text authors' names are linked to the facts described whereby the form (Author, year) designates the year of the discovery, usually in a short communication, and the form (Author, year R) the appearance of the respective full paper or review. The complete citation can then be easily retrieved via consultation of Chemical Abstracts. A desired side-effect is to familiarize the student with author's names and their fields of endeavor. The many coworkers, who actually did the work, may forgive us that only the name of the respective boss is given.

Among our own coworkers who helped to bring this English Edition to completion, the native speakers Pamela Alean (Great Britain, now a resident of Zürich, Switzerland) and James Hurley (USA; resident of Marburg, Germany) stand out. They went a long way to eliminate our worst excesses of “Gerglish”. The bulk of the structural formulae was drawn by one of the authors (A.S.) thereby keeping things in the right perspective and making the book easy to use. Monika Scheld, Marburg, helped with the preparation of the indexes and by checking the cross references. We are grateful to the editor Dr. Michael Weller and the production manager Bernd Riedel (both of VCH Publishers) for a pleasant form of cooperation and their toleration of several last-minute changes. Finally, the authors mutually acknowledge their unflagging support during the various stages of the enterprise.

Ch. Elschenbroich
Marburg
Germany

March
1989

A. Salzer
Zürich
Switzerland
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