Organometallic chemistry continues to be an exciting and rapidly expanding field, which has changed considerably over the 18 years between the first edition of our textbook and the appearance of the third edition. Since 1997, nine organometallic chemists have been honored as Nobel Laureates because their work has had such an enormous impact, not only on the field, but also on related areas of the chemical sciences, especially organic synthesis. The first edition suggested that π-bond metathesis would have significant bearing on the course of organometallic chemistry. We now realize that the applications of metathesis to organic synthesis constitute one of the most significant advances in the ability to construct complex molecules in the past 50 years. In the second edition we emphasized Pd-catalyzed cross-coupling reactions, which constitute one of the most useful ways to construct new carbon–carbon bonds. In recognition of the importance of such reactions, three organometallic chemists were awarded the Nobel Prize in 2010 for their fundamental work in developing widely applicable cross-coupling methodology.

The ready availability of user-friendly software and high-speed computers has made computational chemistry and molecular modeling an important and routinely used tool for the elucidation of organometallic reaction mechanisms. High-level molecular orbital (MO) calculations have helped unravel the mysteries of catalytic cycles and have allowed chemists to develop new chemistry based on the results and predictions of these computations. Recent developments in organometallic chemistry have been highly beneficial to practitioners of materials science, who produce exciting new substances, often through organotransition metal–catalyzed polymerization reactions.

DISTINCTIVE FEATURES OF THE THIRD EDITION

Written with both undergraduate and graduate students in mind, Organometallic Chemistry introduces both audiences to their first in-depth study of the subject. The undergraduate audience will appreciate the logical progression of
topics in the early chapters that carefully, rigorously, but gently, introduces them to concepts of structure and bonding of organometallic compounds. We anticipate the graduate audience will find these early chapters a useful review of organic and inorganic chemistry concepts now applied specifically to organotransition metal complexes. Later chapters build on this foundation and take both undergraduate and graduate to new levels of understanding by introducing rigorous coverage of organometallic reaction mechanisms, more advanced topics of catalysis, carbene complexes, metathesis, transition metal–catalyzed polymerization reactions, applications of organometallic chemistry to organic synthesis, and bioorganometallic chemistry. Both audiences will benefit from the careful explanations, numerous exercises, clear illustrations, and experimental coverage.

Numerous in-chapter worked examples and exercises and expansive end-of-chapter problem sets reinforce fundamental concepts covered in the chapters. End-of-chapter problems cover a wide range of difficulty, from basic practice problems to more advanced analytical types of problems; many of these are referenced directly to the current chemical literature.

An experimental approach is used to not only teach students what is known about organometallic chemistry, but also how we know what we know. Therefore, the text includes discussions of both the classic and contemporary experiments that have revealed the fundamental concepts underlying the subject.

Real-world applications are highlighted throughout the text to engage students and reveal the relevance of organometallic chemistry to everyday life, especially as it affects the world of industry.

WHAT IS NEW IN THE THIRD EDITION

The focus of the third edition remains organotransition metal chemistry, and the order of topics is substantially the same as that found in the second edition. As thematic overview, readers will benefit from the following changes:

• **Updated and expanded coverage** of the latest developments from the field, including catalysis; carbene complexes, especially N-heterocyclic carbene (NHC) complexes; metathesis and polymerization; and applications of cross-coupling reactions to organic synthesis.

• **A new chapter on applications of organometallic chemistry to biochemistry and medicinal chemistry**, describing the synthesis and efficacy of organometallic compounds used as anticancer drugs and other kinds of pharmaceuticals.

• **Increased presentation of industrial applications**, including metathesis and Ziegler–Natta polymerization, Grubbs and Schrock metal carbene catalysts, palladium-catalyzed crossed couplings, and more.
• **Thorough discussion of carbon–hydrogen bond activation and functionalization**, which is a rapidly growing field of organic synthesis.

• **Expanded emphasis on green chemistry**, which reveals how well the principles of organotransition metal catalysis meld with the principles of green chemistry.

• **Expanded discussion of computational approaches** to molecular orbital calculations that includes coverage of the latest developments in density functional theory and a new section on applications of the quantum mechanics/molecular mechanics (QM/MM) method to the study of the structure and reactions of organometallic compounds.

• **Increased number and variety of end-of-chapter problems and worked examples.** The third edition includes 229 end-of chapter problems and 113 in-chapter exercises, a 20% increase overall compared to the preceding edition. The problems cover a broad range of difficulty, and many of the end-of-chapter exercises are referenced directly to the original literature.

• **More molecular model illustrations.** The text now includes more than 1100 illustrations and structures, about a 28% increase over the second edition. In addition to the hundreds of new illustrations, all preexisting figures have been checked and often revised for clarity and consistency. Chapter 2 features many more computer-generated MO surfaces than appeared in the second edition.

• **An emphasis on spectroscopic methods, such as nuclear magnetic resonance (NMR), infrared, and mass spectroscopy.** A special table of contents and bolded entries in the index direct readers to the sections of the text that cover these methods.

**Detailed Chapter-By-Chapter Revisions**

**Chapter 2** retains its emphasis on a qualitative approach to MO theory. However, we have also upgraded the section on computational chemistry to describe the latest developments in the use of density functional theory. A new discussion of the QM/MM method emphasizes the power of this method in calculating the structures of organometallic complexes with large ligands. The computational chemistry section introduces readers to approaches to MO calculations used by readily available commercial software packages. We make no attempt to thoroughly explain the theory behind these approaches, but instead we emphasize what each method can do and how it is applied to real chemical systems. Both qualitative and computational approaches to MO theory appear again throughout the text.

**Chapter 3** introduces the 18-electron rule as a basis to help understand the bonding of several types of ligands to transition metals. These ligand types are covered in Chapters 4 to 6, where readers will discover how ligands combine
with metals to form many unique and exquisitely beautiful structures, which are quite distinct from those found in organic chemistry. In response to reviewers’ suggestions, we have added a short section on Feltham-Enemark notation of nitrosyl complexes to Chapter 4. In addition, we have condensed the discussion of the isolobal analogy and transition metal cluster compounds—originally in Chapter 13—and moved this material to the last part of Chapter 4. Because metallocene complexes containing ansa bridges between the rings have been growing in interest, particularly in the realm of potential pharmaceutical applications, we have added a new section on these complexes to Chapter 5. In addition to covering traditional organometallic ligands, including carbenes, alkyls, hydrides, and phosphines, Chapter 6 introduces readers to new and interesting π ligands, such as extended carbon chains, graphene, and fullerenes. The sections on NMR and mass spectra in Chapters 5 and 6 have been revised and expanded. Chapters 4 to 6 contain numerous end-of-chapter problems where spectroscopic information is an essential part of the exercise. Subsequent chapters have additional spectroscopy problems.

Once readers understand the basic tenets of structure and bonding, they are ready to become acquainted with several kinds of reactions that involve organo-transition metal complexes. Chapter 7 covers reactions that occur primarily at the metal. The sections on the theory of C−H and C−C bond activation have been upgraded. Chapter 8 looks at reactions that occur primarily on ligands attached to the metal, and the material in this chapter remains substantially the same as found in the second edition. A small section on abstraction of methide and hydride from metal complexes has been added. The reactions discussed in these two chapters appear again extensively in Chapters 9 to 12. We have tried wherever possible in Chapters 7 and 8 to point out obvious parallels of organometallic reactions to those in organic chemistry.

Catalysis plays an increasingly important role in all areas of chemistry. Reactions catalyzed by organotransition metals play key roles in industrial process and in the laboratories of synthesis chemists. Chapter 9 has been shortened to eliminate the section on hydrocyanation because of space limitations, although hydrocyanation appears briefly as an end-of-chapter problem. One of the major tenets of green chemistry is the use of catalysts instead of stoichiometric reagents wherever possible. Originating in the industrial sector, green chemistry now plays an important role in the teaching laboratory where significant efforts to make experiments more environmentally friendly are ongoing and bearing fruit. Chapter 9 also contains an expanded section on green chemistry, discussing some of its basic tenets and treating more fully the concept of the environmental factor (E-Factor). Green applications to organometallic chemistry are mentioned often, especially in Chapter 12, where applications of organometallic chemistry to organic synthesis are covered.
Chapter 10 in the first edition covered metal–carbene complexes, metathesis, and polymerization reactions. This chapter was split into two chapters in the second edition, an arrangement that continues in the latest edition. Chapter 10 emphasizes the chemistry of carbene complexes. The sections on NHCs have been completely revised, and the section describing the synthesis of Schrock Mo- and W-carbene complexes has been substantially updated. New material on the dirhodium-catalyzed synthesis of cyclopropanes has been included. Chapter 11 considers metathesis and polymerization. Up-to-date material on the discovery of new metathesis catalysts by Schrock, Grubbs, and Hoveyda has been included. The synthetically useful discovery of Z-selective Schrock and Grubbs metathesis catalysts is described in a new section of the chapter. The discussion of both metathesis and Ziegler–Natta polymerization reactions has been brought up to date.

Application of organometallic chemistry to the synthesis of complex organic molecules continues to be one of the most interesting and exciting areas of organo-transition metal chemistry. Chapter 12 updates material on asymmetric hydroge- nation by Rh, Ru, and Ir complexes. One of the most exciting recent developments in organic synthesis is the development of methodology that allows C–H bonds to be activated and converted to other functional groups. Chapter 12 contains a large section on the discussion of this useful chemistry. The Pd-catalyzed conversion of aryl and alkyl halides to the corresponding C–F, C–O, C–N, and C–CF$_3$ compounds represents an outstanding achievement in synthesis that has occurred over the past 5 to 10 years. Chapter 12 details much of the chemistry related to these conversions. Most of Chapter 12 emphasizes the use of organo-transition metal compounds to catalyze the formation of new C–C bonds, often under asymmetric conditions. Accordingly, this chapter includes updated coverage of the Tsuji–Trost reaction, Heck olefination, and Stille, Suzuki, Sonogashira, and Negishi cross-coupling reactions. A new section on the Kumada-Corriu cross-coupling demonstrates that even normally reactive organomagnesium compounds can usefully serve as sources of carbon groups. Expanded coverage also appears that describes how cross-coupling reactions can construct C(sp$^3$)–C(sp$^3$) bonds.

Chapter 13, “Bioorganometallic Chemistry,” is entirely new to this edition. After a brief discussion of naturally occurring bioorganometallic compounds, this chapter provides a review of platinum-based antitumor agents. This serves as background for the following discussion of organometallic complexes that have been studied in the quest for new, more selective anticancer agents with less severe side effects than current treatments. Chapter 13 concludes with selected additional applications of organometallics—for example, in the treatment of malaria and use in radiopharmaceutical and other tracers.

Organometallic compounds are unique, useful, and esthetically pleasing. We hope readers of our book will also find this to be true and will learn much about a most important and interesting field of chemistry.
SUPPLEMENTS

The following supplementary items are available to instructors who adopt the third edition:

The Ancillary Resource Center (ARC) is a convenient, instructor-focused single destination for resources to accompany your text. Accessed online through individual user accounts, the ARC provides instructors access to up-to-date ancillaries at any time while guaranteeing the security of grade-significant resources. The ARC for Organometallic Chemistry includes all of the figures from the text in electronic format, and the solutions manual files containing the solutions to all of the exercises and problems from the textbook in a series of editable Word files.

COMPANION WEBSITE

(www.oup.com/us/spessard) The companion website houses answers to selected exercises and a list of key abbreviations found in the text.

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