

1 Introduction

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Organometallic chemistry needs no special ideas if general chemical concepts are accepted. Many organic chemists feel that metals, especially those of the transition series, have various types of bonding schemes with molecules, atoms and ligands, and that the valency of the metal may change arbitrarily. In fact, molecular compounds of transition metals have well-defined structures, such as octahedral, square planar, trigonal bipyramidal, etc, depending on the electronic state of the metal. On the other hand, organometallic compounds are generally believed to be very air- and moisture sensitive, since very well known organometallic compounds such as alkyl lithiums and Grignard reagents are vigorously hydrolyzed in solution and organoaluminums are even flammable on exposing to air. Furthermore organotransition metal complexes are active intermediates in many catalyses. These facts probably make many researchers hesitate to use apparently unstable organometallic species in the laboratory. However in recent years, by virtue of the versatility of organometallic compounds in organic synthesis under mild conditions, many organic chemists are now using organometallic compounds as catalysts as well as reagents for creating new highly regio- and stereoselective reactions. Significant developments in these fields are now considered to be highly dependent on the organometallic reagents.

Organometallic chemistry is essentially based on coordination chemistry and organic chemistry. It is not too much to say that Werner's concept of coordination compounds began the development of coordination chemistry in the last 100 years, since it provided the basis for understanding complex inorganic compounds at a molecular level. However, inorganic and organic chemistries unfortunately tended to develop quite independently. Coordination chemists have concentrated on structure and bonding in relation to spectroscopy both experimentally and theoretically, whereas organic groups have used compounds containing metal-carbon bonds as a tool of organic synthesis based on organic chemistry. As a result, inorganic chemists have provided very important structural and theoretical concepts relating to coordination compounds, though they still had resistance to handling air-sensitive organometallic compounds. Coordination chemists are now attempting to resolve problems both in solid state materials by building clusters and on the roles of metals in biology at a molecular level. On the other hand, many highly selective and efficient organic synthetic reactions and catalyses using transition and main-group metals are still developing and attracting growing interest. Selectivities in metal mediated organic reactions are now competing with those of enzymes. It is generally considered that, after the discovery of ferrocene

in 1951, organometallic chemistry has achieved explosive development. Organometallic chemists have helped to eliminate the barrier between organic and inorganic chemistry by dealing with all inorganic and organic compounds at a molecular level. As a result, the important concepts such as π -back bonding, agostic interaction, β -hydrogen elimination, reductive elimination, insertion, etc., have been introduced into the field of chemistry.

In recent years, scientists and chemists in fields other than organometallic chemistry have been frequently required, for their own purposes, to handle organometallic compounds which are believed to be very unstable and toxic. However, the problem is really not so difficult if one knows the general techniques for handling under inert gases and in vacuum. General concepts in organometallic chemistry are also not unusual, if both organic and inorganic chemistries are treated together. The purpose of this textbook is to serve as a practical guide to understand the general concepts of organometallic chemistry and methods of handling unstable compounds for graduate and undergraduate students and scientists who are not specialists in organometallic chemistry.

This book is divided in two parts: general concepts and the chemistry of individual metals, including practical synthetic methods for representative organometallic compounds. Chapters 2 and 3 summarize important fundamentals in organometallic chemistry. Chapter 4 describes experimental techniques, where the simplest ways to manipulate air-sensitive compounds are also included. Specialized techniques requiring expensive facilities are not mentioned in detail, since they have already been described in references. In Chapters 5–17, the general chemistry of individual metals is summarized with references. Half of each chapter includes practical methods for the synthesis of organometallic compounds, including experimental tricks, which are usually not found in books, although some of them are referred to the original references.