

ORGANOMETALLIC SYNTHESES

Volume 3

Edited by

R. Bruce King

John J. Eisch

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INTRODUCTION

1. Organization of the Chosen Procedures

Over 180 detailed and tested procedures for the preparation of specific organometallic compounds are offered in this Volume. In Part I are gathered procedures for the synthesis of some 87 transition metal organometallic compounds. This section is subdivided according to the principal or characteristic type of ligand bonded to the metal and is composed of these subsections: a) lanthanide and early transition metal compounds; b) metal carbonyl derivatives; c) cyclopentadienylmetal carbonyl and nitrosyl derivatives; d) compounds having two π -bonded aromatic rings; e) olefin, cyclobutadiene and acetylene π -complexes; f) allyl and pentadienyl transition metal derivatives; g) alkyl transition metal derivatives; h) methylene and methyldiene transition metal complexes; i) transition metal complexes containing organophosphorus ligands; j) transition metal derivatives containing chalcogen ligands; k) organometallic derivatives containing two different transition metals; and l) coinage metal derivatives.

In Part II are given procedures for the synthesis of some 102 nontransition metal organometallic compounds. Since the electronic hallmark of such metal centers is the absence of d or f shells in any commonly occurring oxidation state, this section is subdivided into these subsections: a) Group IA; b) Group IIA; c) Group IIB; d) Group IIIA; e) Group IVA; f) Group VA; and g) Group VIA.

In both parts the editors have sought to include procedures that give the safe, reliable synthesis of organometallic compounds that can lay some claim to significance in current chemical research. This significance may be based on various factors such as the following: a) the synthesis describes the formation of an unusual or less common structural type; b) the compound prepared is a useful intermediate in other syntheses; c) the compound is a model reagent for investigating the mechanisms of various fundamental or industrial processes, such as the Fischer-Tropsch reaction; d) the compound is a useful reagent in organic synthesis; and e) the techniques employed in the synthesis of the compound are unusual and worthy of further application, such as

metal-atom and electrochemical procedures.

Each specific or generalized procedure is organized into the following sections: an Introduction section, which discusses the available procedures and the reasons guiding the choice of the one selected; a Procedure section, which strives to describe the modus operandi, the safety concerns and pitfalls in the preparation; a Properties section that offers further physical and chemical data on the product and, where appropriate, indications of how the compound can be employed in research; and finally a Reference section, which gives both leading literature citations and supplemental comments on the procedure.

2. General Procedural Observations

Unless explicitly specified to the contrary, all reactions, purifications, and transfers involving organometallics (except Group IVA members) should be conducted under an atmosphere of anhydrous, oxygen-free nitrogen or argon. Conventions in presenting data are generally those currently observed by journals of the American Chemical Society. For spectral data, proton nmr chemical shifts are given in parts per million on the scale with reference to internal tetramethylsilane. (In some trimethylsilyl derivatives the intramolecular Me_3Si group serves as the standard for 0 ppm). Coupling constants are in units of hertz. All temperatures are given in degrees Celsius; infrared absorptions are in reciprocal centimeters; and ultraviolet peaks are in nanometers.

Hazards are inherent in most organometallic laboratory procedures. Although every effort has been made to stress particular hazards in the individual procedures, it is assumed that those chemists attempting to carry out these syntheses are experienced with the techniques for manipulating compounds that are air-, moisture-, and heat-sensitive. If not, before attempting any such work the chemist should consult Volumes 1 and 2 of "Organometallic Syntheses" (Academic Press, 1965 and 1981) for detailed discussions of appropriate techniques and safety precautions.

PREFACE

Compounds containing carbon-metal bonds continue to occupy a prominent position in many aspects of modern chemistry. During the past thirty years these organometallic compounds have revolutionized the practice of both fundamental and industrial chemical synthesis: they are now recognized as superb stoichiometric reagents for the selective formation of C-C, C-H, C-O, C-X, C-N and other carbon-metal bonds and, especially among the transition-metal representatives, they display unusual catalytic activity in a host of oxidation, reduction, isomerization, oligomerization, carbonylation and polymerization processes that have reshaped the chemical industry. Moreover, the diversity in chemical bonding exhibited by organometallic compounds has attracted the curiosity of both structural chemists and kineticists, who employ these compounds to test and refine their understanding of equilibrated and dynamic molecular structure.

In view of the broad importance of organometallic compounds, chemists of diverse backgrounds and interests are faced with the problem of preparing pure organometallic compounds in a safe and reliable manner. Because many organometallic compounds are poisonous, spontaneously flammable in air and generally prone to be chemically changed by oxygen, moisture and heat, their preparation requires specialized laboratory techniques and explicit instructions for their manipulation and isolation. Indeed, procedures for the preparation of the more common organometallic compounds have, accordingly, been included from time to time in the authoritative compilations, "Organic Syntheses" and "Inorganic Syntheses". However, many important procedures must still be ferreted out of the voluminous chemical literature. Selection of a reliable procedure or the location of descriptions of essential techniques or apparatus is a formidable task for the research chemist, who must sift through the copious literature of organometallic chemistry.

These considerations motivated the editors more than twenty years ago to launch the series, "Organometallic Syntheses". The purpose of this publication has been the presentation of clear, safe and reliable procedures for the preparation of important types of organometallic compounds. Accordingly, Volume 1, written by R. B. King and published in 1965, presented detailed descriptions for the preparation of various transition-metal organometallic compounds, as well as a general discussion of special laboratory techniques necessary for the safe and successful performance of such procedures (reactions under pressure or with photochemical promotion; procedures for the purification, identification, and analysis of the products; and safety precautions). Volume 2, written by J. J. Eisch and published in 1981, analogously offered reliable descriptions for the preparation of nontransition-metal organometallic compounds and

a discussion of relevant experimental techniques (purification of sensitive solids and liquids; provision for an inert atmosphere; transfers of sensitive compounds; diverse analytical methods; and the safe manipulation of pyrophoric and explosively hydrolyzable substances).

With the appearance of Volume 3 of "Organometallic Syntheses", several major changes in the series have been made. In light of the burgeoning of organometallic chemistry in the twenty years since the appearance of Volume 1, the editors have decided to avail themselves of the rich experience of the organometallic chemistry community in the ongoing task of offering reliable preparative procedures. Thus with this Volume, "Organometallic Syntheses" has been transformed from an authored work to an edited work. With this change has also come a change in publisher and in format. In moving from Academic Press to Elsevier Science Publishers, this enterprise has the backing of an outstanding publisher of the organometallic chemical literature. Elsevier has published the Journal of Organometallic Chemistry since its inception in 1962.

In moving to publishing in a camera-ready format, the editors hope to reduce the time between the selection of the organometallic procedures and their availability to the chemistry community. This same international community of chemists has played the key role in the preparation of Volume 3. The editors have reviewed the research literature for the last five years and have sought to identify those types of organometallic compounds of greatest current interest in research and to contact those chemists most experienced with the synthesis of such compounds. This effort was greatly aided by the opinions of the Editorial Advisory Board. Upon the basis of this literature survey, then, invitations for the submission of procedures were sent to those chemists judged to be most competent to prepare safe and reliable descriptions of their work. The proposals received from this solicitation were evaluated by the editors and those of greatest interest were selected for this volume. The chosen proposers were then invited to submit detailed manuscripts for the preparation of specific compounds. All such manuscripts were subjected to external review and the comments from the reviewers and from the editors were transmitted to the authors. The authors then prepared the final camera-ready copy in the light of such criticisms and editorial comment.

The editors wish to declare their intention to prepare further volumes of "Organometallic Syntheses", on a biennial or triennial cycle. We would therefore be grateful to receive both general suggestions concerning the mode of preparing such volumes, as well as specific suggestions as to syntheses for inclusion in Volume 4 and subsequent volumes.

R. B. King

J. J. Eisch

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B.J.M. Bennetau and J.P. Dunogues
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M. Ishikawa
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