# INORGANIC SYNTHESES

## Volume 25

Harry R. Allcock, Editor-in-Chief

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**HARRY R. ALLCOCK**

*Department of Chemistry*
*Pennsylvania State University*

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WILEY

A Wiley-Interscience Publication
JOHN WILEY & SONS
*New York Chichester Brisbane Toronto Singapore*

Published by John Wiley & Sons, Inc.

***Library of Congress Catalog Number: 39-23015***

ISBN 0-471-61874-8

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

This volume is dedicated to W. Conard Fernelius (1905–1986), outstanding teacher, researcher, and scholar, who was one of the founders of *Inorganic Syntheses* and who continued throughout his life to be a leader in its development.

# PREFACE

The synthesis of chemical compounds is the bedrock on which all other areas of chemistry depend. In this sense, *Inorganic Syntheses* represents an evolving compilation of techniques and ideas that provide a cross section of activity in the field at a particular time. Providing such a cross section is no easy task. At the present time, the field of inorganic synthesis is undergoing significant changes. Starting from its traditional foundation in small-molecule nonmetal chemistry and metal coordination chemistry, it has in recent years absorbed the dramatic expansion of activity in transition metal organometallic chemistry and cluster chemistry. More recently, connections have been developed to polymer chemistry, ceramic science, electroactive solids, and pharmacology.

The increasing involvement of inorganic chemists with the fields of polymer chemistry, solid state science, and ceramic science is based on the precept that the experimental techniques, theories, and models of small-molecule inorganic chemistry can be applied to the infinitely more complex molecules found in these other areas. Synthetic chemists can play a major role in the design and preparation of new materials if a significant conceptual hurdle can be overcome. This hurdle is the dividing line between the well-understood behavior of small molecules (2–500 atoms) and the more complex behavior of linear macromolecules and three-dimensional, covalently bonded solids. It is a dividing line between compounds that can be characterized easily by modern methods and those that cannot, and between species with absolute compositions and precise molecular weights and substances with variable formulas and structures that can be understood only in statistical rather than absolute terms. Yet the knowledge and experience available within the community of inorganic chemists could have a profound influence on the development of new supramolecular systems, on which much of our advanced technology increasingly depends.

For this reason I have included in this volume a few examples of inorganic polymer syntheses (Chapter 2) and preparations of inorganic ring

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Previous volumes of *Inorganic Syntheses* are available. Volumes I–XVI can be ordered from R. E. Krieger Publishing Co., Inc., P.O. Box 9542, Melbourne, Florida 32901; Volume XVII is available from McGraw-Hill, Inc.; subsequent volumes can be obtained from John Wiley & Sons, Inc.

systems (Chapter 1), which constitute models for more complex molecules and may eventually serve as reaction intermediates for polymers or for main group solid state syntheses. Chapter 3 provides a brief glimpse of the emerging role being played by synthesis in the development of pharmacologically active inorganic compounds. Chapter 4 contains examples of small-molecule coordination complexes and related compounds—the traditional core of inorganic chemistry. In addition, and in accordance with the format of previous volumes of *Inorganic Syntheses,* a section (Chapter 5) is set aside for transition metal organometallic compounds, including species with metal–metal bonds and cluster molecules. In this respect, I have been fortunate to be assisted by Gregory L. Geoffroy, who gathered together and edited the syntheses in this section. I thank him for his contribution to this volume.

Synthetic chemistry of any kind is not a trivial activity, and it should be pursued only by those who can recognize and avoid the inherent safety risks that exist. Thus, most of the procedures given in this volume should be undertaken only by individuals who are already competent synthetic chemists or who are working directly under the close supervision of someone who is. Potential hazards are identified throughout this volume, and these warnings should be taken seriously.

The main purpose of *Inorganic Syntheses* is to provide illustrative synthetic methods that are *reliable.* Thus, all the syntheses reported here have been checked experimentally by independent investigators. I greatly appreciate the contributions of those who submitted the syntheses and the truly essential efforts of the individuals who did the checking. Major assistance with the routing of correspondence and manuscripts to authors and checkers, and maintaining the overall momentum and organization of this volume, was provided by Noreen Allcock. I would also like to thank the members of the Editorial Board for their helpful suggestions and support. The contributions by Thomas Sloan, who compiled the index and answered nomenclature questions, and the advice of Duward Shriver on procedural matters, are particularly appreciated.

HARRY R. ALLCOCK

*University Park, Pennsylvania*
*February 1988*

# NOTICE TO CONTRIBUTORS AND CHECKERS

The *Inorganic Syntheses* series is published to provide all users of inorganic substances with detailed and foolproof procedures for the preparation of important and timely compounds. Thus the series is the concern of the entire scientific community. The Editorial Board hopes that all chemists will share in the responsibility of producing *Inorganic Syntheses* by offering their advice and assistance in both the formulation of and the laboratory evaluation of outstanding syntheses. Help of this kind will be invaluable in achieving excellence and pertinence to current scientific interests.

There is no rigid definition of what constitutes a suitable synthesis. The major criterion by which syntheses are judged is the potential value to the scientific community. For example, starting materials or intermediates that are useful for synthetic chemistry are appropriate. The synthesis also should represent the best available procedure, and new or improved syntheses are particularly appropriate. Syntheses of compounds that are available commercially at reasonable prices are not acceptable. We do not encourage the submission of compounds that are unreasonably hazardous, and in this connection, less dangerous anions generally should be employed in place of perchlorate.

The Editorial Board lists the following criteria of content for submitted manuscripts. Style should conform with that of previous volumes of *Inorganic Syntheses*. The introductory section should include a concise and critical summary of the available procedures for synthesis of the product in question. It should also include an estimate of the time required for the synthesis, an indication of the importance and utility of the product, and an admonition if any potential hazards are associated with the procedure. The Procedure should present detailed and unambiguous laboratory directions and be written so that it anticipates possible mistakes and misunderstandings on the part of the person who attempts to duplicate the procedure. Any unusual equipment or procedure should be clearly described. Line drawings should be included when they can be helpful. All safety measures should be stated clearly. Sources of unusual starting materials must be given, and, if possible, minimal standards of purity of reagents and solvents should be stated. The scale should be reasonable for normal laboratory operation, and any problems involved in scaling the procedure either up or down should be discussed. The criteria for judging the purity of the final product should be delineated clearly. The section on Properties should supply and discuss those physical and chemical characteristics that are relevant to judging the purity of the product and to permitting its handling and use in an intelligent manner. Under References, all pertinent literature citations should be listed in order. A style sheet is available from the Secretary of the Editorial Board.

The Editorial Board determines whether submitted syntheses meet the general specifications outlined above, and the Editor-in-Chief sends the manuscript to an independent laboratory where the procedure must be satisfactorily reproduced.

Each manuscript should be submitted in duplicate to the Secretary of the Editorial Board, Professor Jay H. Worrell, Department of Chemistry, University of South Florida, Tampa, FL 33620. The manuscript should be typewritten in English. Nomenclature should be consistent and should follow the recommendations presented in *Nomenclature of Inorganic Chemistry*, 2nd ed., Butterworths & Co., London, 1970, and in *Pure and Applied Chemistry*, Volume 28, No. 1 (1971). Abbreviations should conform to those used in publications of the American Chemical Society, particularly *Inorganic Chemistry*.

Chemists willing to check syntheses should contact the editor of a future volume or make this information known to Professor Worrell.

# TOXIC SUBSTANCES AND LABORATORY HAZARDS

Chemicals and chemistry are by their very nature hazardous. Chemical reactivity implies that reagents have the ability to combine. This process can be sufficiently vigorous as to cause flame, an explosion, or, often less immediately obvious, a toxic reaction.

The obvious hazards in the syntheses reported in this volume are delineated, where appropriate, in the experimental procedure. It is impossible, however, to foresee every eventuality, such as a new biological effect of a common laboratory reagent. As a consequence, *all* chemicals used and *all* reactions described in this volume should be viewed as potentially hazardous. Care should be taken to avoid inhalation or other physical contact with all reagents and solvents used in procedures described in this volume. In addition, particular attention should be paid to avoiding sparks, open flames, or other potential sources that could set fire to combustible vapors or gases.

A list of 400 toxic substances may be found in the *Federal Register,* Vol. 40, No. 23072, May 28, 1975. An abbreviated list may be obtained from *Inorganic Syntheses,* Volume 18, p. xv, 1978. A current assessment of the hazards associated with a particular chemical is available in the most recent edition of *Threshold Limit Values for Chemical Substances and Physical Agents in the Workroom Environment* published by the American Conference of Governmental Industrial Hygienists.

The drying of impure ethers can produce a violent explosion. Further information about this hazard may be found in *Inorganic Syntheses*, Volume 12, p. 317. A hazard associated with the synthesis of tetramethyldiphosphine disulfide [*Inorg. Synth.,* **15,** 186 (1974)] is cited in *Inorganic Syntheses,* Volume 23, p. 199.

# CORRECTION TO VOLUME 24

## DICARBONYL($\eta^5$-CYCLOPENTADIENYL)(2-METHYL-1-PROPENYL-$\kappa C^1$)IRON AND DICARBONYL($\eta^5$-CYCLOPENTADIENYL)($\eta^2$-2-METHYL-1-PROPENE)IRON(1+) TETRAFLUOROBORATE

### SUBMITTED BY MYRON ROSENBLUM*

The preparation of dicarbonyl($\eta^5$-cyclopentadienyl)(2-methyl-1-propenyl-$\kappa C^1$)iron requires 3-chloro-2-methyl-1-propene (methallyl chloride), not the reagent given in Reference 1, p. 165.[1]

### *References*

1. M. Rosenblum, W. P. Giering, and S.-B. Samuels, *Inorg. Synth.* **24,** 163 (1986).

*Department of Chemistry, Brandeis University, Waltham, MA 02254.

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