Organometallic Compounds

SYNTHESIS, STRUCTURE, AND THEORY

Proceedings of the First Symposium
of the
Industry-University Cooperative Chemistry Program
of the
Department of Chemistry, Texas A&M University
April 17–20, 1983

Editor

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Published for the IUCCP by Texas A&M University Press College Station, Texas

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Library of Congress Cataloging in Publication Data Main entry under title:

Organometallic compounds.

Includes bibliographical references and indexes.

1. Organometallic compounds—Congresses. I. Shapiro,
Bernard L. II. Texas A & M University. Industry—University
Cooperative Chemistry Program.

QD410.07324 1983 547'.05 83-45137
ISBN 0-89096-170-0

Foreword

The Department of Chemistry at Texas A&M University has been pleased to initiate its IUCCP Symposium series with the symposium on the Structure, Theory and Synthesis of Organometallic Compounds. This theme is appropriate not only because it occupies a currently important position in both industrial and academic chemistry, but because it allows us to further honor our former colleague, Professor Minoru Tsutsui, an outstanding organometallic chemist who was instrumental in the development of the IUCCP.

Through the support of the IUCCP sponsors and the dedicated work of many individuals, the Symposium proved to be extremely successful both scientifically and socially, and has set a high standard for the future symposia in this series. My sincere thanks go to all who have helped to make this possible.

May 1983

Joseph B. Natowitz

Professor and Head Department of Chemistry Texas A&M University

Preface

The Industry-University Cooperative Chemistry Program (IUCCP) was formed as a means of effecting closer cooperation between academic and industrial scientists. Through the vigorous efforts of Professors C. S. Giam, A. E. Martell and M. Tsutsui, and, later, Professors J. B. Natowitz and A. Clearfield, the interest of a number of industrial firms was aroused.

A steering committee was formed in 1982 under the chairmanship of Dr. Howard L. Pilat, Vice President - Technology, of the Celanese Chemical Company. After a year's deliberation this committee formulated what has become the Industry-University Cooperative Chemistry Program (IUCCP). industrial firms enrolled as charter sponsors; their cooperation and support has been largely responsible for the success of this Symposium on Organometallic Compounds, the IUCCP's first major undertaking. It presages a long and fruitful collaboration as our program grows and enlarges its scope.

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We also wish to thank the New York Academy of Sciences for their support of, and participation in, this conference. These involvements clearly demonstrate the high esteem in which the Academy holds Minoru Tsutsui.

May 1983

Abraham Clearfield

Professor of Chemistry Director, IUCCP

This volume is the first in an annual series of Proceedings of the Research Symposia sponsored by the Industry-University Cooperative Chemistry Program of the Department of Chemistry of Texas A&M University. The subject matter of these symposia will change from year to year, but will in all cases be focussed on some specific area of great current

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interest to chemists in industry, the academic world, and elsewhere.

Consistent with the guidelines of timeliness and importance, it is planned to have these Proceedings volumes appear as rapidly as possible after the Symposia. To this end, the articles have been prepared by the authors in a camera-ready form. For the present volume, the authors have mostly provided manuscripts based quite closely on their lectures at the Symposium, while in a few cases a somewhat more widely based document on the same subject has been prepared. The articles appear in the order in which the corresponding lectures were presented at the Symposium.

Enquiries concerning the Research Symposia, as well as other aspects of the IUCCP, should be directed to: Professor Abraham Clearfield, Director, IUCCP, Department of Chemistry, Texas A&M University, College Station, Texas 77843, U.S.A.

May 1983

Bernard L. Shapiro

Professor of Chemistry Editor, IUCCP Proceedings Volumes

Acknowledgments

The planning and execution of a symposium as large and complex as this one is a major undertaking requiring the cooperation and participation of a number of dedicated people.
The selection of topics and speakers was largely due to the
Organizing Committee: John F. Cole (Shell), John F. Knifton
(Texaco), P. Larry Kuch (Sohio), Jerry D. Unruh (Celanese),
and David E. Bergbreiter and Donald J. Darensbourg (Texas
A&M). We tried to have as speakers a blend of both established leaders in their respective fields and relatively
young chemists whose work was judged to be outstanding. The
Committee's wisdom in this respect contributed immeasurably
to the success of the Symposium.

Special thanks must also go to the session Chairpersons Marcetta Y. Darensbourg (Texas A&M), Jerry Unruh (Celanese), Tom Johnson (Shell), Dave Bergbreiter (Texas A&M) and Larry Kuch (Sohio), who handled their duties so ably.

I am indebted more than I can say to those who worked behind the scenes. First and foremost is my indomitable

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secretary and assistant Elizabeth Porter who helped in a thousand different ways. A special thanks is also due to Phil Rudolf and his able staff of graduate students who unobtrusively provided transportation, slide projection, and generally saw to our needs and comforts. John Richards and his staff, especially Paula Tallant, arranged the facilities in the University Center and prepared the conference materials. Finally, a special thanks to Dr. Lela Edwards and the staff of our very fine Continuing Education Program which make it possible to carry out symposia such as this at Texas A&M.

May 1983

Abraham Clearfield

Professor of Chemistry Program Chairman, 1983 IUCCP Symposium

Minoru Tsutsui 1918–1981



The first IUCCP Symposium and this Proceedings volume which arose from it are respectfully dedicated to the memory of Dr. Minoru Tsutsui, Professor of Chemistry at Texas A&M University, 1968–1981.

It is a pleasure and an honor to write a few words about a good friend and colleague, Minoru Tsutsui, former Professor of Chemistry in our Department, who died unexpectedly on March 10, 1981.

Born in Japan, Minoru received the B.A. degree in chemistry at Gifu University, and an M.S. in organic chemistry at Tokyo University of Arts and Sciences. After coming to the U.S., he received an M.S. degree in 1953 and the Ph.D. in organic chemistry in 1954 at Yale University, working under H. H. Zeiss. His dissertation on polyphenyl chromium compounds described in detail the synthesis of these compounds and correctly formulated them as π -bonded complexes. This initial work was part of the modern renaissance in organometallic chemistry.

In 1968, after eight years at New York University, Minoru joined the faculty at Texas A&M University, where he pioneered the synthesis of unusual metalloporphyrins and carried out several other studies in organometallic chemistry. His extensive list of publications, monographs and edited books in these areas speaks for itself.

Having seen at first hand the destruction wrought by the second World War, he long ago resolved to work for world peace through international cooperation in the scientific community on a global scale, and it is this type of achieve-

ment that stands out as his major contribution - the art of bringing scientists together to exchange ideas, to promote research and to advance international understanding. There are few scientists anywhere who could match his skills in this respect. The following are a few examples of these activities:

As an officer of the New York Academy of Sciences, he stimulated the conference activities of the Academy and led a vigorous drive for increased federal funding for scientific research.

He provided the initiative that resulted in the establishment of the Journal of Coordination Chemistry, which he served as co-editor for ten years.

He established the Southwest Science Forum as an affiliate of the New York Academy of Sciences.

Professor Tsutsui was a co-organizer of the International Conference on Organometallic Chemistry, held in Corpus Christi, Texas in 1978.

He was the principal activator and organizer of the first Three-Nation Conference on Organometallic and Inorganic Chemistry involving China, Japan, and the United States, held in Peking, Peoples Republic of China in 1980. The second such conference was held in 1982 in Shanghai, and will be followed by other meetings in the

participating countries.

Finally we should look at our own IUCCP, for it was Minoru Tsutsui who had the magnetic personality to bring industry and the Texas A&M University Chemistry Department together and to start the IUCCP ball rolling.

In accordance with their educational ideals, Minoru and Ethel Tsutsui endowed "The Minoru and Ethel Tsutsui Distinguished Graduate Research Award in Science," administered by the New York Academy of Sciences. This bequest provides a yearly award of \$1,500 to an American doctoral student for excellence in graduate research.

After Minoru's death, which was shocking because of its untimeliness, many messages were received from his friends throughout the world:

"His love of organometallic chemistry and his deep concern for the future of mankind qualify him for honorary citizenship in the international organometallic chemistry community." (Dr. Oren F. Williams, National Science Foundation, Washington, D.C.)

"He was very much respected by all who knew him because of his kindness and friendly attitude and because of his scientific achievements. He wholeheartedly supported scientific cooperation between our countries."

(Professor A. Shilov, Academy of Sciences, Moscow, USSR)

"He was the most active advocate of the organization of co-investigation between the chemists of the USA and the Soviet Academy of Sciences." (Professor G. Razuvaev, USSR)

"We are all deeply impressed with his enthusiasm both in scientific activity and in promotion of friendship among scientists of our three countries [U.S., Japan, China]." (Professor Dai Lixin, Academy of Sciences, Shanghai, People's Republic of China)

"A big loss to the American chemistry community as well as to the international chemistry community, especially in the field of organometallic chemistry." (Dr. Jennie Liu, Academy of Sciences, Peking, People's Republic of China)

"His friends all over the world miss him very much and wish to have some suitable activity to commemorate his great contributions to organometallic chemistry and homogenous catalysis." (Professor Yoshio Ishii, Chubu Institute of Technology, Nagoya, Japan)

"He was a great chemist and a dear friend, and we shall miss him." (Professor Harry B. Gray, California Institute of Technology, Pasadena, California)

With Harry, I would like to state in behalf of all of us, Minoru was a great chemist, a good friend, a unique organizer, and we miss him very much.

May 1983

Arthur E. Martell

Distinguished Professor of Chemistry Head, Department of Chemistry, 1966-1980 Texas A&M University

In his lifetime, Minoru Tsutsui had a major impact upon the scientific activities and the leadership functions of the New York Academy of Sciences. His contributions to the Academy spanned a period of more than 25 years. He was chairman of the Chemistry Section in 1962; he organized the Organometallic Section in 1963 and served as its first chairman. He served in the offices of Councillor (1963-1968) and Vice President (1965-1966), and in 1968, he was elected President of the New York Academy. Professor Tsutsui's commitment to the Academy did not diminish when he moved to Texas A&M University; he continued to serve as a member of the Board of Governors. He also founded "The Southwest Science Forum" as a regional affiliate of the New York Academy of Sciences.

Professor Tsutsui was honored several times by the Academy. In recognition of his scientific accomplishments,

he was elected as a fellow of the Academy in 1962. He was the recipient of the Academy's A. Cressy Morrison award for his pioneering research in the field of organometallic chemistry. In recognition of his scientific achievements and his service to the international scientific community, he was chosen to be a life member of the Academy in 1968.

To honor Professor Tsutsui's lifelong commitment to the education of young scientists, the New York Academy of Sciences has created "The Minoru and Ethel Tsutsui Distinguished Graduate Research Award in Science." This award will be granted each year to an outstanding graduate student to recognize his or her research accomplishments. It is quite fitting that the first recipient of this award was a graduate student at Texas A&M University.

Throughout his association with the Academy, Professor Tsutsui was interested in scientific policy and often spoke out on important issues. Aspects of his concern for the future of science in the United States and abroad were expressed in his Presidential Address which was delivered to the New York Academy of Sciences in 1968. The theme of the address focussed upon the means by which scientific cooperation between nations could be improved. He "proposed the creation of private organizations within every nation, free from government control and allowing the greatest number of

scientists to contribute their hearts and minds to solving those problems which are common to all nations and above international politics. Such organizations must be concerned with the stimulation and development of science; with the education of the world's people as their first priority; and with teaching that science creates economy, strength and human well-being." Throughout his life, Professor Tsutsui expressed his concern for the development of science for mankind. As he stated, "Science is for a better life and for construction of a better world. It is for the buildup of a peaceful human life, not for politics and, of course, not for war. Science is not a weapon for making rich countries richer but is for us and for all human welfare."

Minoru Tsutsui's influence on science policy extended beyond the Academy. Because of his reputation as a scientist and spokesman for the scientific community, his advice was sought by important government leaders, including a President of the United States. He spoke out strongly for what he believed in. In a still relevant statement he made in 1968, Professor Tsutsui remarked that "We in the United States are facing a very real budget cut and, even worse, an unrealistic disproportion of funds allocated between applied and basic research. If allowed to continue, can we expect anything less than a disastrous undermining of our ability to educate,

encourage, and produce continued economic growth and further public well-being?"

The New York Academy of Sciences has benefitted greatly from the loyal support of Minoru and Ethel Tsutsui. Their contributions will have a continuing and lasting influence upon the Academy.

April 1983

Stephen A. Koch

Chairman, Organometallic Section New York Academy of Sciences

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