

Organometallic Chemistry

edited by H. ZEISS

Ed. 542
Z-17

ORGANOMETALLIC CHEMISTRY

Edited by

H. ZEISS

Research Associate

Monsanto Chemical Company

Dayton, Ohio



American Chemical Society

Monograph Series

1963.4 9-

REINHOLD PUBLISHING CORPORATION, NEW YORK
CHAPMAN & HALL, LTD., LONDON

Copyright © 1960 by
REINHOLD PUBLISHING CORPORATION

All rights reserved

Library of Congress Catalog Card Number: 60-15994

Photocomposed by THE SCIENCE PRESS, INC., Lancaster, Pa.

Printed in the United States of America

THE GUINN CO., INC.
New York 14, N. Y.

CONTRIBUTORS

- HERBERT C. BROWN, *Department of Chemistry, Purdue University, Lafayette, Indiana*
- J. CHATT, *Akers Research Laboratories, Imperial Chemical Industries, Ltd., Welwyn, Herts., England*
- G. E. COATES, *Chemistry Department, University of Durham, England*
- HENRY GILMAN, *Department of Chemistry, Iowa State University, Ames, Iowa*
- F. GLOCKLING, *Chemistry Department, University of Durham, England*
- ROLF HUISGEN, *Institut für Organische Chemie, University of Munich, Germany*
- H. D. KAESZ, *Department of Chemistry, Harvard University, Cambridge, Massachusetts*
- P. L. PAUSON, *Department of Chemistry, Royal College of Science and Technology, Glasgow, Scotland*
- JAMES W. RICHARDSON, *Department of Chemistry, Purdue University, Lafayette, Indiana*
- F. G. A. STONE, *Department of Chemistry, Harvard University, Cambridge, Massachusetts*
- L. M. VENANZI, *Chemistry Department, Oxford University, England*
- HANS J. S. WINKLER, *Department of Chemistry, Iowa State University, Ames, Iowa*
- H. ZEISS, *Research and Engineering Division, Monsanto Chemical Company, Dayton, Ohio*
- KARL ZIEGLER, *Max-Planck-Institut für Kohlenforschung, Mülheim/Ruhr, Germany*

GENERAL INTRODUCTION

American Chemical Society's Series of Chemical Monographs

By arrangement with the Interallied Conference of Pure and Applied Chemistry, which met in London and Brussels in July, 1919, the American Chemical Society was to undertake the production and publication of Scientific and Technologic Monographs on chemical subjects. At the same time it was agreed that the National Research Council, in cooperation with the American Chemical Society and the American Physical Society, should undertake the production and publication of Critical Tables of Chemical and Physical Constants. The American Chemical Society and the National Research Council mutually agreed to care for these two fields of chemical progress. The American Chemical Society named as Trustees, to make the necessary arrangements of the publication of the Monographs, Charles L. Parsons, secretary of the Society, Washington, D. C.; the late John E. Teeple, then treasurer of the Society, New York; and the late Professor Gellert Alleman of Swarthmore College. The Trustees arranged for the publication of the ACS Series of (a) Scientific and (b) Technological Monographs by the Chemical Catalog Company, Inc. (Reinhold Publishing Corporation, successor) of New York.

The Council of the American Chemical Society, acting through its Committee on National Policy, appointed editors (the present list of whom appears at the close of this sketch) to select authors of competent authority in their respective fields and to consider critically the manuscripts submitted.

The first Monograph of the Series appeared in 1921. After twenty-three years of experience certain modifications of general policy were indicated. In the beginning there still remained from the preceding five decades a distinct though arbitrary differentiation between so-called "pure science" publications and technologic or applied science literature. By 1944 this differentiation was fast becoming nebulous. Research in private enterprise had grown apace and not a little of it was pursued on the frontiers of knowledge. Furthermore, most workers in the sciences were coming to see the artificiality of the separation. The methods of both groups of workers are the same. They employ the same instrumentalities, and frankly recognize that their objectives are common, namely, the search for new knowledge for the service of man. The officers of the Society therefore combined the two editorial Boards in a single Board of twelve representative members.

Also in the beginning of the Series, it seemed expedient to construe rather broadly the definition of a Monograph. Needs of workers had to be recognized. Consequently among the first hundred Monographs appeared works in the form of treatises covering in some instances rather broad areas. Because such necessary works do not now want for publishers, it is considered advisable to hew more strictly to the line of the Monograph character, which means more complete and critical treatment of relatively restricted areas, and, where a broader field needs coverage, to subdivide it into logical subareas. The prodigious expansion of new knowledge makes such a change desirable.

These Monographs are intended to serve two principal purposes: first, to make available to chemists a thorough treatment of a selected area in form usable by persons working in more or less unrelated fields to the end that they may correlate their own work with a larger area of physical science discipline; second, to stimulate further research in the specific field treated. To implement this purpose the authors of Monographs are expected to give extended references to the literature. Where the literature is of such volume that a complete bibliography is impracticable, the authors are expected to append a list of references critically selected on the basis of their relative importance and significance.

AMERICAN CHEMICAL SOCIETY

BOARD OF EDITORS

WILLIAM A. HAMOR, *Editor of Manuscripts*

Associates

L. W. BASS
E. W. COMINGS
HENRY EYRING
WILLIAM A. GRUSE
NORMAN HACKERMAN
C. G. KING

S. C. LIND
C. H. MATHEWSON
LAURENCE L. QUIL
W. T. READ
ARTHUR ROE
OLIVER F. SENN

PREFACE

The extraordinary convergence of organic and inorganic chemistry in the metallocene and metallarene structures has provided a new area of mutual interest shared by experimental and theoretical chemists alike. Yet this is only one of the truly exciting resurgences occurring in organometallic chemistry. The enthusiasm readily discernible in the communications appearing on this subject is documented by the rapidly increasing numbers of papers and scientists devoted to the study of the carbon-metal compounds. The universality of effort and the increase in scientific intercourse between inorganic and organic chemists permit the optimistic view that the artificial barriers which existed formerly between organic and physical disciplines are being leveled at this border also.

As is true in all fields undergoing rapid expansion, the problem of merely reporting significant advances is difficult enough. To attempt a critical evaluation of the accumulating data and results for inclusion in a permanent reference text is next to impossible at this stage. On the other hand, the chemical literate must be informed of new lines of progress having significance and, one hopes, major scientific merit. This latter consideration led to the present effort.

This monograph, then, is not a comprehensive survey of organometallic chemistry. In fact, it does not contain an exhaustive treatment of any one subject. It does consist of a series of research subjects which are *under active investigation—at the present time—by their respective authors*. Nor can it be claimed that the choice of subjects encompasses the entire reach of organometallic research. It is true, however, that the selection includes some of the chemical foci currently producing new knowledge in prodigious quantity; and further, the information to be found in these pages is straight from the source. The intent of this monograph, therefore, is to bring to the graduate student and the more advanced chemist a reliable account of contemporary research in organometallic chemistry.

The arrangement of chapters in this volume is arbitrary and the responsibility of the editor. Little justification can be offered for the particular order chosen beyond the choice of the topic of "Carbon-Metal Bonding" for Chapter 1. In this case a consideration of the present state of theory regarding this type of chemical combination will be useful and rewarding when encountering the specific sigma- and pi-bonded compounds and complexes in subsequent chapters.

No attempt has been made to equate styles of presentation, since it is held that each author best knows how to present his own work. Indeed it is

hoped that each chapter will delineate the character and personality of its author.

Finally, I wish to acknowledge personally my indebtedness to former students at Yale and to my associates, past and present, who have aided and in many ways stimulated and advanced my own interest in organo-metallic chemistry. I wish also to thank Eva J. Cox, Magdalene B. Peacock and Betty D. Zeiss for their invaluable assistance in preparing manuscript and reading proof.

Sulphur Grove, Ohio
August, 1960

HAROLD H. ZEISS

CONTENTS

PREFACE	vii
1. CARBON-METAL BONDING, James W. Richardson	1
Introduction	1
Single Bonds, Polar and Nonpolar	2
MO Description of HeH^+	2
The Antibonding Wave Function	4
Correlation Diagram	5
Octahedral Transition-Metal Complexes	6
Orbitals for Octahedral Complexes	7
Complexes With Simple Ligands	7
Unsaturated Ligands— $\text{Fe}(\text{CN})_6^{-4}$	10
Carbonyl Compounds	12
Correlation Diagram for $\text{Ni}(\text{CO})_4$	12
Sigma Bonding Systems	14
Pi Bonding Systems	15
Charge Distribution in $\text{Ni}(\text{CO})_4$	16
Bond Orders in $\text{Ni}(\text{CO})_4$	18
Bis-Cyclopentadienyl Compounds	20
Orbitals for Bis-Cyclopentadienyl Compounds	21
Correlation Diagram and Bond Properties	22
Magnetic Properties	25
Charge Distributions	26
Representation of Bonding by "Equivalent Orbitals"	26
Stability of Alkyl and Aryl Transition-Metal Compounds	28
Review	28
Comparison of Methyl and Halogen Bonding	29
Conditions for Stability	32
Conclusion	34
2. BENZYNE CHEMISTRY, Rolf Huisgen	36
Benzyne Type Intermediates in Nucleophilic Aromatic Substitutions	36
History and Formulation of Benzyne	37
Evidence from Rearrangements in Nucleophilic Aromatic Substitutions	38
The Mechanism of Aryne Formation	51
Two-step Reaction in Liberation of Benzyne with Organolithium Compounds	52

The Reaction of Halobenzenes with Alkali Amide in Liquid Ammonia	54
Kinetics of the Reaction of Halobenzenes with Lithium Piperidide in Ether	55
Rate and Nature of the Metalating Agent	58
Rate and Nature of the Aryl Group	60
Other Routes to Arynes	62
Relation to Other Eliminations	63
Typical Reactions of Arynes	65
Phenylation of Carbanions	65
Benzyne as Dienophile	66
Ring Closure Reactions	68
Catalytic Arylation of Aryl Chlorides	71
Quantitative Data from Competition Experiments and the Nature of Arynes	73
Characterization of Benzyne as Intermediate	73
Selectivity Differences of Arynes	74
The Nucleophilicity Scale towards Aryne as Reference Acid	76
Orientation in Addition to Arynes	78
Structure of benzyne	81
3. VINYLMETALLICS, <i>H. D. Kaesz and F. G. A. Stone</i>	88
Introduction	88
Vinyl Compounds of Alkali Metals and Magnesium	89
Alkali Metals	89
Magnesium	91
Vinyl Compounds of the Group IIb Metals	92
Vinyl Compounds of the Group III Elements	102
Boron	103
Aluminum	113
Thallium	114
Silicon	115
Germanium	118
Tin	121
Lead	127
Vinyl Compounds of the Group V Elements	128
The Infrared Spectra of Some Vinyl Compounds	136
4. ORGANOBORANES, <i>Herbert C. Brown</i>	150
Introduction	150
Synthesis of Organoboranes <i>via</i> Organometallics	151
Hydroboration	152
Early Observations	152

Experimental Procedures	156
Scope and Stoichiometry	158
Directive Effects	160
Bis-3-methyl-2-butylborane as a Selective Hydroborating Agent	164
Cyclic Olefins. Stereochemistry of Hydroboration	166
Hydroboration of Dienes	169
Hydroboration of Acetylenes	170
Reactions of Organoboranes	171
Thermal Behavior	171
Isomerization	173
Displacement Reactions	177
Redistribution Reactions	181
Protonolysis	182
Mercuration	184
Oxidation	184
Addition Compounds of Organoboranes	186
Conclusion	189
•	
5. ORGANO-ALUMINUM COMPOUNDS, <i>Karl Ziegler</i>	194
Introduction	194
Synthesis and Classification of Organo-Aluminum Compounds	194
The New "Direct Synthesis" of Aluminum Trialkyls	194
Other Routes to Organo-Aluminum Compounds	197
Different Types of Organo-Aluminum Compounds with Three Substituents Bound to Aluminum	198
Coördination Complexes of Organo-Aluminum Compounds	199
Interconversion of Organo-Aluminum Compounds	202
Molecular Structure and Properties of Organo-Aluminum Com- pounds	207
Organo-Aluminum Compounds and Intermolecular Forces	207
Spectroscopic and Miscellaneous Physical Properties of Organo- Aluminum Compounds	212
Reactions of Organo-Aluminum Compounds	214
Introduction	214
Reactions in which the Sum of Al—C + Al—H Bonds (+ Free Al) Remains Constant	215
Reactions of Organo-Aluminum Compounds with Cleavage of Al—C and Al—H Bonds	236
Reactions in which Al—C Bonds Are Broken but Total Number of Metal-Carbon Bonds Remains Constant (Synthesis of Other Metal Alkyls)	242
Electrolysis of Organo-Aluminum Compounds	251

6. ORGANOSILYLMETALLIC CHEMISTRY, <i>Henry Gilman and Hans J. S. Winkler</i>	270
Historical Review	270
Preparation of Organosilylmetallic Compounds	272
Metal Cleavage of Bond between Silicon and Hydrogen	273
Metal Cleavage of Bond between Silicon and Silicon	274
Metal Cleavage of Bond between Silicon and Group IV Elements other than Silicon	277
Metal Cleavage of Bond between Silicon and Group VI Elements	280
Metal Cleavage of Bond between Silicon and Group VII Elements	281
Analytical Chemistry of Organosilylmetallic Compounds	286
Reactions of Organosilylmetallic Compounds	287
With Elements	287
With Inorganic Compounds	288
With Organic Compounds	291
Comparison Between Organosilylmetallic and Organogermymetallic Chemistry	331
Reactivity of Organosilylmetallic Compounds	335
7. CYCLOPENTADIENYL METAL COMPOUNDS, <i>P. L. Pauson</i>	346
Introduction	346
Compounds with Two Hydrocarbon Ligands	346
Compounds with One Hydrocarbon Ligand	350
Preparation of Dicyclopentadienylmetal Derivatives	355
Some Properties and Structures	359
Reactions not Involving the Cyclopentadienyl Group	363
Aromatic Substitution Reactions	364
Friedel-Crafts Acylation	365
Sulfonation	367
Mercuration	367
Arylation	369
Condensation with Formaldehyde	369
Aldehydes	369
Metalation	371
8. ARENE COMPLEXES OF THE TRANSITION METALS, <i>H. Zeiss</i>	380
Introduction	380
Hein's Polyphenylchromium Chemistry	381
Origin of the π -Bis-Arene Concept	383
Experimental Basis	383
Onsager's Proposal	386
Bis-Arene Chromium	388
Fischer-Hafner Synthesis	388

Properties of Bis-Benzene-Chromium	389
Grignard Synthesis	392
Triphenylchromium Synthesis	392
Bis-Arene Metal Complexes	397
Arene Complexes of V and Fe	397
Bis-Arene Complexes of Re, Ru, Os, Co, Rh, and Ir	405
Acetylenic Synthesis of Cr, Mn, and Co Bis-Arene Complexes	406
Mixed Arene and Arene Carbonyl Metal Complexes	407
Nonbenzenoid Arene Metal Complexes	408
Heterocyclic Metal Complexes	410
Acetylenic Metal Complexes	411
Cyclic Condensation on Chromium	411
Cyclic Condensation on Nickel	414
Cyclic Condensation on Cobalt	415
Addition Reactions	416
The Job-Cassal Reaction	417
 9. TRANSITION METAL ALKYLs AND ARYLs, <i>G. E. Coates and F. Glockling</i>	 426
Introduction	426
Group III	427
Group IV	428
Group V	430
Vanadium, Niobium and Tantalum	430
Group VI	
Chromium, Molybdenum and Tungsten	430
Group VII	432
Manganese and Rhenium	432
Group VIII	433
Iron, Ruthenium and Osmium	433
Cobalt, Rhodium and Iridium	434
Nickel, Palladium and Platinum	434
Group Ib	446
Copper	446
Silver	447
Gold	449
Transition Metal Olefin-Complexes	451
Structure of Metal-Olefin Complexes	456
Acetylenic Derivatives of Transition Metals	458
Acetylene Derivatives of Type (a)	458
Acetylene Complexes of Type (b)	461
Acetylene Complexes of Type (c)	462

10. METAL CARBONYLS AND RELATED COMPOUNDS, <i>J. Chatt, P. L. Pauson and L. M. Venanzi</i>	468
Structure	468
Considerations Governing the Constitution of Metal Carbonyls	468
Structures	472
Nature of the Metal-Carbon and Carbon-Oxygen Bonds	474
Preparation	480
Simple Carbonyls	480
The Polynuclear Carbonyls	482
Substitution Reactions in Metal Carbonyls	482
Displacement without Change in Oxidation State	483
Displacement with Disproportionation	491
Reactions with Acetylenes	492
The Carbonyl Hydrides and Related Compounds	498
Introduction	498
Preparation of Carbonyl Hydrides	499
Properties	499
Salts of the Hydrocarbonyls	503
Alkyl Metal Carbonyls	506
Metal Carbonyl Halides and Related Compounds	509
Preparation of the Noble Metal Derivatives	511
The Manganese, Iron and Cobalt Carbonyl Halides	512
Displacement Reactions of Carbonyl Halides	513
Carbonyl Sulfides and Related Compounds	513
Metal Nitrosocarbonyl and Nitrosoisonitrile Complexes	516
Cationic Isonitrile Complexes	517
AUTHOR INDEX	529
SUBJECT INDEX	545

1. CARBON-METAL BONDING

JAMES W. RICHARDSON

Purdue University, Lafayette, Indiana

INTRODUCTION

The major objective of this chapter is to collect together some of the more important points in the qualitative theoretical description of chemical bonds, especially as applied to such heteropolar systems as occur in organometallics. These principles are developed mostly in connection with problems associated with carbon compounds of transition elements, with, however, the general applicability of the discussion to other organometallics indicated from time to time.

The language developed in the discussion is mainly qualitative molecular orbital (MO) theory, although appropriate translation is occasionally made into the more familiar valence bond (VB) language. One of the hopes of this effort is that the newer MO viewpoint will enhance and complement present understanding in the area. The theoretical development begins with an analysis of bonding in HeH^+ , in order to gain a feeling for the application of MO theory to the simplest heteropolar system. Basic principles developed there are applied to some nonorganic derivatives of transition elements and then successively to selected cyanide, carbonyl and cyclopentadienyl derivatives, thus furnishing a background for more specific applications in later chapters. Considerable detail is presented, which on first reading might be omitted. It is included not only to describe the diversity of bonding interactions present in transition metal compounds but also to indicate the way in which MO theory is used in such problems.

Various observations on bonding in those compounds are then collected and used to suggest some reasons why normal alkyl and aryl bonds had rarely been reported and to speculate about the conditions under which they are more stable.

For the sake of being specific, the discussion proceeds in terms of compounds of the first transition series only; but the same general description applies to the later series as well. Furthermore, not all types of transition metal-carbon systems are considered here. The significant omissions—particularly square planar complexes and the unusual bonds to ethylenic and acetylenic molecules—are analyzed, however, in later chapters in conjunc-

tion with their chemical properties. They represent direct applications of the bonding pictures presented in this chapter.

SINGLE BONDS, POLAR AND NONPOLAR

The chemistry of metal-carbon bonds is, by and large, the chemistry of heteropolar bonds; so it is well to begin by studying the simplest of them all, the bond in HeH^+ .[†] In VB language the He to H bond is largely ionic, being best represented by the structure $\text{He}:\text{H}^+$, though there is some contribution from the covalent structure $(\text{He}-\text{H})^+$. Thus the charge distribution in HeH^+ is rather like that in free He, there being only a moderate polarization toward the proton as represented by the covalent structure.

MO Description of HeH^+

An alternative description of the HeH^+ molecule is provided by the Coulson and Duncanson MO wave function (10) (some details of which are given later), from which a theoretical charge density may be calculated and compared with that for free He. The approximate contour maps are given in Fig. 1.1. From this drawing one can qualitatively view the bonding as a deformation of the He atom charge cloud caused by the approach of the proton.

The process of deformation can be described in another way. If the charge on the proton in the molecule were zero, then, of course, the electron distribution would be that of neutral He. As it is increased to 1 (i.e., as the electron affinity of the H center increases from 0) there is a continuous deformation to that indicated in Fig. 1.1 by the dashed line. If the charge at the proton center were to be increased still further to 2, then the electronic charge would become equally distributed between the two ends of the molecule; that is, the bond would become nonpolar (or completely covalent in VB language).

The concept of continuous change from extreme polarity to complete covalency is familiar in much of chemistry; it is to be emphasized that it applies equally to the chemistry of all bonding systems, including alkali halides, metal-carbon bonds and transition-metal complexes. The description of HeH^+ applies qualitatively as well to such a molecule as LiCl , for example. One might say that the Li^+ ion imbeds itself somewhat in the charge distribution of the Cl^- ion and causes some polarization in its

[†]For a similar treatment of the simplest homopolar molecule H_2^+ , see the discussion in Coulson's book (9), p. 77. This book affords a more general introduction to the molecular orbital treatment of bonding and its comparison with valence bond theory.

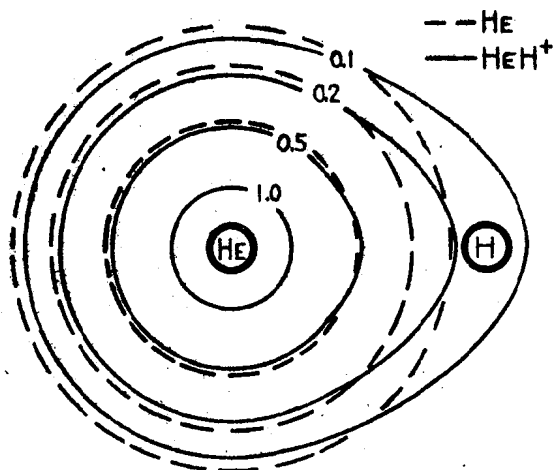


Fig. 1.1. Charge density distribution in He and HeH⁺. The numbers assigned to the various charge density contour lines are on a relative scale. The internuclear distance is taken to be 0.8 Å, i.e., approximately at the calculated energy minimum.

direction, or that there is a small but significant covalent bonding. A similar sort of behavior might be expected in the Li—CH₃ bond, although the valence-shell charge density might well be shifted more to the Li in this case.

It is apparent even from Fig. 1.1, that dividing up the bond charge density into contributions from atoms at either end of the bond must be somewhat arbitrary, and, except for finer details, largely a matter of computational or descriptive convenience. In speaking of such division, one must keep firmly in mind the theoretical framework within which the discussion proceeds.

It is instructive to look a little deeper into the nature of the continuous deformation as revealed in the simple MO wave function. The coefficients in the ground state MO $\psi_{\text{HeH}^+} = C_{\text{He}}(1s_{\text{He}}) + C_{\text{H}}(1s_{\text{H}})$, calculated by Coulson and Duncanson, give

$$\psi_{\text{HeH}^+} = 0.85(1s_{\text{He}}) + 0.25(1s_{\text{H}}). \quad (1.1)$$

If the molecule were completely polar (ionic) then C_{H} would be 0; if it were completely nonpolar (covalent) then C_{H} would equal C_{He} . The charge distribution corresponding to Eq. 1.1 is given by

$$\psi^2_{\text{HeH}^+} = 0.72(1s_{\text{He}})^2 + 0.22 \frac{(1s_{\text{He}})(1s_{\text{H}})}{S} + 0.06(1s_{\text{H}})^2, \quad (1.2)$$

where $S = \int (1s_{\text{He}})(1s_{\text{H}})d\mathbf{v} = 0.55$ is the overlap integral. This is to say that