THE HYDROGEN SERIES

Volume 1

TRANSITION METAL HYDRIDES

Edited by Earl L. Muetterties

CENTRAL RESEARCH DEPARTMENT

EXPERIMENTAL STATION

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Transition Metal Hydrides

THE HYDROGEN SERIES

edited by Earl L. Muetterties

Volume 1: Transition Metal Hydrides Volume 2: Chemistry of Boron Hydrides

Other Volumes in Preparation

Preface to the Series

The Hydrogen Series represents a first attempt to characterize important or timely areas of hydrogen chemistry with principal emphasis on the hydrogen nucleus and its impact on chemical and physical properties. The ubiquitous hydrogen nucleus is too often an ignored facet of chemistry. Generally the major focus is on the other elements present in a molecule, despite the fact that hydrogen can be theoretically considered with greater accuracy than any other nucleus. importance of hydrogen chemistry hardly needs elaboration. Hydrogen is the chameleon of the chemical elements with broad areas wherein protonic, H⁺, or hydridic, H⁻, character to the HX bond essentially sets the chemical background. In addition, there is the vast organic area in which the carbon-hydrogen bond generally has nonpolar character. Hydrogen bonding is a phenomenon of great import. It is the genesis of the unique properties of water and is a critical secondary and tertiary structure factor in synthetic and biological macromolecules. Another example of the hydrogen atom's "adaptability" is its ready participation in multicenter, two-electron bonds, as evidenced in the structurally and chemically beguiling boron hydrides.

The sincere hope of the Editor is to ultimately present in a holistic fashion a definitive treatment of hydrogen. Every attempt will be made in the development of the series to achieve breadth and depth. In all these, the theme will be, so to speak, a "hydrogen view" of chemistry. There will, however, be some gaps in the series. The "gaps" will occur in areas where definitive books on aspects of hydrogen chemistry already exist. Duplication will be avoided. For example, the whole of organic chemistry or biochemistry is not to be rewritten or rephrased in this series, although these areas will not be neglected where there are opportunities to cogently emphasize a "hydrogen view" of some subarea.

These are the goals of this series, but no judgment can be made of the series based on this preface. Only the products, the various volumes in the series, will establish whether these goals have been realistically achieved and whether the series will be of unique value to the scientific community.

E. L. Muetterties

Preface

On the jacket of this book is a mapping of the hydrogen atom positions in a remarkable transition metal hydride, the ReH_9^{2-} ion (see also page 59). This unusual nonohydridorhenium ion began its literature existance in a rather inauspicious fashion, stripped bare to the core and characterized as the rhenide ion, Re . As years passed, the ion gathered charge and hydrogen atoms and became successively ReH_4^{2-} , ReH_8^{2-} , and ReH_9^{2-} . Final resolution of composition was not realized until complete X-ray and neutron diffraction studies were made. Although this is an exceptional case from transition metal hydride history, it is not far from being exemplary. Many other critical facets of transition metal hydride chemistry have had an analogous, checkered history, e.g., the nature of the metal-hydrogen bond, synthesis of hydrides and mechanistic details of reactions catalyzed by metal hydrides. Only in the last five to ten years have fundamentals been established. Compositional and structural definitions of metal hydrides have been greatly facilitated by advanced nuclear magnetic resonance techniques and by the now relatively rapid structural analysis afforded by diffraction studies. It is a tribute to the early investigators that they accomplished so much with so little spectral and diffraction information. The very early work of Hieber and coworkers and the later (to present) studies of Chatt and of Wilkinson and their coworkers are most notable.

Principles underlying structure, bonding, stereochemistry, synthesis and chemistry are reasonably in hand for discrete transition metal hydride molecules and ions. Hence, there is fundamental justification for a volume devoted to these subjects. However, such an argument could be made for many other areas of hydrogen chemistry. Current interest in metal hydride chemistry is at a very high level. The research activity is international in scope with significant

activities in Japan, Europe, England, and the United States. A major point of interest in recent years has been the structure and stereochemistry of the transition metal hydrides. In addition, the chemistry of the metal-hydrogen bond has been examined rather extensively in recent years. Of particular note is the fact that the metal-hydrogen bond can interact reversibly with a number of organic substrates. Accordingly, it is a key element in many kinds of homogeneous catalytic reactions. This facet of metal hydride chemistry is a major point in the current, high-level interest in this area. Essentially within a decade many aspects of laboratory synthesis and industrial processes have felt the impact of transition metal hydride chemistry.

There has been an unfortunate division between solid state and molecular inorganic chemistry. The barrier between these two areas is beginning to fall, but as yet an extensive communication between scientists in these two areas has not been achieved. This volume on transition metal hydride chemistry is directed to molecular transition metal hydride chemistry. This is not an attempt to further maintain the barrier between molecular and solid state inorganic chemistry. The emphasis on molecular chemistry within this volume is a result of two considerations: (1) a number of quite comprehensive volumes have appeared on solid state transition metal hydride chemistry and (2) a definitive treatment of solid state inorganic chemistry and the associated, important area of heterogeneous catalysis involving hydrogen and hydrogen compounds cannot be presented at this time. Accordingly, the subject of solid state transition metal hydride chemistry, hydrogen chemisorption, and heterogeneous catalysis is only briefly reviewed in Chapter 2. Adequate reference is made to the existing, more comprehensive reviews available today. Chapter 1, which is devoted to a concise summary of properties of hydrogen, deuterium, and tritium molecules, is included only to provide the transition metal hydride chemist with a ready source of information, particularly of physical properties that may be of value in research associated with transition metal hydride chemistry.

In general, the recommended nomenclature rules have been followed. This extends to the prevailing rules for sequential listing of elements in coordination compounds. This procedure is rigorously followed

through Chapter 4. In the last two chapters, where the emphasis is on the metal-hydrogen chemistry, this sequential rule is not followed; rather the hydrogen nuclei appear before the metal atom or atoms. We believe that this departure from convention is justified because the nature of interactions of the metal-hydrogen bond with various molecules or ions and mechanistic details thereof are more readily apparent following this alternative method. In Chapters 3 through 5 the treatment is critical and relatively comprehensive. The major objective in Chapter 6 is an outline of the metal-hydrogen bond in homogeneous catalysis. This outline is as definitive as the available data allow, and it is not comprehensive.

The material presented in this volume covers the literature through 1970.

Many contributed substantially to the preparation of this volume. We are especially indebted to Mrs. Judy Truitt for proofreading and for typing the final manuscript for the offset printing process and to Mr. Ames Schuck and his associates for all drawings, lettering, and book jacket design. In addition, the typing assistance of Mrs. Kathy Jones and Mrs. Susan Kelly is gratefully acknowledged.

E. L. Muetterties

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