HYPERCARBON CHEMISTRY

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FOREWARD

The periodic nature of the properties of atoms and the nature and chemistry of molecules are based on the wave property of matter and the associated energetics. Concepts including the electron pair bond between two atoms and the associated three-dimensional properties of molecules and reactions have served the chemist well, and will continue to do so in the future.

The completely delocalized bonds of π aromatic molecules, introduced by W. Hückel, also provided a basis for rational description of molecular orbitals in these systems. Extended Hückel theory allowed a study of molecular orbitals throughout chemistry at a certain level of approximation.

The localized multicentered orbital holds a certain intermediate ground, and is particularly useful when there are more valence orbitals than electrons in a molecule or transition state. First widely used in the boron hydrides and carboranes, these three-center and multicenter orbitals provide a coherent and consistent description of much of the structure and chemistry of the upper left side of the periodic table, and of the interactions of metallic ions with other atoms and molecules.

Skeletal electron counts (the sum of the styx numbers), first proposed by Wade, Mingos and Rudolph, have also provided a guide for synthesis, and have given a basis for filled bonding descriptions of polyhedral species and their fragments. Together with the isolobal concept, diverse areas of chemistry have thereby been unified.

In this book one sees the remarkable way in which these ideas bring together structure and reactivity in a great diversity of novel carbon chemistry and its relationship to that of boron, lithium, hydrogen, the metals, and others. The authors are to be congratulated.

Rather than ask why it has taken some 30 years for these concepts to become widely known, one can be amazed that the background for this fine book developed at all. It is due in no small part to reluctance of chemists to adapt to the dynamic changes of chemistry. One can also hope that chemistry will recover from the recent neglect of support of research in mechanistic organic chemistry and synthesis of compounds of the main group elements. In addition, much of the molecular structure determination that is so central to these arguments had to await the newer methods of X-ray diffraction and nuclear magnetic resonance, and the theory had to await the modern developments in methods and computers. Thus the emergence of the depth and breadth of these concepts in this book is a tribute to the dedication of the authors and to the vitality of the ideas themselves.

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May 1986

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PREFACE

Organic chemistry is concerned with carbon compounds. Over 6 million such compounds are now known, and their number is increasing rapidly. They range from the simplest compound methane, the major component of natural gas, to the marvelously intricate macromolecules that nature uses in life processes.

Within such a rich and diverse subject, it is difficult for someone deeply familiar with one area to keep abreast of developments in others. This can hinder progress if discoveries in one field that can have significant impact on others are not recognized in a timely fashion. For example, developments in the chemistry of carbohydrates, proteins, or nucleotides are traditionally exploited by biochemists and biologists more than by organic chemists. Developments in organometallic chemistry, while increasingly attracting the attention of inorganic chemists, are not as well appreciated by mainstream organic chemists.

In this book we have attempted to alleviate this problem by pooling our diverse experience and backgrounds but centering on a common interest in the fascinating topic of hypercarbon chemistry. The book centers around the theme that carbon, despite its firmly established tetravalency, can still bond simultaneously to five or more other atoms. We refer to such atoms as *hypercarbon atoms* (short for hypercoordinated carbon atoms) since four valency (hence four coordination using normal two-center, two-electron type bonds) is the upper limit for carbon (being a first-row element it can accommodate no more than eight electrons in its valence shell). Since their early detection in bridged metal alkyls, where they helped advance the concept of the three-center, two-electron bond (and later the four-center, two-electron bond), hypercarbon atoms have now become a significant feature of organometallics, carborane, and cluster (carbide) chemistry, as well as of acid catalyzed hydrocarbon chemistry and the diverse chemistry of carbocations.

First we survey the major types of compounds that contain hypercarbon. The relationships that link these apparently disparate species are demonstrated by showing how the bonding problems they pose can be solved by use of three- or multicenter electron-pair bond descriptions or simple MO treatments. We also show the role played by hypercoordinated carbon intermediates in many familiar reactions (carbocationic or otherwise). Our aim here is to demonstrate that carbon atoms in general can increase their coordination numbers in a whole range of reactions.

In our original plans for the book, we were privileged to have our friend and colleague Paul v. R. Schleyer participate, and we regret that other obligations made it impossible for him to continue. We gratefully acknowledge his many suggestions and thank him for his continued encouragement. We have mainly focused our attention on experimentally known hypercarbon systems and are not discussing only computationally studied ones (these are reviewed by Paul Schleyer elsewhere).

Most chemists' familiarity with chemical bonding evolved in electron-sufficient systems, where there are enough electrons not only for (2*e*–2*c*) bonds but also for nonbonded electron pairs. Hypercarbon atoms are generally found in electron-deficient systems where electrons are in short supply and thus have to be spread relatively thinly to hold molecules or ions together. A relative deficiency of electrons is not uncommon in chemistry, particularly in the chemistry of the metallic elements. The (3*c*–2*e*) and multicenter bonding concept of boranes and carboranes, pioneered by Lipscomb, further emphasizes this point. Thus it is not surprising that the concept of hypercarbon bonding was accepted by inorganic and organometallic chemists earlier than by their organic colleagues. The well-publicized spirited debate over the classical–nonclassical nature of some carbocationic systems preceded their preparation and their spectroscopic study under long-lived stable ion conditions, which unequivocally established their structures. Debate and even controversy is frequently an essential part of the "growing pains" of a maturing field, and they should be welcomed as they help progress in finding answers. The importance of hypercoordination in carbocations and related hydrocarbon chemistry is now firmly established. At the same time hypercoordinate carbocations are but one aspect of the much wider field of hypercarbon chemistry.

It is significant to note that almost all carbocations have known isoelectronic and isostructural neutral boron analogs. Boron compounds also provide useful models for many types of intermediates (transition states) of electrophilic organic reactions.

The field of hypercarbon chemistry is already so extensive that it is impossible to give an encyclopedic coverage of the topic. Instead we have taken the liberty of organizing our discussion around selected topics with representative examples to emphasize major aspects. Our choices were arbitrary and we apologize for inevitably omitting much significant work.

Multiauthor books frequently lack the uniformity that a single-author book is able to convey. Our close cooperation, made possible by the Loker Hydrocarbon Research Institute, has helped us give a homogeneous presentation that merges our individual viewpoints to reflect our common goal. If we have succeeded in calling attention to the ubiquitous presence of hypercarbon compounds, breaching the conventional boundaries of chemistry, and have aroused the interest of our readers, we shall have achieved our purpose.

We thank Ms. Cheri Gilmour for typing the manuscript and our editor, Dr. Theodore P. Hoffman, for helping along the project in his always friendly and efficient way. Many friends and colleagues offered helpful comments and suggestions and we are grateful to them all.

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chapter 1

INTRODUCTION AND GENERAL ASPECTS

1.1. AIMS AND OBJECTIVES

The chemistry of carbon compounds is generally referred to as organic chemistry. This book is intended to draw attention to an important but generally neglected area of carbon chemistry that has recently undergone a period of extremely rapid growth, yet which is still hardly touched on in most organic textbooks. This is the chemistry of compounds in which carbon atoms are covalently bonded to more neighboring atoms than can be explained in terms of classical, two-center, electron-pair bonds. We refer to such carbon atoms as *hypercarbon atoms*[1a] (short for *hypercoordinated carbon atoms*) because of their *unexpectedly high coordination numbers*.

Carbon contains four atomic orbitals (AO's) in its valence shell (the $2s$, $2p_x$, $2p_y$, and $2p_z$ AO's), and so can accommodate at most four bonding electron pairs (in accordance with the "octet rule").[1b] Commonly, these electron pairs are used to form four single bonds (as in alkanes), two single bonds and one double bond (as in alkenes), one single and one triple bond (as in alkynes), or two double bonds (as in cumulenes). With only four bond pairs, carbon atoms cannot bond covalently to more than four neighboring atoms using only two-center, electron-pair bonds. If attached to more than four neighboring atoms, they must resort to some form of *multicenter* σ *bonding*, in which the bonding power of a pair of electrons is spread over more than two atoms. All carbon atoms with coordination numbers greater than four are therefore necessarily hypercoordinated, and compounds containing such atoms (of which there are now many known examples) will be the main concern of this book. However, there are circumstances in which carbon atoms with only three or four neighbors may participate in multicenter sigma bonding to two or even three of these neighbors, and we shall include them in our discussion where appropriate.

We have four main objectives:

1. *To illustrate the wide and developing scope of hypercarbon chemistry* by indicating the variety of compounds now known to contain hypercarbon atoms (carbocations,[2] organometallics,[3] carboranes,[4] and other cluster compounds,[5,6] carbides), including many familiar systems such as alkyllithium reagents $(LiR)_n$[7-10] (n = 4 or 6) in which the hypercoordinated nature of the carbon atoms (and, by implication, the roles that the attached metal atoms play in their chemistry) is often ignored.
2. *To discuss ways in which the bonding in such systems can be described.* Notably, in terms of three-center, electron-pair bonds as well as classical two-center bonds, but also in terms of simple molecular orbital (MO) treatments that shed useful light on some of the more symmetrical systems.
3. To demonstrate that, far from being exotic species remote from mainstream organic chemistry, *hypercarbon compounds are closely related to many classically bonded systems, and to aromatic systems,* comparisons with which are of mutual benefit.
4. To show how *the study of hypercarbon compounds helps us to understand the mechanisms of many organic reactions.* These are reactions in which carbon atoms become hypercoordinated in intermediates or transition states, even though the reagents and products of these reactions contain only normally coordinated carbon atoms.

In introducing the subject in Section 1.2, we define some of the terms we shall be using. In Section 1.3 we illustrate the various types of hypercarbon compounds now known. Since we shall rely heavily on the concept of the three-center, electron-pair bond in our discussion of their bonding, and since the usefulness of this concept is perhaps less widely appreciated in organic chemistry than in inorganic or organometallic chemistry, we devote Section 1.4 of this introductory chapter to discussion of the three-center bond concept and illustration of its value for treating specific systems. We also demonstrate the relevance and value of some simple MO arguments applied to hypercarbon systems (Sections 1.4 and 1.5), and conclude this introductory chapter by indicating the types of reactions that are now thought to involve hypercarbon systems. More detailed treatments of particular types of systems, and of specific reactions, follow in subsequent chapters.

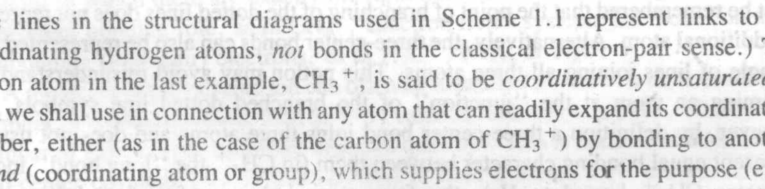
1.2. SOME DEFINITIONS

Throughout this book we shall be concerned with the twin issues of coordination and bonding. The terminology by which chemists refer to these issues tends to vary considerably from area to area. It is, therefore, important to define and to illustrate the sense in which certain terms will be used here.

The *coordination number* of an atom is defined here as the *number of neighboring atoms* by which that atom is directly surrounded, and to each of which it is attached by the direct sharing of electronic charge. All the coordinating atoms may not be at the same distance—some may be bonded more strongly than others, and so be closer to the atom under consideration—but all will be located in directions and at distances that indicate some sharing of electronic charge with the central atom, rather than linkage to the central atom via a second neighboring atom.

On occasions, the term "valence" is used as if it were synonymous with "coordination number." We shall not use it in that sense here. We define the *valence of an atom* as the *number of bonding electron pairs* used by that atom. Normally, carbon is *tetravalent* (i.e., the octet rule is obeyed), and hypercarbon compounds are no exception. On the other hand, in hypervalent compounds the number of valence electrons exceeds the number of bonding orbitals available. Carbon being a small first row element cannot expand its valence shell (vide infra). In the same way that the carbon atom of methane is tetravalent in forming four two-center, two-electron (2*c*–2*e*) bonds to the neighboring four hydrogen atoms, so it is tetravalent but pentacoordinate in the product of protonation of methane. The methonium cation (CH_5^+) is an energetic, highly reactive species[11] believed to have a structure in which three hydrogen atoms are at a normal single bond distance while the other two are at a greater distance.[11,12] In contrast, the methyl cation (CH_3^+) into which CH_5^+ decomposes contains a triply coordinated, *trivalent* carbon atom (Scheme 1.1).

Scheme 1.1



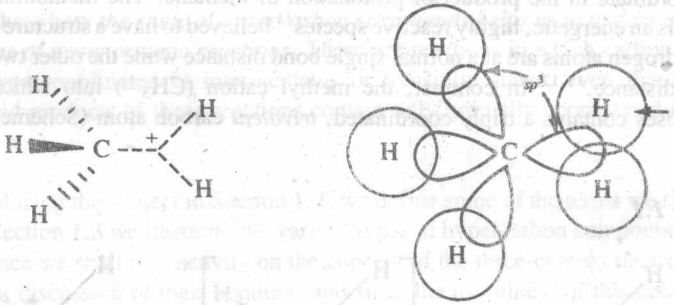
(The lines in the structural diagrams used in Scheme 1.1 represent links to the coordinating hydrogen atoms, *not* bonds in the classical electron-pair sense.) The carbon atom in the last example, CH_3^+, is said to be *coordinatively unsaturated*, a term we shall use in connection with any atom that can readily expand its coordination number, either (as in the case of the carbon atom of CH_3^+) by bonding to another *ligand* (coordinating atom or group), which supplies electrons for the purpose (e.g., $CH_3^+ + X^- \longrightarrow CH_3X$), or by using electrons that were previously *nonbonding*, as occurs when coordinately unsaturated carbanions are protonated, that is, when nonbonding lone-pair electrons are converted into bond pairs (Scheme 1.2).

Scheme 1.2

$$R_3{-}C^- \xrightarrow{H^+} R_3CH$$

When discussing bonding, we shall find it convenient to retain wherever practicable the concept of single, double, and triple bonds, that is, links between pairs of atoms that involve the sharing between those atoms of two, four, or six electrons, respectively, and shall refer to them as two center, two electron [i.e., (2*c*–2*e*)] bonds, two center, four electron (2*c*–4*e*) bonds, and two center, six electron [i.e., (2*c*–6*e*)] bonds. However, as already indicated, we shall find it necessary, in discussing hypercarbon compounds, to use the concept of *multicenter σ bonds*, bonds in which the bonding power of a pair of electrons is considered to extend over three or occasionally four atoms. In CH_5^+, for example, a three-center, two-electron (3*c*–2*e*) bond can account for the bonding between the carbon atom and the two hydrogen atoms furthest from the carbon atom, represented as follows in Scheme 1.3.

Scheme 1.3



For simplicity it is suggested[2a] that three-center bonds be depicted by triangular dotted lines drawn from and meeting each other between the three participating atoms; full straight lines are generally used to symbolize two-center, two-electron bonds. Such a formulation best illustrates the overlap of bonding orbitals; however, it must be remembered that the point of branching of the dotted lines does not represent an additional atom. Alternatively, the three-center bonds can also be represented by a triangle of lines joining all three atoms. This notion may avoid misunderstandings assuming an atom at the "junction" of the branched dotted line symbols. As, however, by definition a three-center bond joins three atoms and does not usually represent equal bonding character between them (in CH_5^+ the "long bond" indeed indicates CH_3^+ bound to H_2), the former symbol is preferred and is gaining acceptance.

Such a bond is envisaged as resulting from the mutual overlap of a suitable AO from each of the atoms involved, an sp^3 hybrid AO on carbon and a 1*s* AO on each hydrogen atom, as illustrated in Scheme 1.3.

It should be stressed that although such a three center, two electron bond shares the bonding pair of electrons between three atoms instead of two as in classical bonds and therefore is sometimes referred to as delocalized, the description of the bonding in CH_5^+ by three (2*c*–2*e*) bonds and one (3*c*–2*e*) bond is nevertheless a description in terms of *localized bonds*. It is a valence bond description of this cation that attempts to account for the distribution of the atoms and the internuclear distances by allocating pairs of electrons to localized regions between pairs of atoms or within triangular arrays of three atoms. A *delocalized* bonding description of this cation would allocate the four pairs of electrons to MOs embracing all six atoms, each or most making some contribution to all of the pairwise interactions, bonded or nonbonded, in CH_5^+, but generating overall much the same electron density in particular regions as the localized bond model. Thus, electron density corresponding to essentially one pair of electrons would be found in each of the "normal" C—H bonds, but the electron density associated with each long C—H link, and also in the H—H link between the two anomalous (hypercoordinated) hydrogen atoms, would approximate to two thirds of an electron apiece (for electron bookkeeping purposes, the sharing of a pair of electrons between three atoms, as in a (3*c*–2*e*) bond, corresponds to the allocation of two thirds of an electron to each edge of the triangle defined by those three atoms).

An additional term that we may occasionally find useful, though we shall restrict its use to avoid ambiguity, is *electron deficient*. This term has at least three different senses in which it has been used in connection with organic systems. It is often applied as meaning "center for nucleophilic attack" to refer to carbon atoms bearing electron-withdrawing substituents. Secondly, it is also used in referring to compounds with coordinatively unsaturated carbon atoms like those of carbenium ions, R_3C^+, which can accommodate an extra pair of electrons. The third usage[13,14a] is as a label for molecules, or sections thereof, that contain too few electrons to allow their bonding to be described exclusively in terms of two-center, electron-pair bonds. In this book we prefer to restrict our discussion to compounds wherein molecules or sets of atoms are held together by multicenter bonding (i.e., by electron-deficient bonding). Similarly, "electron precise"[14a] is a term that can be used as a label for systems in which there are exactly the right number of electrons to give each pair a two-center bonding role, as in CH_4. "Electron rich" systems are those containing nonbonding (lone-pair) electrons, as in H_3C^-, NH_3, or H_2O.

A molecule or polyatomic ion can often be identified as *electron deficient* from its formula, if it contains fewer than $(n - 1)$ valence shell electron pairs, where *n* is the number of atoms in the molecule or ion in question. This is because at least $(n - 1)$ two-center covalent links will be needed to hold *n* atoms together, whatever the structure may be. Thus, the methonium ion, CH_5^+, with six atoms held together by only four valence shell electron pairs, is clearly electron deficient in this sense. In the CH_6^{2+} dication[14b] seven atoms are involved, further increasing the electron deficiency.

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