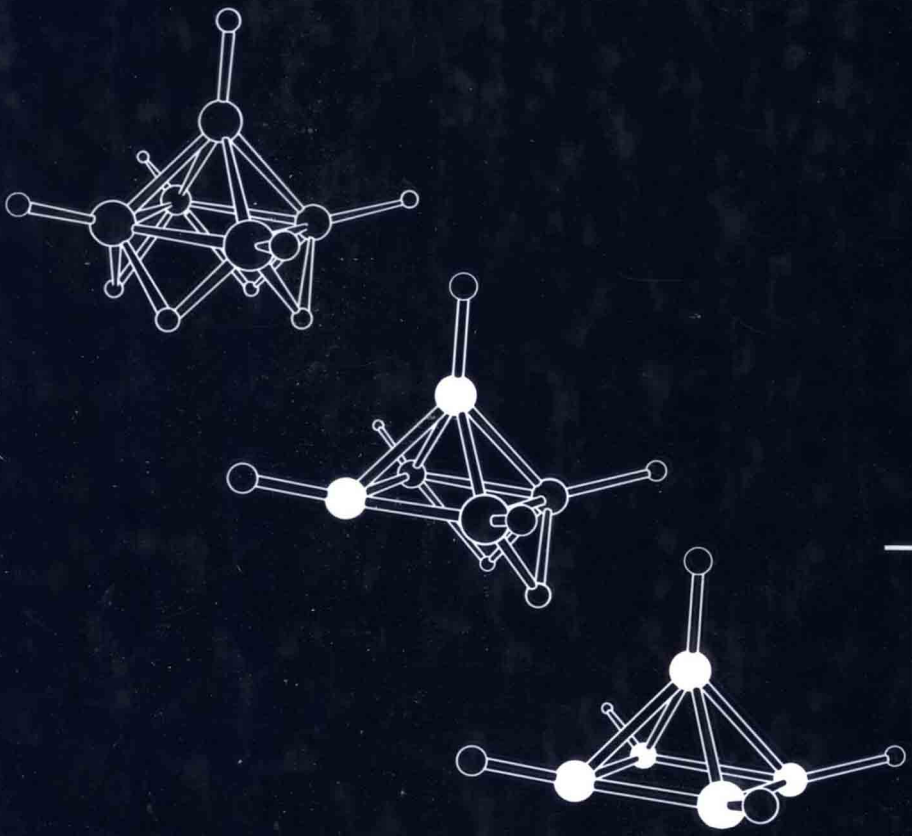
THE BORANE, CARBORANE CARBOCATION CONTINUUM



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FOREWORD: THE PATTERNMAKER

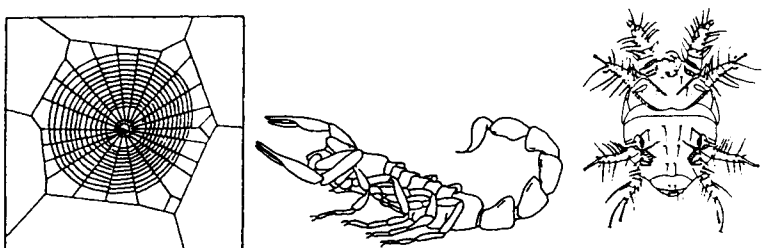
During the past 45 years, Bob Williams has made numerous seminal contributions to at least three aspects of borane chemistry: (1) the discovery and subsequent characterization of the first carboranes; (2) the nomenclature of cluster species; and (3) the structral patterns and significant relationships between the various types of carborane clusters. As is clear from his contribution in this volume, he continues to make subtle and penetrating observations that invariably stimulate us to further thought and experimentation.

His original work on the carboranes (1953–1961) was classified by the U.S. government and the first publication only appeared in 1962.[1] It opened up an enormous field of novel cluster chemistry that has been of great theoretical importance and industrial significance. This has been fully reviewed many times and need not be further elaborated here.

Bob was one of the first to deprecate the continuing and constricting use of what he termed "the shibboleth of the icosahedron"[2] as the main structural basis for borane cluster geometry and was the first to point out the unifying relations involving triangulated polyhedra.[2,3] Before that (and even afterward), as is clear from various ACS and IUPAC Nomenclature Committee Reports,[4] classification had been based on the idea of closed and open networks of boron atoms distinguished by the prefixes *closo* and *nido*, respectively. Perhaps Bob disliked the emphasis on the idea of a *network of boron atoms* divorced from the structural influence of the hydrogen atoms, and he may even have recalled Samuel Johnson's famous definition in the very first Dictionary of the English Language: "*Network*: anything reticulated or decussated, at equal distances, with interstices between the intersections." In any event, he pointed out that, "for bookkeeping purposes" all carborane–borane chemistry can be divided into

three categories: *closo*, *nido*, and *arachno*, though these last were at first considered as a subset of *nido*.[2,5]

His choice of the prefix *arachno*, in allusion to a spider's web, reveals that Bob was a much better boron chemist than zoologist because, as any observant naturalist knows, spiders' webs never feature triangular units, only quadrilaterals and occasional pentagons (see **a**). Indeed, the class *Arachnida* includes not only the 32,000 species of spiders, but also the scorpions (see **b**), and this reminds us of another of Bob's endearing traits. For, though he is one of the most generous and charming of people and a delightful colleague, he also sees it as his role to sting us into action by his provocative thoughts, and this without doubt has stimulated all of us to think more deeply about our subject.



It might be thought less than seemly to remind Bob that, in addition to spiders and scorpions, the arachnids also include some 30,000 species of mites and ticks. These minute creatures are rarely more than 0.5–0.9 mm long, but many have bizarre patterns of behavior. Perhaps the most remarkable is the mite *Acarophenax tribolii*. The female (see **c**) produces 15 eggs, including but a single male, which all develop within the mother's body. The male emerges within his mother's shell, copulates with all his sisters and dies before birth.[16] It may not sound like much of a life, even for a boron chemist, but is suggests that there are still innumerable developments possible in our field. I am confident that Bob will continue to goad us into searching for them.

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NORMAN N. GREENWOOD

FOREWORD: A BRIEF OVERVIEW

Bob Williams was the codiscoverer, along with C. D. Good, of the smaller carboranes $C_2B_3H_5$, $C_2B_5H_7$, and two isomers of $C_2B_4H_6$.[1] Good isolated the pure samples, following preliminary very-low-yield mixtures obtained by H. Landesman (in 1953) and B. Keilin. Bob established the number of hydrogens using mass spectra and deduced the polyhedral structures from the ^{11}B and ^{1}H NMR spectra. These structures became public knowledge on September 8, 1961.[2] Bob comments [3] that only 17 days later, I included them in a paper then submitted to the *Proceedings of the National Academy of Sciences*.[4]

At about the same time, several industrial research groups were beginning to prepare the icosahedral $C_2B_{10}H_{12}$ and its derivatives. For example, an application was filed on May 13, 1959 by J. W. Ager Jr. [5] At least two other patents filed in 1959 were issued in 1962.[6,7] Although an X-ray diffraction structure indicated [8] that $C_2B_{10}H_{12}$ consisted of a —CH=CH— unit bridging the 6,9 positions of a decarborane-like B_{10} unit, the icosahedral structure was clearly proven in two other studies.[9,10] These discoveries in the smaller carboranes and $C_2B_{10}H_{12}$ demonstrated that carbon could show the high coordination (5,6) that boron was known to have in "electron-deficient" bonding situations.

The rapture attendant upon these discoveries was tempered by slow acceptance of the ideas, reduction in funding of the rocket propellant program, and termination of support for most of main-group inorganic chemistry (including my grant) by the National Science Foundation, which became abnormally preoccupied with transition-metal catalysis.

The invention of Olin's Dexil polymers based on alternating units of $C_2B_{10}H_{12}$ with siloxanes,[11] and of similar polymers involving $C_2B_5H_7$ and siloxanes,[12] produced materials of unprecedented thermal stability and decreased viscosity–temperature dependence. These latter materials were produced by Chemical Systems, Inc., which Bob founded in 1970. At about the time that his company was acquired by the Purolator Corporation (1980), Bob became a Senior Fellow of the Loker Hydrocarbon Research Institute (1979 to the present).

Bob's poineering and continuing advances in the geometrical (and charge) systematization of polyborane and carborane cluster compounds have been a major contribution. Starting from the structures of *closo*-(polyhedral), *nido*-(one vertex B or C missing), and *nido*-(two adjacent vertices missing) species, Bob extended the coordination number patterns beyond the then established octahedral- and icosahedral-based structure relationships to the B_N *closo*-series for $5 \leq N \leq 14$, and their *nido*- and *arachno*-fragments, including both polyboranes and carboranes.[13,14] The electron-count rules for polyhedral-like species [15,16] were developed in a background that included these coordination patterns, the simplifying omission of the external outward-pointing bonds,[17] and the *styx* numbers,[18] which encompass the electron counts.[19]

In a publication of 1976, Bob greatly extended his "coordination number pattern recognition theory" of the carboranes and boranes.[20] Supplementary new rules were presented on the placement of bridge and endo-hydrogens (of BH_2 groups), the placement of carbon and other heteroelements in the framework, and the coordination of boron. He showed us enlarged patterns of relationships, predictions of new molecular geometries, and positions of heteroatoms and of bridge and endo-hydrogens. In addition, relative stabilities of isomers were judged. As exemplified in Bob's most recent surveys [3,21] this empirical approach accommodates the known structures of carboranes, and predicts fewer candidates for undiscovered or controversial structures than other theoretical proposals.

Even as Bob began his tenure at the Loker Hydrocarbon Research Institute, he was interested in the relationship between the then controversial nonclassic carbocations (e.g., norbornyl cation) and delocalized bonding in analogous polyboranes.[22] At IMEBORON-4 (Snowbird, Utah), he more than held his own against an alternative view held by a well-known organic chemist, a discussion that was ended only when the final bus had to leave!

In the case of norbornyl cation, the resolution of the classic versus the nonclassic description was eventually resolved by experiment: ^1H NMR and ^{13}C spectroscopy,[23] Raman spectroscopy,[23] X-ray photoelectron spectroscopy,[23] solid-state NMR [24] and X-ray diffraction;[25,26] and by theory.[27]

Bob continues to pursue his extended interests in the borane, carborane, and nonclassic carbonium ion analogies,[28–30] and in doing so he shows us the great value of pattern recognition, the hallmark of original science.

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WILLIAM N. LIPSCOMB

PREFACE

In December 1995, a symposium entitled "The Borane, Carborane, Carbocation Continuum," a part of the Richard Kimbrough Research Symposium series, was held at the Loker Hydrocarbon Institute of the University of Southern California. The symposium was assembled to honor the 70th birthday of Robert E. Williams. Dr. Williams has been one of the leading contributors to the field of preparative and structural carborane chemistry over a period of four decades. The symposium title reflects one of the key research interests of the Institute—the preparation, characterization, and reactions of carbocations and the related boron analogs—the area of principal scientific contributions of Bob Williams. The choice of symposium topic also focuses attention on an emerging understanding regarding the similarity of properties and behavior of carbocations, boranes, and carboranes. These highly electron-deficient species exhibit structural features and chemical properties that sufficiently parallel each other so that a meeting of international experts in these three areas of research, to jointly discuss their fields, seemed most appropriate. The novelty of the symposium topic and the freshness of the work presented at the symposium made it natural for us to reduce the presentation to print. This volume is the result of that effort.

In the early 1950s, Lipscomb and Kaspar reported the correct structures for pentaborane and decaborane, among the many discoveries that led to the award of the Nobel Prize in 1976 to Bill Lipscomb. But, prior to the 1950s, there were no recognizable carboranes. Following his baccalaureate work at DePauw University and doctorate at the University of New Mexico, Williams accepted a job at the Pasadena laboratories of the Olin Matheson Corporation; the job involved vacuum line work and the company's interest in high-energy materials. This placed him in a good position to discover the first four carborane compounds.

Between 1956 and 1958, Williams, with the help of coworkers at Olin Matheson, determined the structures of these novel compounds using 12.8 MHz ^{11}B NMR. By the early 1960s, three classes of carboranes had been identified. The rich and novel cage structures of these compounds, resulting from their incorporation of unusual three-center two-electron bonds, which had been described and popularized by Lipscomb, gave Williams an opportunity to display a talent for which he has become widely known—that is, the ability to recognize patterns relating geometry and electron distribution in these compounds and the special insight to draw structural inferences regarding classes and families of compounds depending on molecular composition and electron count. During this early period, similar pioneering efforts of Earl Muetterties and Fred Hawthorne in carborane and metallocarborane chemistry were signal in developing an understanding of these compounds. Williams regards the boranes, carboranes, and carbocations as offering organized examples of the simplest, most elementary electron-deficient clusters in all of chemistry. Since there are many more possible electron-deficient boranes (BH) and carboranes (BCH) than there are equivalent electron-deficient carbocations (CH), the incorporation of all three groups of structures under a unified structural rubric offers widespread utility and understanding. At the same time, the close relationship of boranes and carboranes, as neutral analogs of carbocations, the study of which earned George Olah his Nobel Prize, opened up a fresh new field of cooperative studies in which Bob Williams has been able to extend his interests.

Today, integration of high-level ab initio theory and concomitant IGLO and GIAO calculations with NMR experiments is bearing fruit and has become the structure marker of these electron-deficient compounds for the 1990s. Several contributions to this volume directly reflect these developments. Williams continues to be an active participant in these currently ongoing efforts.

In the name of all participants and contributors to this volume, I wish Bob not only a happy birthday, but continuing good health. We are certain that he will continue to contribute to his beloved field for many years to come. We take special pleasure in bringing together the chapters contributed here by distinguished researchers in the field, assembled as a tribute to the outstanding efforts of Bob Williams over a period of four decades. During these four decades, Bob and I have been good friends and colleagues, and we hope that this will remain so during the next four decades.

The editor is greatful to Robert Greatrex, John D. Kennedy, and Kenneth Wade for editorial suggestions.

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