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Boron Chemistry: Introduction

This thematic issue is intended to attract the attention of chemists to the exciting area of boron cluster compounds, which forms a bridge between organic chemistry, inorganic chemistry, and the chemistry of metals.

The fortunes of boron chemistry portray, in a characteristic way, how the degree of interest in a branch of science depends on its perceived practical utility. After the discovery of the first boranes in 1912, these compounds were considered to be of only academic importance. The first borane boom started in 1941, when the use of the volatile uranium borohydride was proposed for the separation of uranium isotopes. Subsequently, more convenient procedures were developed and support for borane work subsided. Large-scale preparation of sodium borohydride and of diborane were the main achievements.

The second boom for cage boranes started in 1946 when liquid (B_5H_9) and solid ($B_{10}H_{14}$) boranes were believed to be most powerful rocket fuels and more than 100 million dollars, along with a similar number of millions of rubles, were invested in the research and development of these materials. This idea, too, was eventually abandoned, but a great effort of more than 2000 chemists created a firm base for the future development of borane chemistry. During this long decade, several new boranes and many hydridopolyborates were discovered. Their structures were determined, and economical synthetic methods and many interconversions were elaborated. In the next three decades, gradual systematic but less well-supported research continued.

At present, in spite of the great amount of information available, the chemistry of boron skeletons is not yet nearly as developed as organic chemistry. Attempts to predict with a sufficient reliability the chemical behavior of a given compound, or to carry out a controlled synthesis of desired compounds, only succeed relatively rarely. This shows that our understanding of electron-deficient compounds is inadequate, and systematic study of reaction mechanisms and search for further preparative methods offer very promising fields for further research.

Currently, the significance of work with deltahedral boron compounds lies in two areas: (i) in revealing the principles determining the chemical behavior of electron-deficient compounds and (ii) in recognizing the particular properties of boron-cluster compounds that are of most use for science and in practical applications.

In this issue, only a part of this huge area is reviewed. Architectural patterns of polyboranes, carboranes, and carbocations are discussed by R. E. Williams. While his earlier papers dealt mainly with the optimum location of hydrogen bridges and of heteroatoms and, consequently, with the most stable isomer or isomers of a given stoichiometric formula, the present contribution deals with the distribution of electrons within the clusters, with their stability, and with the size of the open face, all of which helps to predict the most stable isomer for almost each new compound.

Two papers deal with the chemistry of carboranes. V. Bregadze reviews the *o*-, *m*-, and *p*-dicarba-*closo*-dodecaboranes $C_2B_{10}H_{12}$ and their derivatives. Of particular interest are the preparation of C- and B-metalated derivatives, which provide access to other types of substitution. B. Štíbr treats other types of mono- to tetracarbaboranes. Especially interesting are open-skeleton anionic carboranes which can be used as precursors for numerous metallacarboranes.

R. N. Grimes reviews boron–carbon ring ligands, which can be attached to two metal atoms, one on each side, and open access to a new class of multimetal sandwiches. A review discussing potential applications of boron cluster compounds by J. Plešek lists the known applications and offers several new ideas of potential uses.

There are two contributions that deal with spectroscopy. S. Heřmánek presents the first systematic treatment of ^{11}B NMR chemical shifts and formulates several general rules for their prediction. L. A. Leites summarizes the IR and Raman spectra of carboranes and parent boranes, which are particularly valuable for species of high symmetry.

This issue covers only a part of boron cluster chemistry. Both the Editor and the Guest Editor hope, however, that many readers will find inspiration in the ideas presented here and that some of them will be interested in borane chemistry to such a degree that they will try to contribute to the solution of some of the outstanding problems.

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