



CONTEMPORARY
*boron
chemistry*

edited by M. G. DAVIDSON, A. K. HUGHES,
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Contemporary Boron Chemistry

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The proceedings of the 10th International Conference on the Chemistry of Boron, IMEBORON X, held at the University of Durham on 11–15 July 1999.

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Contemporary Boron Chemistry

Preface

This book reports chemistry of boron and its compounds which was presented in lectures given at the Tenth International Conference on Boron Chemistry, IMEBORON X, held at the University of Durham, United Kingdom, 11–15 July 1999. The conference featured 49 invited and 37 contributed lectures as well as 80 poster presentations. In all, over 200 chemists contributed to a truly international meeting with participants representing Australia, Belgium, the Czech Republic, Finland, France, Germany, Hong Kong, India, Ireland, Japan, Korea, Mexico, New Zealand, Poland, Puerto Rico, Russia, Spain, Sweden, Switzerland, the USA as well as the UK.

The invited lecturers included both senior members of the boron chemistry community, who have been important contributors to the field for many years, and younger scientists whose research has already had a significant impact. Topics covered included inorganic and organic compounds as well as polymers and solid-state materials, medicinal aspects and theoretical studies.

Contemporary Boron Chemistry contains 80 reports in nine chapters. Clearly, since much research is interdisciplinary in nature, our decision to include a report in one particular section rather than another was sometimes an arbitrary one. With this caveat in mind, the sections are as follows: Applications to Polyolefin Catalysis; Materials and Polymers; Medicinal Applications; Cluster Synthesis; Carboranes; Metallaboranes; Metallaheteroboranes; Organic and Inorganic Chemistry of Mono- and Di-boron Systems; and Theoretical and Computational Studies.

The continued and evolving significance of boron chemistry to the wider chemical community is illustrated by the broad range of topics covered at IMEBORON X and in this book (e.g. boron clusters, metal catalysed boration reactions of organics, synthesis and optical properties of conjugated boron-containing polymers, boron neutron capture therapy, theoretical studies of rare earth borides, weakly coordinating anions, metal boryl and borylene compounds, and boronates as dienophiles to name a few). It is hoped that this book will encourage further interdisciplinary research and new collaborative ventures. With this prospect in mind the editors look forward with optimism to the next IMEBORON meeting to be held in 2002.

Matthew Davidson, Andrew Hughes, Todd Marder and Ken Wade

Durham, January 2000

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The editors thank Janet Freshwater and Sue Askey of the Royal Society of Chemistry for their help and advice in the preparation of this book.

Professor Stanislav Heřmánek

13th June 1929–16th August 1999



This volume, reporting boron chemistry presented at IMEBORON X in Durham, UK, July 11–15, 1999, is dedicated to the memory of Professor Stan Heřmánek. It was Stan whose vision and enthusiasm for boron chemistry led to the establishment of that series of meetings in 1971, when he and Jaromír Plešek hosted the first IMEBORON meeting in Liblice, Czechoslovakia. In those bleak days, indeed for nearly two more decades, opportunities for meetings and scientific exchanges between researchers separated by the iron curtain were severely limited, and it is to the great credit of scientists like Stan Heřmánek that their efforts to bring about or attend such meetings eventually led to the changed political climate in which such barriers could be dismantled.

Stan Heřmánek was born in Tábor, Bohemia, in 1929, and studied chemistry at Prague Technical University, where he obtained his master's degree in 1952, and then stayed on until 1958 as an assistant to Professor Rudolf Lukeš, one of the leading Czech organic chemists of his day. His young assistant helped with teaching, textbook writing and researches that included borohydride chemistry. Communist purges then required Stan to move to the Research Institute of Natural Drugs in Prague. In 1961, however, he joined what is now the Institute of Inorganic Chemistry of the Czech Academy of Sciences at Řež near Prague, establishing the boron chemistry research group that he led with distinction from 1961 to 1974 and again from 1990 to 1994. This group has been internationally recognised for decades as one of the leading centres of boron chemistry research and, incidentally, its associated commercial laboratory is now one of the best places from which to purchase samples of higher boranes and carboranes. Stan received his Ph.D. from the Technical University at Pardubice in 1966, and much later (1996) was appointed to a chair of chemistry at Charles University (Prague).

At Řež, Stan pioneered a number of approaches to boron hydride research. He developed thin-layer chromatographic methods to separate products, and progressively more sophisticated multinuclear NMR methods to identify new substances. A key early breakthrough, of which he was rightly proud, was his recognition that the kinetics of the thermal gas-phase conversion of diborane into higher boranes, and ultimately decaborane, implied that better yields would be obtained by working at the higher pressures other workers were then avoiding for safety reasons. His success with the production of decaborane in large enough quantities to allow its chemistry to be developed, and higher carborane chemistry to be opened up, proved invaluable to later workers.

A penetrating lateral thinker, Stan also recognised the capacity of carborane icosahedra to transmit electronic effects directly across the cage (antipodal effects), probed using NMR chemical shifts. He also showed how powerful ^{11}B - ^1H coupling constants could be in reflecting the local bonding environment of BH units in boranes. Indeed, he identified various NMR-borane structure correlations of considerable use long before modern IGLO methods were devised. Undaunted by the complexities of borane structures, he demonstrated how localised bond treatments, and sequences of bond cleavages as electron numbers are increased, were powerful aids in rationalising the more open structures of *nido*, *arachno* and *hypho* boranes and carboranes (his 'seco' principle). He also developed the solvent extraction of radionuclides using bis(dicarbollide)cobaltate anions.

The value of his contributions was recognised in 1968 by a Czechoslovak Academy of Sciences Award, and most recently by the award of the highly prestigious Heyrovský Medal of the Academy of Sciences of the Czech Republic, a belated tribute to his lifelong achievements recorded in some 200 publications. The intervening years would have been even more productive, and more fully recognised, had he found his politics more in tune with those who then ran his country, but following the brief flirtation of Czechoslovakia in the 1960s with a more open style of government, and the reimposition of a stricter regime, Stan and others found themselves playing more junior roles than before. As Stan himself put it, with his uncanny feeling for the capacity of the English language to express double meanings, 'having been appointed to a senior position under one regime, I was dis-appointed under its successor'. His ability to play on words even in English, and his endearing modesty, were elsewhere evident in his subtle use of word transposition, as in his deliberate use of the words 'least, but not last' in signalling a change of topic in a lecture.

Despite the various set-backs in his career, Stan retained a wonderfully optimistic outlook on life, great enthusiasm for his subject, and an inspirational capacity to infect the young with his own insatiable curiosity to find out more about the fascinating networks of atoms that so enrich borane chemistry. Unselfishly keen to help when hosting conferences in his native country, as at Liblice in 1971 and Bechyně in 1987, a charming, interesting, courteous guest when visiting other countries, he characteristically made light of the problems that his final fatal illness generated. He battled bravely with leukaemia over the last few years of his life, coping so well and making so little of his problems as to lull all of us into thinking that he was winning the battle. It was characteristic of this brave man to show the resilience and determination that allowed him to attend his last IMEBORON meeting in Durham in July 1999, only five weeks before he finally succumbed on August 16th, 1999. It was characteristic of him that at that meeting, he dismissed expressions of concern about himself, endeavouring to behave as if he were in good health, touchingly solicitous of the welfare of his wife Věra, who herself had had to cope with substantial surgery from which she had not fully recovered.

With Stan's death, boron chemistry has lost an original thinker and researcher with the vision to see how much can be achieved by bringing the community together at regular intervals, one who inspired many others with his own great enthusiasm for his subject. His widow and sons Jan and Ivan have lost a wonderful husband and father, and we share that loss. The lives of all who knew him have been enriched by this kind, gentle man.

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