inorganics

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Editorial

Fifth Element: The Current State of Boron Chemistry

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Citation: Stogniy, M.Y. Fifth Element: The Current State of Boron Chemistry. *Inorganics* **2024**, *12*, 10. https://doi.org/10.3390/inorganics12010010

Received: 21 November 2023
Revised: 12 December 2023
Accepted: 22 December 2023
Published: 25 December 2023

The fifth element of the Periodic Table is boron. Boron belongs to the class of metalloids; that is, to elements that combine the properties of metals and non-metals at the same time [1]. It has fewer valence electrons than valence orbitals, which is typical for metals, but due to its high ionization energy, low electron affinity and small atom size, boron does not form a metallic crystal lattice, but instead forms unique and complex structures with multicenter bonds in which a pair of electrons holds three or more atoms together. Even elementary boron does not consist of individual boron atoms, but mainly B_{12} icosahedral motifs, within which each boron atom is bonded to five other atoms [2]. That is why, despite the simple electronic structure of the atom, boron forms a variable system of substances, ranging from inorganic oxides, nitrides, halides and borides to numerous organoboron compounds and unusual cluster structures in which an atypical electron-deficient bond is realized.

Although some boron compounds such as borax have been known since ancient times, the intensive development of boron chemistry began with the systematic study of binary compounds of boron with hydrogen of the general formula B_xH_y, undertaken by German chemist Alfred Stock [3]. Between about 1912 and 1936, Stock synthesized a whole family of such compounds, the simplest of which is diborane B_2H_6, containing two bridging hydrogens. In addition to the fact that boron hydrides exhibited complex properties, their structures were also very unusual and could not be described using the then known theories of chemical bonding [4]. The main contribution to understanding the structure of boron hydrides was made by American chemist William N. Lipscomb, for which he was awarded the Nobel Prize in Chemistry in 1976 “for his studies on the structure of boranes illuminating problems of chemical bonding” [5–7].

The investigation of borohydride structures led to the development of the theory of two-electron three-center bonds, which explained the properties and behavior of compounds with electron-deficient bonds [8,9].

Moreover, the study of the reactions of diborane with various organic molecules undertaken by American chemist Herbert C. Brown in the earlier 1950’s became the starting point in the development of organoboron chemistry, and in 1979 he shared the Nobel Prize in Chemistry for the “development of the use of boron containing compounds into important reagents in organic synthesis” [10].

Another important organic process involving organoboron compounds that should be mentioned here and the associated 2010 Nobel Prize in Chemistry is the Suzuki cross-coupling reaction, which is currently actively used for the synthesis of polyolefins, styrene, substituted biphenyls, etc., [11,12].

The next key moment in the development of boron chemistry was the synthesis of polyhedral boron hydrides in the 50–60s of the twentieth century. Currently, a large number of such unusual structures are known. One of the most important examples is the *closo*-dodecaborate anion $[B_{12}H_{12}]^{2-}$, which has a structure similar to the B_{12} icosahedral unit of elemental boron, but with each boron atom bonded to one hydrogen atom [13]. In addition, it should be noted that the aromatic nature of polyhedral boron hydrides determines many unusual properties which distinguish them from most boron hydrides and organoboron compounds. First of all, this is the high thermal and kinetic stability of the boron cluster, as well as a pronounced tendency towards substitution and, accordingly, modification.

Replacing one or more boron atoms in a cluster with carbon atom(s) leads to the formation of a class of carboranes [14]. It is also possible to remove one or more boron vertices, which significantly expands the range of structural types of carboranes. As a result, in addition to closed structures (*closo*-carboranes), the open ones (*arachno*- and *nido*-carboranes) become available. Moreover, open structures, such as, for example, the 7,8-dicarba-*nido*-undecaborate anion (*nido*-carborane) and its derivatives, are very promising ligands for the synthesis of metal complexes [14].

Despite intensive development over more than a hundred years, boron chemistry still remains one of the most diverse and rapidly developing areas of modern chemistry. This is also promoted by a wide variety of applications of boron and boron-containing compounds, including the synthesis of organic fine chemicals, pharmaceuticals and medicines, and polymers, ceramics, heat-resistant materials, semiconductors, etc.

These twelve articles form a *Special Issue* of *Inorganics* to reflect data on the latest advances in synthetic and applied boron chemistry. The papers illustrate the very comprehensive world of heteroborane, organoboron and inorganic boron chemistry from simple zinc borates to mono- and a tri-metallic tungstaboranes and *closo*-ruthenacarborane complexes, boron-based oxadiazoles and thiadiazoles, as well as novel approaches to the synthesis of 3-halogen and 3,6-dihalogen derivatives of *ortho*-carborane and NHC-haloboranes.

A simple and effective approach to the synthesis of zinc borate powders in the form of nanoparticles agglomerates with an average size of 43 nm exhibiting low bulk density and high reactivity was developed by a group of Prof. S. P. Gubin (contribution 1). Zinc borates were prepared by the thermal treatment of a concentrated water–carbohydrate solution of a zinc salt until finely dispersed ZnO was formed, followed by its hydrothermal treatment at 90–300 °C as part of a suspension based on a hot aqueous solution of H_3BO_3. Due to high thermal stability, the prepared zinc borates can be used in industry as a flame retardant in the production of plastics, rubber or other polymer compositions.

The design and synthesis of a series of seventeen boron-based benzo[c][1,2,5] oxadiazoles/thiadiazoles was carried out by Prof. B. C. Das and co-workers. The compounds were synthesized in two steps in an efficient manner via boronic acid pinacol esters followed by subsequent hydrolysis to give boronic acid derivatives in good yields. These are the first boron-based compounds that can be used as anticancer agents targeting tumor hypoxia (contribution 2).

New advances in the chemistry of organoboron compounds were highlighted in the *Special Issue* by one more article presented by Dr. S. S. Sen and co-workers. The authors prepared a series of SNHC-haloboranes adducts and investigated their further nucleophilic substitutions to put unusual functional groups at the central boron atom such as $–ONO_2$, –OTf, etc., (contribution 3).

Two novel mono- and a tri-metallic tungstaborane clusters were presented by a group of Prof. J.-F. Halet and co-workers. The first complex is *arachno*-$[Cp^*W(CO)_2B_3H_8]$, which has the geometry of an open butterfly cluster and can be utilized for further cluster build-up chemistry. The second complex is tungstaborane $[(Cp^*W)_3(\mu\text{-}H)_2(\mu_3\text{-}H)(\mu\text{-}CO)_2B_4H_4]$ and represents a rare *oblato-nido* hexagonal-bipyramidal cluster with a W_3B_4 core (contribution 4).

A large block of articles in the *Special Issue* are devoted to the chemistry of polyhedral boron hydrides. Thus, a convenient two-stage method for the preparation of important 3-halogen and 3,6-dihalogen *ortho*-carborane derivatives $3\text{-X-1,2-}C_2B_{10}H_{11}$ and $3,6\text{-}X_2\text{-1,2-}C_2B_{10}H_{10}$ (X = Cl, Br, I) via Cu-assisted halodeboronation of the corresponding pinacolborate derivatives was proposed by the group of Prof. I. B. Sivaev (contribution 5). This approach allows us to avoid the use of highly aggressive boron trihalides and liquid ammonia. The authors demonstrated that a chlorine atom can effectively protect the boron atom bound to two carbon atoms from nucleophilic attack.

The preparation of novel nitrilium derivatives of *closo*-dodecaborate anion $[B_{12}H_{11}NCR]^-$, R = $n\text{-}C_3H_7$, $i\text{-}C_3H_7$, $4\text{-}C_6H_4CH_3$, $1\text{-}C_{10}H_7$, which are very good substrates for the following modification of the boron cluster, was presented by a group of Prof. K. Yu. Zhizhin and Prof. N. T. Kuznetsov (contribution 6). The work is supported by X-ray and DFT analysis.

Another contribution of Prof. K. Yu. Zhizhin and co-workers concerns the theoretical investigation of monomethyl derivatives of *closo*-borate anions of the general formula $[B_nH_nCH_3]^{2-}$ (n = 6, 10, 12) and monocarboranes $[HCB_nH_nCH_3]^-$ (n = 5, 9, 11) (contribution 7). An analysis of the main bonding descriptors of *exo*-polyhedral B–C bonds was performed using modern approaches such as QTAIM (quantum theory of "Atoms in Molecules"), ELF (electron localization function), NBOs (natural bond orbitals) analyses and some others. Based on the data obtained on electron density descriptors, the authors conclude that orbital interaction increases with increasing boron cluster size. This investigation provides a better understanding of *exo*-polyhedral B–C bond phenomena in boron cluster systems.

Gold(III) complexation with the octadecahydrido-eicosaborate anion $[B_{20}H_{18}]^{2-}$ was studied for the first time by a group of Prof. E. A. Malinina (contribution 8). It was found that when gold(III) complexes $[Au(L)Cl_2]BF_4$ (L = bipy, phen) react with $[B_{20}H_{18}]^{2-}$, complexes $[Au(L)Cl_2]_2[B_{20}H_{18}]$ can be isolated. The compounds consisted of a cationic gold(III) complex $[Au(L)Cl_2]^+$ and the hydridoborate cluster as a counterion. The work is supported by X-ray diffraction studies that reveal weak B–H…Au interactions in prepared compounds.

Two articles in the Special Issue are devoted to the synthesis of ruthenacarboranes, which can be potential catalysts for many organic processes. The first one was presented by Prof. I. D. Grishin and co-workers and deals with so-called POP ligands (Xanthos, NiXantphos, DPEphos) that have the ability to show either κ^2- or κ^3-binding modes which are valuable for catalytic application and internal stabilization of intermediates (contribution 9). The authors proposed two novel approaches to the synthesis of *closo*-ruthenacarboranes with POP ligands and, as a result, six new 17-e (3,3-(POP)-3-Cl-*closo*-3,1,2-$RuC_2B_9H_{11}$) and 18-e (3,3-(POP)-3-$NCCH_3$-*closo*-3,1,2-$RuC_2B_9H_{11}$) clusters were prepared. The article is supported by electrochemical studies that showed the reversibility of the Ru(II)-Ru(III) transition, which makes the resulting complexes suitable for use in catalysis of polymerization.

Another work on ruthenacarboranes was presented by the group of Prof. D. A. Loginov and was devoted to the reactions of monocarboranes [6-Ph-*nido*-6-$CB_9H_{11}]^-[Et_4N]^+$ and [*arachno*-6-$CB_9H_{14}]^-[Et_4N]^+$ with $RuCl_2(PPh_3)_3$ (contribution 10). It was shown that a *nido*-carborane derivative reacts unselectively due to the undesired coordination of ruthenium to a phenyl substituent in the carborane cage and phosphine ligands, giving a series of new classical and non-classical metallacarborane complexes. At the same time, the *arachno*-carborane forms the only product, the 10-vertex 20-electron *isocloso*-structured metallacarborane.

The *Special Issue* also contains two important reviews concerning the chemistry of polyhedral boron hydrides. The first one, presented by a group of Prof. I. B. Sivaev, summarizes data on the main types of charge-compensated *nido*-carborane derivatives (contribution 11). It has been shown that onium derivatives of *nido*-carborane compared to organic analogs have increased stability due to the stabilizing electron-donating effect of the boron cage and are important precursors for the preparation of functional *nido*-carborane derivatives and, based on them, metal complexes.

The second review, provided by a group of Dr. V. V. Avdeeva, systematizes data on the coordination ability of mono- and disubstituted derivatives of boron cluster anions containing B–X *exo*-polyhedral bonds (X = N, O, S, Hal) in complexation with transition metals (contribution 12). The authors describe the synthesis and structural features of complexes known to date and analyze the effect of complexing metal and substituents attached to the boron cage on the composition and structures of the final complexes.

Thus, this Special Issue combines the latest achievements in the field of experimental boron chemistry, along with a review of previously obtained results. We thank all the authors who took part in this issue and look forward to further interesting and useful developments in the chemistry of boron.

Funding: The author considers it necessary to express his gratitude to the Ministry of Science and Higher Education of the Russian Federation (075-03-2023-642).

Conflicts of Interest: The author declares no conflict of interest.

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