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Review

Recent aspects of the ten-vertex dicarbaborane chemistry

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Dedicated to Professor Narayan S. Hosmane on the occasion of his 70th birthday

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A B S T R A C T

A review on recent developments in the chemistry of ten-vertex dicarbaboranes is presented. This chemistry is essentially derived from that of the *nido*-5,6-$C_2B_8H_{12}$ dicarbaborane, the most significant compound of the 10-vertex dicarbaborane series. This carborane gave rise to all the three *closo*-$C_2B_8H_{10}$ isomers and to *arachno*-6,9-$C_2B_8H_{14}$ that serve as substrates for various reactions outlined in this work. Individual chemical transformations are discussed within the context of possible reaction mechanisms and NMR consequences. The work demonstrates that this chemistry resulted in the isolation of the whole series of other compounds that may now start playing ever increasing role in developing new carborane chemistry in this almost forgotten area.

Contents

1. Introduction

The chemistry of the title class of dicarbaboranes has already been outlined in three review articles [1–3]. The most efficient synthetic routes to the ten-vertex dicarbaboranes have been developed in our group, being generally based on chemical transformations of the *nido*-5,6-$C_2B_8H_{12}$ (**1**) [4–7]. The original procedure shown in Scheme 1, so called Plešek's reaction, is based on oxidative removal of the BH9 vertex in the open face of the well known [*nido*-7,8-$C_2B_9H_{12}$]$^-$ anion [8–10] by the action of acidic $FeCl_3.6H_2O$ solution (yield 50–60%):

As shown in the next Scheme 2, carborane **1** has become a source of several neutral compounds of the 10-vertex

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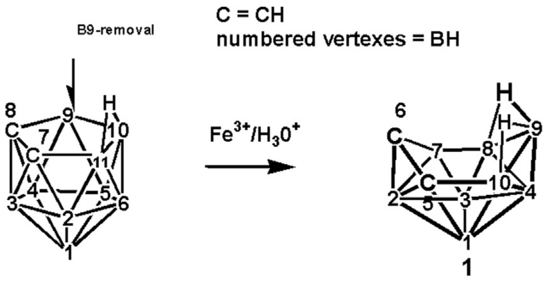


Scheme 1. Oxidative degradation of the [*nido*-7,8-$C_2B_9H_{12}$]$^-$ (dicarbollide) anion giving the neutral *nido*-5,6-$C_2B_8H_{12}$ dicarbaborane (**1**).

dicarbaborane series relevant to this review, specifically *closo*-1,2-$C_2B_8H_{10}$ (**2**), *closo*-1,6-$C_2B_8H_{10}$ (**3**), *closo*-1,10-$C_2B_8H_{10}$ (**4**), and *arachno*-6,9-$C_2B_8H_{14}$ (**5**).

Of the seven possible *closo*-$C_2B_8H_{10}$ isomers adopting a bicapped square antiprism geometry, only three compounds (**2**, **3** and **4**) having one or both carbon atoms in low-coordinate apex positions have been isolated and characterized. Before 2016, the only viable synthesis of carborane **2** had been based on practically a quantitative disproportionation of Na^+[*nido*-5,6-$C_2B_8H_{11}$]$^-$ at 120–200 °C [11]. The *closo* isomer **3** can be, in fact, regarded as a stable intermediate on the **2** → **4** thermal-rearrangement pathway in which it can be isolated or at least detected [11]. Nevertheless, so far the best and quite a specific synthesis of **3** consists in room-temperature oxidation of carborane **1** with elemental iodine in dichloromethane in the presence of triethylamine [7] providing **3** in 85% yield. The reaction is supposed to proceed via several intermediate stages involving two bis-equatorial *closo* isomers, in agreement with theoretical considerations by Gimarc and Ott [12]. Carborane **2** can be converted quantitatively into *closo*-1,10-$C_2B_8H_{10}$ (**4**) by heating at 350 °C in a sealed ampoule. The latter carborane can be also produced directly from **1** via dehydrogenation by passing through a hot tube at ~500 °C [11], although originality was ascribed [1] to a group of innovators who repeated the same procedure 29 years later in a stainless vessel, in which multigram amounts of **4** could be made [13]. The synthetically useful parent *arachno*-6,9-$C_2B_8H_{14}$ carborane (**5**) is best prepared via reduction of carborane **1** with $NaBH_4$ in ethanolic NaOH (yield 37%) [14].

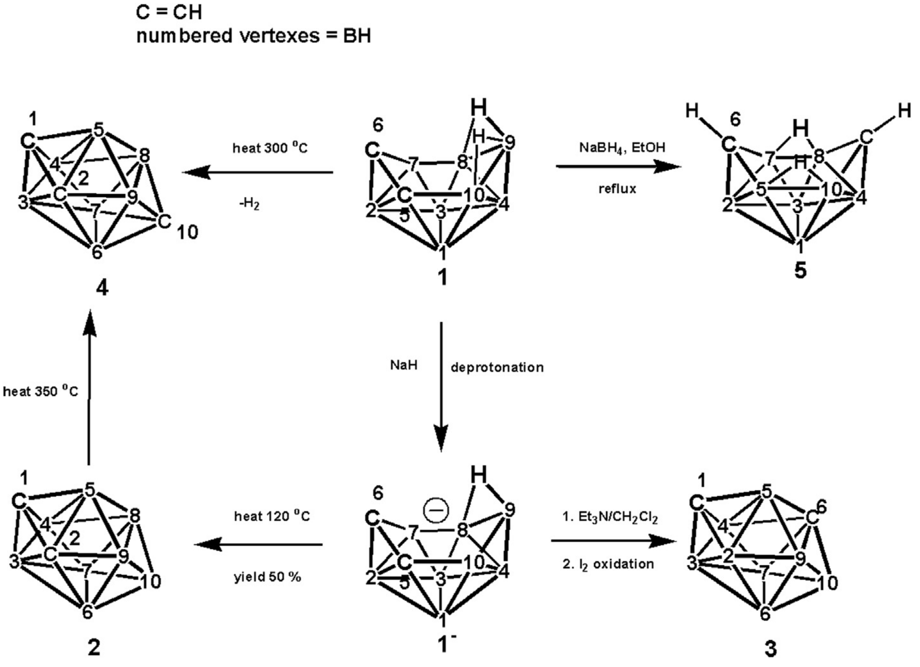
This work should demonstrate that the chemistry of carboranes mentioned above can result in the formation of the whole series of interesting compounds which may play significant role in developing new carborane chemistry. Despite the statement that exploration syntheses in cluster-boron area have been extinct [15].

2. Progress in the chemistry of the *nido*-5,6-$C_2B_8H_{12}$ (1) carborane

2.1. Tautomerism of the [nido-5,6-$C_2B_8H_{11}$] anion ($\mathbf{1}^-$)

Reported was an unprecedented case of carborane-cage tautomerism in the series of C-substituted derivatives of the [*nido*-5,6-$C_2B_8H_{11}$] anion ($\mathbf{1}^-$) in which both tautomers can be isolated in pure state, structurally established and mutually interconverted [16].

As shown in Scheme 3 (path A), deprotonation of the neutral *nido*-5,6-$R_2C_2B_8H_{10}$ dicarbaboranes (5,6-R_2-**1**) (where R = H, alkyls or Ph) and NMe_4OH in water precipitates only one tautomer, NMe_4^+[5,6-R_2-*nido*-5,6-$C_2B_8H_9$-$\mu^{8,9}$] (5,6-R_2-$\mathbf{1a}^-$), the structure of which was determined via an X-ray diffraction analysis. In contrast, path B of Scheme 3 shows that adding a slight excess of Et_3N to hexane solutions of the neutral carborane 5,6-R_2-**1** generates surprisingly the inverse tautomer, Et_3NH^+[*nido*-5,6- $R_2C_2B_8H_9$-$\mu^{9,10}$] (5,6-R_2-$\mathbf{1b}^-$), which was also structurally characterized. Tautomeric anions 5,6-R_2-$\mathbf{1a}^-$ and 5,6-R_2-$\mathbf{1b}^-$ therefore differ in the positioning of the bridging hydrogen, whereby 5,6-R_2-$\mathbf{1a}^-$ is 3.9 kcal mol^{-1} more stable than tautomer 5,6-R_2-$\mathbf{1b}^-$, as assessed by MP2/6-31G* computations on unsubstituted compounds (Fig. 1). As a consequence of this energy difference, tautomer 5,6-R_2-$\mathbf{1b}^-$ exists only in the solid state and is instantly converted into 5,6-R_2-$\mathbf{1a}^-$ on dissolution (Scheme 3, path C) [16].



Scheme 2. The most efficient routes to the isomeric *closo*-$C_2B_8H_{10}$ dicarbaboranes developed in the author's group.

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