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A restricted polyhedral rearrangement of an aminosubstituted 12-vertex ferratricarbollide

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Abstract

The oxidation of anion $[7,8\text{-}CH_2OCH_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$ with aqueous $FeCl_3$ gives the 10-vertex *nido*-carborane $5,6\text{-}CH_2OCH_2\text{-}5,6\text{-}C_2B_8H_{10}$ in 23% yield. Its interaction with Bu^tNC in the presence of proton sponge gives the tricarbollide anion $[7,8\text{-}CH_2OCH_2\text{-}9\text{-}Bu^tNH\text{-}7,8,9\text{-}C_3B_8H_8]^-$ (44% yield) having a short linkage between carbon atoms. Further photochemical reaction of this anion with $[CpFe(C_6H_6)]^+$ is accompanied by room-temperature polyhedral rearrangement giving ferratricarbollide $1\text{-}Cp\text{-}2,3\text{-}CH_2OCH_2\text{-}9\text{-}Bu^tNH\text{-}1,2,3,9\text{-}FeC_3B_8H_8$ (**5**) in 89% yield. The process involves the migration of the amino-substituted carbon atom, while the separation of two other carbons (observed for the non-linked analogue) is restricted by the CH_2OCH_2 bridge. DFT calculations of the hypothetical non-rearranged isomer $1\text{-}Cp\text{-}2\text{-}Bu^tNH\text{-}1,2,3,4\text{-}FeC_3B_8H_{10}$ revealed its strongly distorted geometry with the C2–C3 distance (2.347 Å) being clearly non-bonding, thus explaining the mild conditions of the polyhedral rearrangement. The structure of **5** was confirmed by X-ray diffraction.

Keywords: Boron; Iron; Metallacarboranes; Polyhedral rearrangement; X-ray diffraction; DFT calculations

1. Introduction

Polyhedral rearrangements of 12-vertex metallacarboranes generally occur at high temperatures (>200 °C) [1], although a few examples of low-temperature isomerizations are known [2–4]. Recently, we have reported the reaction of the amino-substituted tricarbollide anion $[9\text{-}Bu^tNH\text{-}7,8,9\text{-}C_3B_8H_{10}]^-$ (**1**) with the $[CpFe]^+$ fragment giving ferratricarbollide $1\text{-}Cp\text{-}12\text{-}Bu^tNH\text{-}1,2,4,12\text{-}FeC_3B_8H_{10}$ (**2b**) (Scheme 1) [5]. The most remarkable feature of this reaction is the room-temperature polyhedral rearrangement involving the separation of all three carbon atoms. It was of interest to restrict the rearrangement by introducing a short linkage between carbon atoms. With this aim in mind, we have prepared the tricarbollide ligand **3** having the CH_2OCH_2 bridge and studied its complexation with the $[CpFe]^+$ fragment.

2. Results and discussion

2.1. Synthesis

The synthesis of anion **3** was performed similar to **1** [6]. The oxidative deboronation of the 11-vertex anion $[7,8\text{-}CH_2OCH_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$ (prepared by reaction of $1,2\text{-}CH_2OCH_2\text{-}1,2\text{-}C_2B_{10}H_{10}$ [7] with KOH/MeOH) with $FeCl_3$ gives the 10-vertex *nido*-carborane $5,6\text{-}CH_2OCH_2\text{-}5,6\text{-}C_2B_8H_{10}$ (**4**) in 23% yield (Scheme 2). Its further interaction with Bu^tNC in the presence of proton sponge (PS, 1,8-bis(dimethylamino)naphthalene) gives the target anion **3** which was isolated as a $[Bu_4N]^+$ salt in 44% yield.

The reaction of **3** with the $[CpFe]^+$ fragment (photochemically generated from $[CpFe(C_6H_6)]^+$ [8]) gives complex $1\text{-}Cp\text{-}2,3\text{-}CH_2OCH_2\text{-}9\text{-}Bu^tNH\text{-}1,2,3,9\text{-}FeC_3B_8H_8$ (**5**,

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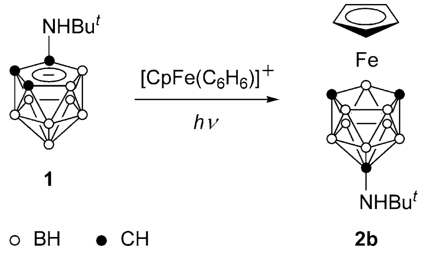
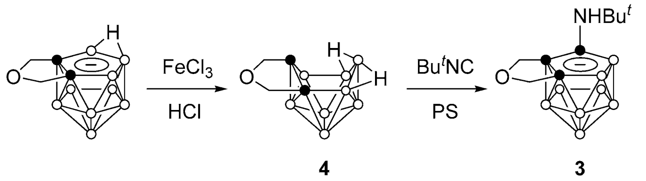
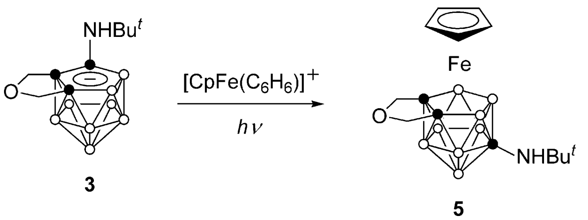


Scheme 1.



Scheme 2.



Scheme 3.

89%) as the only metallacarborane product (Scheme 3). The $^{11}B\{^1H\}$ NMR spectrum of **5** possesses eight singlets of equal intensity indicating that the structure has no symmetry. Accordingly, the ^1H NMR spectrum contains four doublets of equal intensity for protons of the CH_2OCH_2 bridge.

2.2. Structure of ferratricarbollide 5

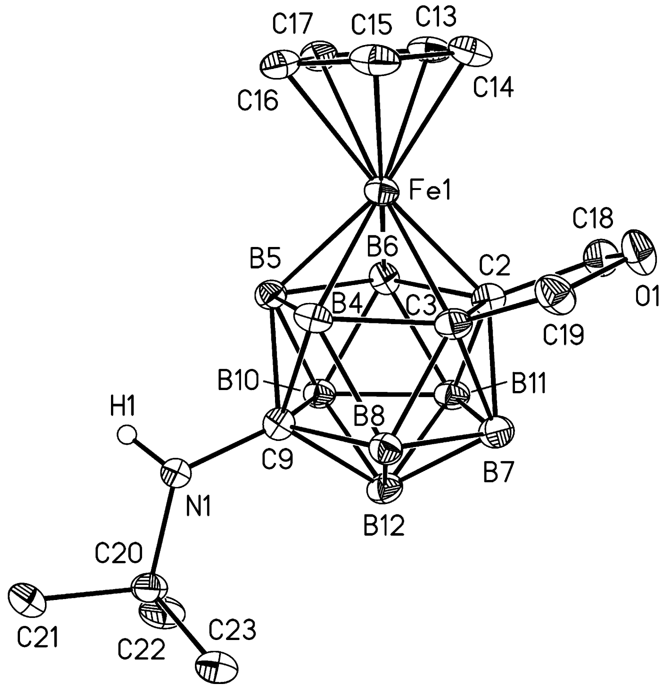


Fig. 1. Structure of **5** (one of two independent molecules). Atoms are represented by 50% thermal ellipsoids. All hydrogen atoms except H1 are omitted for clarity. Selected distances (Å): Fe1–C2 2.033(3), Fe1–C3 2.023(3), Fe1–B4 2.002(4), Fe1–B5 2.051(4), Fe1–B6 2.047(4), Fe1–C13 2.056(3), Fe1–C14 2.072(3), Fe1–C15 2.064(3), Fe1–C16 2.043(4), Fe1–C17 2.055(3), Fe1···Cp 1.668, Fe1···C_2B_3 1.408, C9–N1 1.438(4).

The X-ray diffraction study of **5** revealed that its framework has the 2,3,9-arrangement of the carbon atoms (Fig. 1). In contrast to **2b**, the amino-substituted carbon is located in *meta*-position relative to the iron atom. The C2–C3 bond length (1.602 Å) is typical for metallacarboranes. The C_2B_3 ligand face is notably bent with the B5 atom deviated from the B6–C2–C3–B4 plane for 0.086 Å. Similar effect has been observed previously for the 1-Cp-1,2,3,5-$FeC_3B_8H_{11}$ ferratricarbollide [7]. The Fe···Cp distance in **5** (1.668 Å) is close to that in ferrocene (1.660 Å) [9] and the ferradicarbollide anion [1-Cp-1,2,3-$FeC_2B_9H_{11}]^-$ (**6**) (1.663 Å) [10]. In contrast, the Fe···C_2B_3 distance in **5** (1.408 Å) is notably shorter than in **6** (1.437 Å) presumably due to the stronger acceptor character of the tricarbollide ligand. The crystal cell of **5** contains two independent molecules with essentially the same geometry. The molecules in crystal are assembled by the N–H···O hydrogen bonds between the Bu^{t}NH group and the CH_2OCH_2 bridge (H1···O1 2.56 Å, angle N1–H1–O1 153°, N1···O1 3.328(4) Å).

2.3. DFT calculations

Unlike the reactions of the aminosubstituted anions **1** and **3** (see Schemes 1 and 3), the complexation of the parent tricarbollide anion $[7,8,9\text{-}C_3B_8H_{11}]^-$ proceeds without rearrangement giving 1-Cp-1,2,3,4-$FeC_3B_8H_{11}$ (**7**) [8]. In order to get the explanation for such strong influence of the amino substituent, we carried out DFT calculations (at the PBE/TZV level) on ferratricarbollide 1-Cp-4-Bu^{t}NH-1,2,3,4-$FeC_3B_8H_{10}$ (**2a**) which is presumed to be the initial complexation product of anion **1**.[1]

Surprisingly, the optimized structure of **2a** was found to have strongly distorted framework (Fig. 2). In particular, while the C3–C4 bond (1.547 Å) is just a bit shorter than usually found in metallacarboranes, the C2–C3 connectivity

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[1] The framework geometry of the rearranged complex **2b** (optimized at the same level) is in a good agreement with X-ray data [11] (maximum deviation 0.061 Å, average deviation 0.016 Å), proving the reliability of the calculation results.