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Review

Chemistry related to cluster-borane analogues of the cyclopentadienide anion and ferrocene: New developments

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Abstract

A review on cluster-borane analogues of the cyclopentadienide anion (Cp) and ferrocene is presented. Analogues of Cp that have been so far isolated and characterised are the 11-vertex triheteroboranes of general structure [*nido*-$E_3B_8H_8]^-$ (where E = CH or P and their combinations, the molecules of which contain an open pentagonal face. These anions were used as effective ligands for the preparation of "half- and full-sandwich" complexes [$CpFeE_3B_8H_8$] and [$Fe(E_3B_8H_8)_2$], respectively – analogues of ferrocene. Developments in this area of cluster-borane chemistry that include recent results in the synthesis and Fe-complexation reactions of 11-vertex tricarbaboranes (tricarbollides), phosphadicarbollides, and diphosphacarbollides are the subject of this work.

Keywords: Boron; Boranes; Carboranes; Metallacarboranes; Phosphacarboranes; Metallaphosphacarboranes

Contents

What are cluster-borane analogues of the cyclopentadienide (Cp) anion? The answer is quite straightforward. These compounds should be monoanionic and their structures should contain an open pentagonal face. In the area of cluster-borane chemistry, this condition would be met by the *nido* ($2n + 4$ cage electron, where n = number of polyhedral vertices) anions of general formulation $[E_3B_{n-3}H_8]^-$ (where E = main group-element polyhedral vertex donating three electrons to the cluster bonding proper, such as CH and P). This rule applies just to compounds with $n = 6, 7, 9$, and 11 cluster atoms, as anions with $n = 8$ and 10 vertices are expected to contain a hexagonal open face [1]. Nevertheless, the corresponding anions with $n = 6$, 7, and 9 vertices have not yet been reported and therefore this review

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comprises only the isomeric 11-vertex *nido* triheteroborane anions $[E_3B_8H_8]^-$ (where E = CH and P) that, with the exception of the $[P_3B_8H_8]^-$ anion, have already been prepared. Fe-complexation of these anions then leads to ferrocene analogues, namely to the "half sandwiches" $[CpFeE_3B_8H_8]$ and "full sandwiches" $[Fe(E_3B_8H_8)_2]$, some examples of which have already been known. Most of the key compounds reviewed have been structurally characterised by X-ray diffraction methods or at least by methods of geometry optimisation. Structural formulas in Schemes are presented in a simplified manner: C = CH and unmarked vertices of individual polyhedra denote BH cluster units.

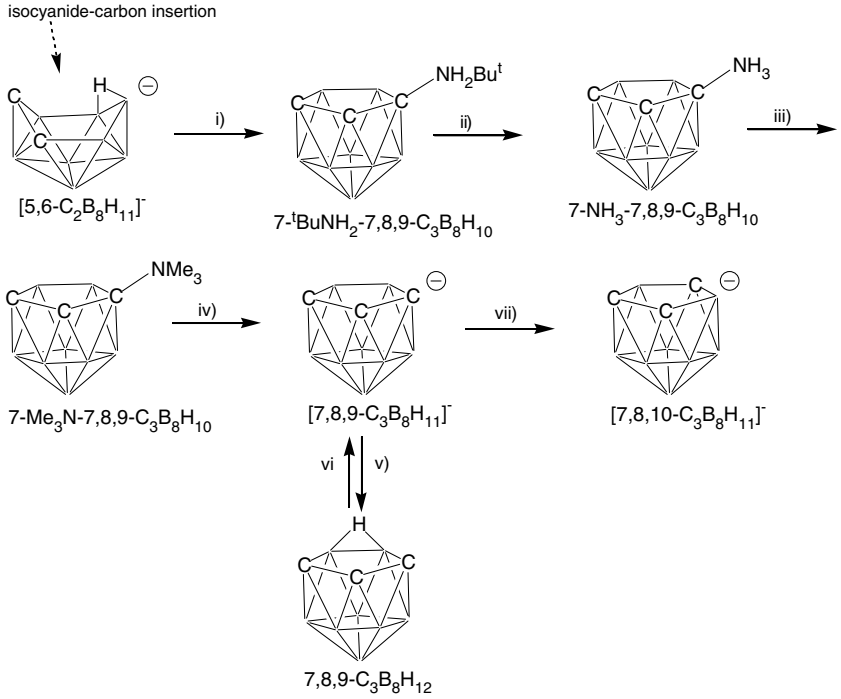
1. 11-Vertex *nido* tricarbaborane (tricarbollide) ligands and ferratricarbollides

It should be noted that this area has already been reviewed in part [2,3] and this work therefore outlines just general features and new aspects of this chemistry. The most straightforward route to the synthesis of compounds of the tricarbollide series is outlined in Scheme 1. The synthesis is based on the reaction between the $[nido\text{-}5,6\text{-}C_2B_8H_{11}]^-$ anion and $t\text{-}C_4H_9NC$ (path (i)) acting as monocarbon insertion agent [4], The reaction is effected via evaporation of a solution of Na^+ $[5,6\text{-}C_2B_8H_{11}]^-$ in neat $t\text{-}C_4H_9NC$, followed by acidification [5], which leads to the isolation of $7\text{-}t\text{-}C_4H_9NH_2\text{-}7,8,9\text{-}C_3B_8H_{10}$ in 90% yield.

This derivative has been converted into $7\text{-}H_3N\text{-}7,8,9\text{-}C_3B_8H_{10}$ (path (ii)) via elimination of isobutylene in the reaction with $AlCl_3$ in refluxing benzene (yield 77%). As also outlined in Scheme 1 (path (iii)), methylation of the H_3N derivative gave $7\text{-}Me_3N\text{-}7,8,9\text{-}C_3B_8H_{10}$, which is an essential starting material for the synthesis of parent compounds of the tricarbollide series. Its deamination with sodium naphthalide in THF (path (iv)) results in the unsubstituted tricarbollide anion, $[7,8,9\text{-}C_3B_8H_{11}]^-$, as the main product (yield 62%) [3,6]. Acidification of this anion with CF_3COOH (path (v)) gives the neutral tricarbaborane $7,8,9\text{-}C_3B_8H_{12}$ (yield 62%). This carborane behaves as a weak acid and can be smoothly deprotonated (path (vi)) to give back the $[7,8,9\text{-}C_3B_8H_{11}]^-$ anion [6].

As demonstrated in Scheme 1 (path (vii)), short heating of $[7,8,9\text{-}C_3B_8H_{11}]^-$ at 350 °C results in the rearrangement of the carbons on the open-face to give the isomeric tricarbollide anion $[7,8,10\text{-}C_3B_8H_{11}]^-$ (yield 63%) [6,7]. Theoretical aspects of the rearrangement mechanism have been published together with a possible rearrangement path [8], It should be also noted that some monosubstituted derivatives of $[7,8,10\text{-}C_3B_8H_{11}]^-$ have been isolated from reactions of the $[6\text{-}R\text{-}nido\text{-}5,6,9\text{-}C_3B_7H_9]^-$ anions (where R = CH_3 and $C_6H_5CH_2$) with $BrBH_2 \cdot SMe_2$ in dichloromethane, followed by deprotonation with PS. The reaction produced the substituted $[7\text{-}R\text{-}7,8,10\text{-}C_3B_8H_{10}]^-$ anions in good yields [9].

Both the parent $[7,8,9\text{-}C_3B_8H_{11}]^-$ anion and its 7-aminosubstituted derivatives, $[7\text{-}R\text{-}7,8,9\text{-}C_3B_8H_{10}]^-$,



Scheme 1. Reactions leading to tricarbollide ligands. (i) Na^+ salt, neat ^{t}BuNC, 0 °C; (ii) $AlCl_3$, benzene, reflux; (iii) OH^-, Me_2SO_4, r.t.; (iv) Na naphthalide, THF, reflux; (v) CF_3COOH; (vi) PS, CH_2Cl_2–hexane, deprotonation; (vii) 350 °C.