

Review

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

Bohumil Štíbr *

Institute of Inorganic Chemistry, Academy of Sciences of the Czech Republic, 250 68, Řež, the Czech Republic

Received 10 October 2004; accepted 28 January 2005

Available online 23 March 2005

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), phosphadiborollides, and diphosphacarbollides are the subject of this work.

© 2005 Elsevier B.V. All rights reserved.

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

Contents

1. 11-Vertex <i>nido</i> tricarbaborane (tricarbollide) ligands and ferratricarbollides.	2695
2. 11-Vertex <i>nido</i> phosphadiborollide (phospha-dicarbollide) ligands and ferra phosphadiborollides	2697
3. 11-Vertex <i>nido</i> diphosphacarbaborane (diphospha-carbollide) ligands and ferra diphosphacarbollides	2699
4. Conclusions.	2699
Acknowledgements	2700
References	2700

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

* Present address: Lecture presented at the EUROBORON 3 meeting, Průhonice-by-Prague, the Czech Republic. September 12–16, 2004. Tel.: +420 2 6617 3106; fax: (internat.) +420 2 6617 3109.
E-mail address: stibr@ic.cas.cz.

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.

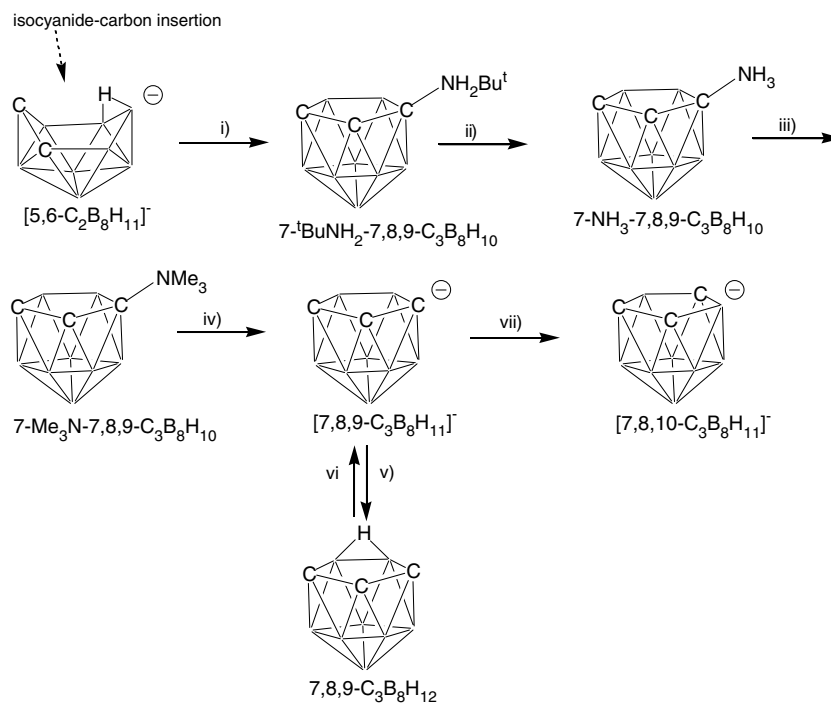
1. 11-Vertex *nido* tricarbaborane (tricarbollide) ligands and ferratricarbollides

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*-5,6- $C_2B_8H_{11}$] $^-$ anion and *t*-C₄H₉NC (path (i)) acting as monocarbon insertion agent [4]. The reaction is effected via evaporation of a solution of Na⁺ [5,6- $C_2B_8H_{11}$] $^-$ in neat *t*-C₄H₉NC, followed by acidification [5], which leads to the isolation of 7-*t*-C₄H₉NH₂-7,8,9- $C_3B_8H_{10}$ in 90% yield.

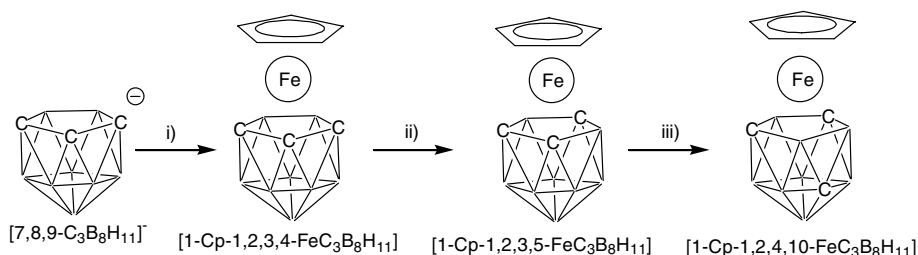
This derivative has been converted into 7-H₃N-7,8,9- $C_3B_8H_{10}$ (path (ii)) via elimination of isobutylene in the reaction with AlCl₃ in refluxing benzene (yield 77%). As also outlined in Scheme 1 (path (iii)), methylation of the H₃N derivative gave 7-Me₃N-7,8,9- $C_3B_8H_{10}$, which is an essential 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, $[7,8,9-C_3B_8H_{11}]^-$, as the main product (yield 62%) [3,6]. Acidification of this anion with CF₃COOH (path (v)) gives the neutral tricarbaborane 7,8,9- $C_3B_8H_{12}$ (yield 62%). This carborane behaves as a weak acid and can be smoothly deprotonated (path (vi)) to give back the $[7,8,9-C_3B_8H_{11}]^-$ anion [6].

As demonstrated in Scheme 1 (path (vii)), short heating of $[7,8,9-C_3B_8H_{11}]^-$ at 350 °C results in the rearrangement of the carbons on the open-face to give the isomeric tricarbollide anion $[7,8,10-C_3B_8H_{11}]^-$ (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 $[7,8,10-C_3B_8H_{11}]^-$ have been isolated from reactions of the [6-*R*-*nido*-5,6,9- $C_3B_7H_9$] $^-$ anions (where R = CH₃ and C₆H₅CH₂) with BrBH₂·SME₂ in dichloromethane, followed by deprotonation with PS. The reaction produced the substituted $[7-R-7,8,10-C_3B_8H_{10}]^-$ anions in good yields [9].

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



Scheme 1. Reactions leading to tricarbollide ligands. (i) Na⁺ salt, neat *t*-BuNC, 0 °C; (ii) AlCl₃, benzene, reflux; (iii) OH⁻, Me₂SO₄, r.t.; (iv) Na naphthalide, THF, reflux; (v) CF₃COOH; (vi) PS, CH₂Cl₂-hexane, deprotonation; (vii) 350 °C.

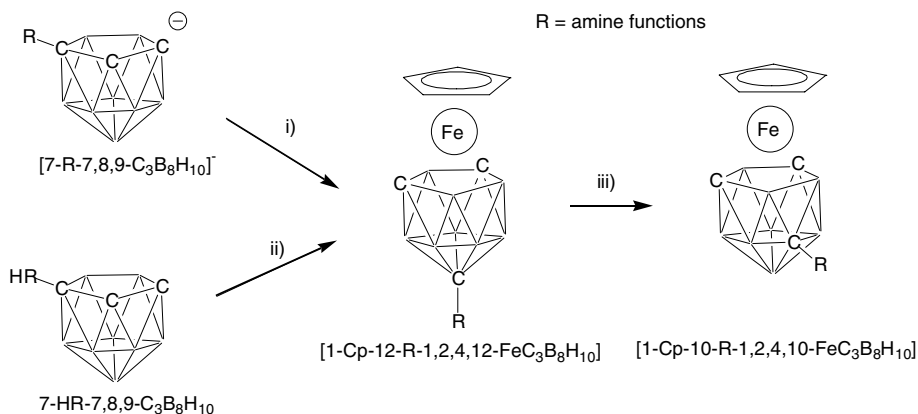


Scheme 2. Reactions leading to unsubstituted “half-sandwich” ferratricarbollides. (i) $[\text{CpFe}(\text{C}_6\text{H}_6)]^+\text{BF}_4^-$, CH_2Cl_2 , irradiation, r. t.; (ii) toluene, reflux; (iii) decane, reflux (160°C).

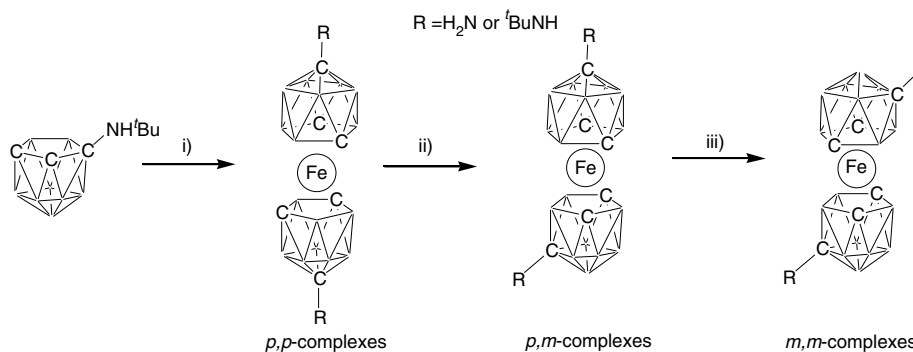
undergo Fe-complexation reactions using organometallic agents that generate in situ the $[\text{CpFe}]^+$ fragment to form the corresponding tricarbollide analogues of ferrocene. Just recently it has been found [10] that a room-temperature photolytic reaction between $\text{NMe}_4^+[7,8,9\text{-C}_3\text{B}_8\text{H}_{11}]^-$ and $[\text{CpFe}(\text{C}_6\text{H}_6)]^+\text{BF}_4^-$ generates in a moderate yield (ca. 40%) the ferratricarbollide $[1\text{-Cp-}1,2,3,4\text{-FeC}_3\text{B}_8\text{H}_{11}]$ (path i) of Scheme 2). The complex then undergoes cluster rearrangement on gentle heating to yield the $[1\text{-Cp-}1,2,3,5\text{-FeC}_3\text{B}_8\text{H}_{11}]$ isomer (path ii), which further rearranges to $[1\text{-Cp-}1,2,4,10\text{-FeC}_3\text{B}_8\text{H}_{11}]$ (path iii) at elevated temperatures (160°C). Theoretical calculations show that the last isomer is 8.5 and $25.8\text{ kcal mol}^{-1}$ more stable than the 1,2,3,5- and 1,2,3,4-isomers, respectively, and the *dsd* rearrangement path for these isomerisation processes has also been proposed [10]. It should be noted for comparison that $\text{Ti}^+[7,8,9\text{-C}_3\text{B}_8\text{H}_{11}]^-$ and $[\text{CpFe}(\text{CO})_2\text{I}]$ generate a mixture of the 1,2,3,5- and 1,2,4,10-isomers in toluene at reflux [11]. The same mixture is also obtained via reaction between the neutral $7,8,9\text{-C}_3\text{B}_8\text{H}_{12}$ and $[\text{CpFe}(\text{CO})_2\text{I}]$ in diglyme at ca. 150°C [10]. In these both cases, higher temperatures are required to eliminate the two CO ligands and, as a consequence, the transient 1,2,3,4-isomer is not isolated.

In contrast to complexation reactions shown in Scheme 2, similar complexations of the substituted $[7\text{-R-}7,8,9\text{-C}_3\text{B}_8\text{H}_{10}]^-$ anions (where $\text{R} = \text{H}_2\text{N}$ and ${}^t\text{BuHN}$)

(see Scheme 3) must proceed with a sharply different mechanism. Treatment of these anions with $[\text{CpFe}(\text{CO})_2\text{I}]$ in refluxing toluene (path i) generates the corresponding $[1\text{-Cp-}12\text{-R-}1,2,4,12\text{-FeC}_3\text{B}_8\text{H}_{10}]$ complexes in moderate yields as single products. The same cage isomers, $[1\text{-Cp-}12\text{-R-}1,2,4,12\text{-FeC}_3\text{B}_8\text{H}_{10}]$ (where $\text{R} = \text{H}_2\text{N}$, Me_2N , ${}^t\text{BuHN}$, and ${}^t\text{Bu}(\text{Me})\text{N}$) were also isolated in moderate yields from reactions of the zwitterionic compounds $7\text{-HR-}7,8,9\text{-C}_3\text{B}_8\text{H}_{10}$ with $[\text{CpFe}(\text{CO})_2\text{I}]$ in refluxing xylene (path ii) [12]. Surprisingly, a complex of the same cluster constitution, $[1\text{-Cp-}12\text{-}{}^t\text{BuNH-}1,2,4,12\text{-FeC}_3\text{B}_8\text{H}_{10}]$, is also formed in a high yield of 82% under very mild reaction conditions, via a room temperature photolytic reaction between $\text{Ti}^+[7\text{-}{}^t\text{BuNH-}7,8,9\text{-C}_3\text{B}_8\text{H}_{10}]^-$ (see also path i) and $[\text{CpFe}(\text{C}_6\text{H}_6)]^+\text{BF}_4^-$ [10]. All these reactions are thus accompanied by severe rearrangement of the cluster carbon atoms, in which the substituted carbon is moved to the bottom of the molecule, even under mild reaction conditions [10]. Theoretical considerations leading to the explanation of the different mode of these rearrangement-complexation reactions are underway. It should be added in this context that all complexes of the $[1\text{-Cp-}12\text{-R-}1,2,4,12\text{-FeC}_3\text{B}_8\text{H}_{10}]$ cluster configuration (where $\text{R} = \text{H}_2\text{N}$, Me_2N , Bu^tHN , and $\text{Bu}^t(\text{Me})\text{N}$) smoothly rearrange at 350°C into their thermodynamically more stable isomers, $[1\text{-Cp-}10\text{-R-}1,2,4,10\text{-FeC}_3\text{B}_8\text{H}_{10}]$ (path iii) [13].



Scheme 3. Reactions leading to aminosubstituted “half-sandwich” ferratricarbollides. (i) $[\text{CpFe}(\text{CO})_2\text{I}]$, toluene, reflux or $[\text{CpFe}(\text{C}_6\text{H}_6)]^+\text{BF}_4^-$, CH_2Cl_2 , irradiation, r. t.; (ii) $[\text{CpFe}(\text{CO})_2\text{I}]$, xylene, reflux; (iii) 350°C .



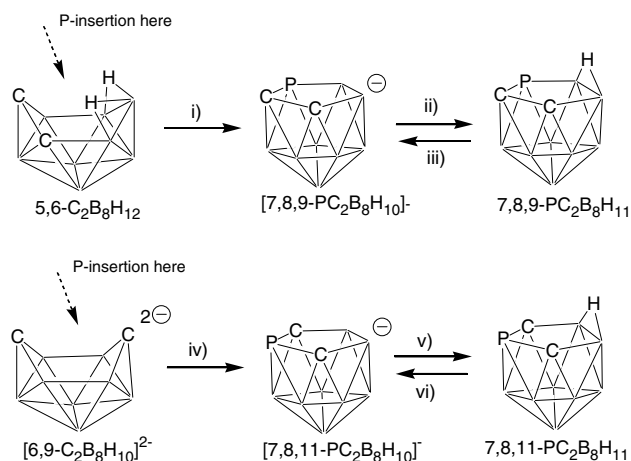
Scheme 4. Reactions leading to aminosubstituted “full-sandwich” ferratricarbollides. (i) Ti^+ or Na^+ salts, FeCl_2 (99.9%), diglyme, reflux, (ii) and (iii) higher temperatures up to $350\text{ }^\circ\text{C}$.

The first representatives of the “full-sandwich” iron(II) complexes, double tricarbollide-cage analogues of ferrocene, have also been prepared (Scheme 4) [14,15]. The best synthesis is based on a reaction between high-purity FeCl_2 and the $[7-(^t\text{BuHN})-7,8,9-\text{C}_3\text{B}_8\text{H}_{10}]^-$ anion that generates, depending on reaction condition (solvent, temperature) *para-para* (*p,p*) type complexes [*commo*-1- $\text{Fe}-(12-\text{R}-2,4,12-\text{C}_3\text{B}_8\text{H}_{10})_2^-$] (where $\text{R} = ^t\text{BuHN}$ or H_2N) as the main products in moderate yields (path (i)). Higher temperatures (paths (ii) and (iii)) promote the formation of the isomeric complexes of the *para-meta* (*p,m*) or *meta-meta* (*m,m*) type in smaller yields. The reaction of individual $^t\text{BuHN}$ -substituted compounds with AlCl_3 generally converts this substituent into the H_2N group via isobutylene elimination. The H_2N -substituted compounds are obviously structurally desired as metallocarborane building units for chemical constructions of linearly or L-shaped oligomeric rod molecules.

2. 11-Vertex *nido* phosphadiborane (phosphadiborane) ligands and ferra phosphadiboranes

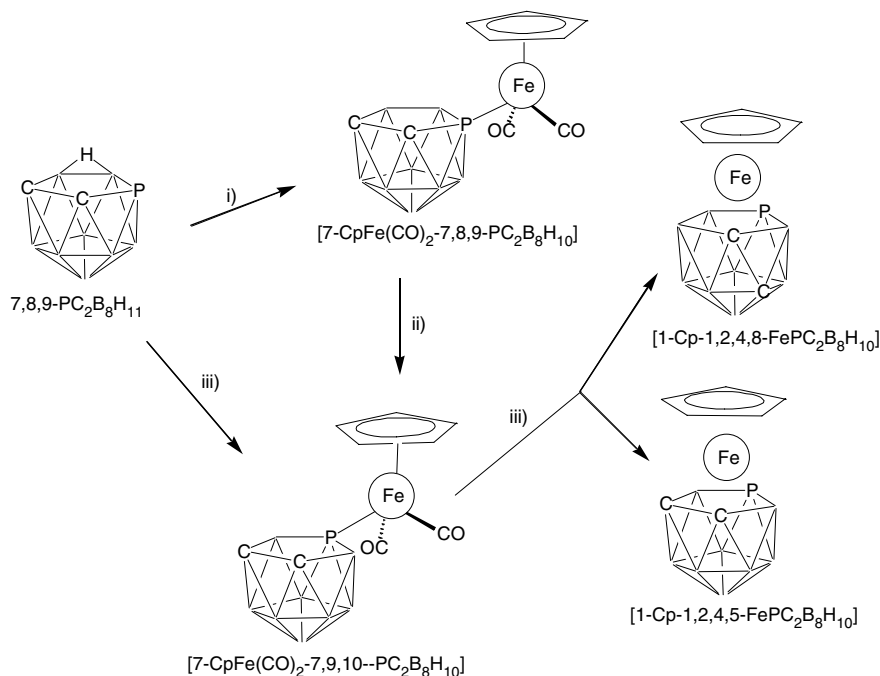
As shown in Scheme 5 (paths (i) and (ii)), the reaction between $5,6-\text{C}_2\text{B}_8\text{H}_{12}$ and PCl_3 in the presence of PS in dichloromethane, followed by acidification, generated $7,8,9-\text{PC}_2\text{B}_8\text{H}_{11}$ as the main reaction product (yield 38%) [16–18]. This phosphadiborane can be deprotonated by PS or NaH (path (iii)) to give the $[7,8,9-\text{PC}_2\text{B}_8\text{H}_{10}]^-$ anion. As also shown in Scheme 6, treatment of $\text{Na}_2[\text{nido}-6,9-\text{C}_2\text{B}_8\text{H}_{10}]$ with PCl_3 in DME at room temperature for 24 h (path (iv)), followed by hydrolysis of the reaction mixture, produces the neutral phosphadiborane $7,8,11-\text{PC}_2\text{B}_8\text{H}_{11}$, (yield 35%, see paths (iv) and (v)) [19]. The compound is isomeric with $7,8,9-\text{PC}_2\text{B}_8\text{H}_{11}$ and can be quantitatively deprotonated by PS to give the corresponding $[7,8,11-\text{PC}_2\text{B}_8\text{H}_{10}]^-$ anion (path (vi)).

So far, only the neutral $7,8,9-\text{PC}_2\text{B}_8\text{H}_{11}$ was used as a starting material for the syntheses of a series of com-

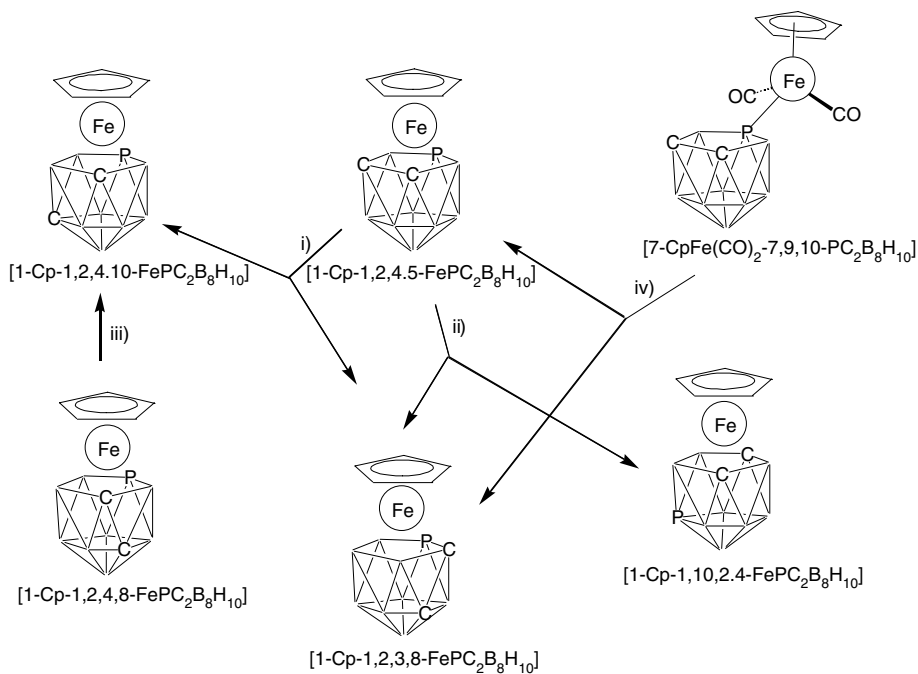


Scheme 5. Reactions leading to 11-vertex *nido* phosphadiboranes. (i) PCl_3 , PS, CH_2Cl_2 , r.t.; (ii) acidification; (iii) PS, CH_2Cl_2 -hexane, deprotonation; (iv) PCl_3 , DME, r.t., 24 h; (v) acidification; (vi) PS, CH_2Cl_2 -hexane, deprotonation.

plexes containing the $[\text{CpFe}]^+$ unit (Scheme 6) [20]. In contrast to the complexation of tricarbollide ligands discussed above, that of their phosphadiborane analogues proceeds via two isomeric η^1 -bonded (σ) $[\text{CpFe}(\text{CO})_2-\text{PC}_2\text{B}_8\text{H}_{10}]$ *nido* complexes (paths (i) and (ii) that undergo full η^5 -complexation at elevated temperatures via CO elimination. As demonstrated in path (i), the reaction between $7,8,9-\text{PC}_2\text{B}_8\text{H}_{11}$ and $[\text{CpFe}(\text{CO})_2]_2$ in benzene at reflux gave an η^1 -bonded complex $[7-\text{CpFe}(\text{CO})_2-7,8,9-\text{PC}_2\text{B}_8\text{H}_{10}]$ in 38% yield. A similar reaction at elevated temperatures (xylene, reflux 24 h, path (iii)) gave, however, the isomeric complex $[7-\text{CpFe}(\text{CO})_2-7,9,10-\text{PC}_2\text{B}_8\text{H}_{10}]$ (yield 28%) together with the fully sandwiched complexes $[1-\text{Cp}-1,2,4,5-\text{FePC}_2\text{B}_8\text{H}_{10}]$ (yield 30%) and $[1-\text{Cp}-1,2,4,8-\text{FePC}_2\text{B}_8\text{H}_{10}]$ (yield 5%). Moreover, heating of both of the carbonyl complexes in refluxing xylene (paths (ii) and (iii)) gives $[1-\text{Cp}-1,2,4,5-\text{FePC}_2\text{B}_8\text{H}_{10}]$ (yields 46% and 52%, respectively) and $[1-\text{Cp}-1,2,4,8-\text{FePC}_2\text{B}_8\text{H}_{10}]$ (yields 4% and 5%, respectively).



Scheme 6. Reactions leading to the Fe-complexation of 7,8,9-PC₂B₈H₁₁. (i) [CpFe(CO)₂], benzene, reflux; (ii) and (iii) [CpFe(CO)₂], xylene, reflux.



Scheme 7. Cage-isomerisation reactions of “half-sandwich” ferraphosphadecarborollides. (i) 350 °C; (ii) mesitylene, reflux; (iii) and (iv) 350 °C.

While the thermolysis of [1-Cp-1,2,4,5-FeC₃B₈H₁₁] leads only to one isomer, (see path (iii) of Scheme 2), that of the isostructural [1-Cp-1,2,4,5-FePC₂B₈H₁₀] compound gives also complexes of other than 1,2,4,10-cluster constitution (see Scheme 7) [21]. Thus, heating of the 1,2,4,5-isomer at 350 °C (path (i)) gave two other isomers, [1-Cp-1,2,4,10-FePC₂B₈H₁₀] (yield 23%) and [1-Cp-1,2,3,8-FePC₂B₈H₁₀] (yield 52%). The last isomer

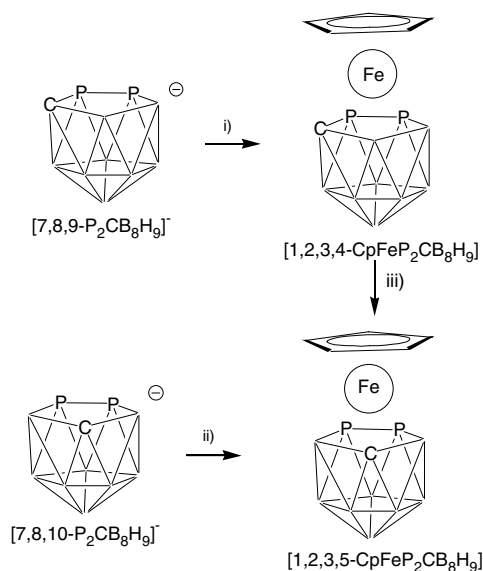
is also formed (yield 15%), along with [1-Cp-1,10,2,4-FePC₂B₈H₁₀] (yield 13%), upon heating in mesitylene at reflux (path (ii)), and the thermolysis of the solid [1-Cp-1,2,4,8-FePC₂B₈H₁₀] at 350 °C (path (iii)) leads to [1-Cp-1,2,4,10-FePC₂B₈H₁₀] (yield 51%). Moreover, the heating of the σ complex [7-CpFe(CO)₂-7,9,10-PC₂B₈H₁₀] at 350 °C (path (iv)) generates complexes [1-Cp-1,2,4,5-FePC₂B₈H₁₀] (yield 52%) and [1-Cp-

1,2,3,8-FePC₂B₈H₁₀] (yield 23%). Therefore, in the [Cp-FePC₂B₈H₁₀] series, five isomers have so far been known [20,21] as compared to the three reported isomers of the corresponding [Cp-FeC₃B₈H₁₁] ferratricarbollide series (see Scheme 2) [10].

3. 11-Vertex *nido* diphosphacarborane (diphosphacarborollide) ligands and ferra diphosphacarborollides

Scheme 8 shows that treatment of a solution of excess PCl₃ and PS with 4-CB₈H₁₄ in CH₂Cl₂, followed by hydrolysis of the reaction mixture, resulted in the isolation of the 11-vertex phosphadecarborane 7,8,9-P₂CB₈H₁₀ (yield 34%, paths (i) and (ii)) as the main product. Other products isolated from this reaction were the phosphacarboranes *nido*-7,8,9,10-P₃CB₇H₈ (yield 5%) and *closo*-2,1-PCB₈H₉ (yield 5%). The neutral 7,8,9-P₂CB₈H₁₀ can be deprotonated by PS in CH₂Cl₂ or NaH in diethyl ether to give the [7,8,9-P₂CB₈H₉][−] anion (path (iii)), which gives back 7,8,9-P₂CB₈H₁₀ on re-protonation (path (ii)). Thermal rearrangement of Na⁺[7,8,9-P₂CB₈H₉][−] at 350 °C (path (iv)) afforded the isomeric, symmetrical [7,8,10-P₂CB₈H₉][−] anion (yield 86%) via clean C migration in the open pentagonal face [22].

Scheme 9 (path (i)) shows that the reaction between Tl⁺[7,8,9-P₂CB₈H₉][−] and [CpFe(CO)₂I] in refluxing mesitylene gives the half-sandwich complex [1-Cp-1,2,3,4-FeP₂CB₈H₉] (yield 63%). Under the same conditions, the isomeric salt [PPh₄]⁺[7,8,10-P₂CB₈H₉][−] and [CpFe(CO)₂I] (path (ii)) generate [1-Cp-1,2,3,5-FeP₂CB₈H₉] (yield 56%), which also results (yield 52%) from the heating of [1-Cp-1,2,3,4-FeP₂CB₈H₉] under argon at ca. 350 °C (path (iii)). Further heating of the 1,2,3,5-isomer at temperatures >400 °C led only to decomposition and no isomer containing CH or P vertices in *m*- or *p*-positions to the Fe vertex was iso-

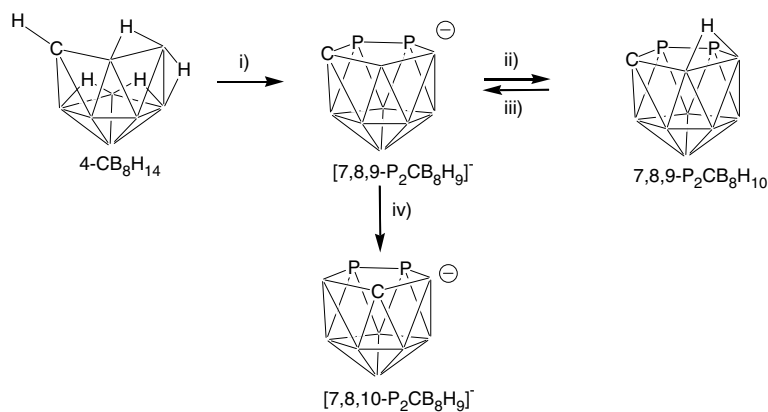


Scheme 9. Reactions leading to half-sandwich^{††} ferradiphosphacarborollides. (i) Tl⁺ salt, [CpFe(CO)₂I], mesitylene, reflux; (ii) PPh₄⁺ salt, [CpFe(CO)₂I], mesitylene, reflux; (iii) 350 °C.

lated. A significant feature of both complexation reactions shown in paths (i) and (ii) is the retention of cluster configuration even at elevated temperatures [23].

4. Conclusions

The review outlines synthetic methods leading to carborane and phosphacarborane ligands of the general 11-vertex [*nido*-E₃B₈H₈][−] constitution (where E = CH or P and their combinations) that are structural analogues of the Cp anion. The ligands can be employed for the preparation of a long series of isomeric “half-sandwich” [Cp-*closo*-FeE₃B₈H₈] cluster-borane analogues of ferrocene



Scheme 8. Reactions leading to 11-vertex *nido* diphosphacarboranes. (i) excess PCl₃ and PS, CH₂Cl₂, r.t.; (ii) acidification; (iii) PS, CH₂Cl₂-hexane, deprotonation; (iv) 350 °C.

via complexation with selected organometallic compounds of iron that generate the $[\text{CpFe}]^+$ fragment, such as $[\text{CpFe}(\text{CO})_2\text{I}]$, $[\text{CpFe}(\text{CO})_2]$, and $[\text{CpFe}(\text{C}_6\text{H}_6)]^+$. It should be anticipated that the Fe-complexation of the unsubstituted, $[\text{E}_3\text{B}_8\text{H}_8]^-$, ligands in its initial stage proceeds with retention of the original ligand configuration to give complexes of structure $[\text{1-Cp-1,2,3,4-FeE}_3\text{B}_8\text{H}_8]$. A complex of this type has so far been isolated only in the tricarbollide series ($\text{E} = \text{CH}$) under very mild reaction conditions; at elevated temperatures; complexes of structures $[\text{1-Cp-1,2,3,5-FeE}_3\text{B}_8\text{H}_8]$ and $[\text{1-Cp-1,2,4,10-FeE}_3\text{B}_8\text{H}_8]$ are most typically isolated as a consequence of cluster rearrangement of the 1,2,3,4-isomer. It should be noted that the $[\text{1-Cp-1,2,4,10-FeE}_3\text{B}_8\text{H}_8]$ isomer is missing in the $[\text{FeP}_2\text{CB}_8\text{H}_9]$ series and, in the $[\text{FePC}_2\text{B}_8\text{H}_{10}]$ series, also other isomers have been isolated, while the 1,2,3,4-isomer is pending. These differences can be attributed to remarkable differences in the strengths of cage C–C, C–P, and P–P bonds. It should be also added that all attempts to synthesize unsubstituted “full sandwiches” of the $[\text{closo-Fe}(\text{E}_3\text{B}_8\text{H}_8)_2]$ constitution have so far failed.

Except for the $[\text{7-R-7,8,9-C}_3\text{B}_8\text{H}_{10}]^-$ anions (where $\text{R} = \text{H}_2\text{N}$, Me_2N , $^t\text{BuHN}$, and $^t\text{Bu}(\text{Me})\text{N}$), no other substituted tricarbollide or phosphacarbollide anions have so far been employed for Fe-complexation. Nevertheless, the corresponding complexation reactions in the substituted tricarbollide series shown in Schemes 3 and 4 provide entirely different rearrangement-complexation scenario in comparison with that established for unsubstituted compounds (see Schemes 2, 6, and 9). The most significant feature is a clean formation, even under very mild reaction conditions, of the $[\text{12-R-1,2,4,12-FeC}_3\text{B}_8\text{H}_{10}]$ isomer which has never been isolated in the unsubstituted series. It can be therefore inferred that the complexation process is severely affected by the nature and cage position of the substituent, its size and electronic effects as well. Naturally, much work in this area is to be done to elucidate these effects.

Acknowledgements

Part of this work was supported with subventions from the Spanish government, Alexander von Humboldt Stiftung (FRG), and Grant Agency of the Czech Republic (Project no. 203/05/2646). Appreciated are helpful suggestions by Professors B. Wrackmeyer (University of Bayreuth (FRG), F. Teixidor (ICMAB Barcelona), and J.D. Kennedy (University of Leeds, UK)

together with the experimental and theoretical work by Drs. J. Holub, B. Grüner, M. Bakardjiev, D. Hnyk, and J. Fusek in this area of chemistry. We also thank Professor A.R. Kudinov (INEOS Moscow) and his group for fruitful collaboration in the field of tricarbollide complexes.

References

- [1] See, for example: R.E. Williams, in: A. Olah, K. Wade, R.E. Williams (Eds.), *Electron Deficient Boron and Carbon Clusters*, G. Wiley, New York, 1991, pp. 11–93.
- [2] B. Štíbr, J. Holub, F. Teixidor, in: W. Siebert (Ed.), *Advances in Boron Chemistry*, Royal Society of Chemistry, Cambridge, England, 1997, pp. 333–340.
- [3] B. Štíbr, *Proc. Ind. Natl. Acad. Sci.* 68A (2003) 487–497.
- [4] B. Štíbr, J. Holub, F. Teixidor, C. Viñas, *Chem. Commun* (1995) 795–796;
B. Štíbr, J. Holub, I. Čisařová, F. Teixidor, C. Viñas, J. Fusek, Z. Plzák, *Inorg. Chem.* 35 (1996) 3635–3642.
- [5] B. Štíbr, J. Holub, J. Plešek, T. Jelínek, B. Grüner, F. Teixidor, C. Viñas, *J. Organomet. Chem.* 582 (1999) 282–285.
- [6] J. Holub, B. Štíbr, D. Hnyk, J. Fusek, I. Čisařová, F. Teixidor, C. Viñas, Z. Plzák, P.v.R. Schleyer, *J. Am. Chem. Soc.* 119 (1997) 7750–7759.
- [7] B. Štíbr, J. Holub, I. Čisařová, F. Teixidor, C. Viñas, *Inorg. Chim. Acta* 245 (1996) 129–131.
- [8] R. Rousseau, S. Lee, E. Canadell, F. Teixidor, C. Viñas, B. Štíbr, *New J. Chem.* 20 (1996) 277–281.
- [9] A.M. Shedlow, P.J. Carroll, L.G. Sneddon, *Organometallics* 14 (1995) 4046–4047.
- [10] J. Holub, D.S. Perekalin, D.G. Golovanov, K.A. Lyssenko, P.V. Petrovskii, A.R. Kudinov, B. Štíbr, *Organometallics* (in press).
- [11] B. Štíbr, J. Holub, F. Teixidor, C. Viñas, *Collect. Czech. Chem. Commun.* 60 (1995) 2023–2027.
- [12] J. Holub, B. Grüner, I. Čisařová, J. Fusek, Z. Plzák, F. Teixidor, C. Viñas, B. Štíbr, *Inorg. Chem.* 38 (1999) 2775–2780.
- [13] B. Grüner, A. Lehtonen, R. Kivekäs, R. Sillanpää, J. Holub, F. Teixidor, C. Viñas, B. Štíbr, *Inorg. Chem.* 39 (2000) 2577–2580.
- [14] B. Grüner, F. Teixidor, C. Viñas, R. Sillanpää, R. Kivekäs, J. Holub, B. Štíbr, *J. Chem. Soc., Dalton. Trans.* (1999) 337.
- [15] B. Grüner, J. Bačkovský, R. Sillanpää, R. Kivekäs, O. Čisařová, F. Teixidor, C. Viñas, B. Štíbr, *Eur. J. Inorg. Chem.* 9 (2004) 1402–1410.
- [16] B. Štíbr, J. Holub, M. Bakardjiev, D. Hnyk, O.L. Tok, W. Milius, B. Wrackmeyer, *Eur. J. Inorg. Chem.* 7 (2002) 2320–2326.
- [17] B. Štíbr, *Collect. Czech. Chem. Commun.* 67 (2002) 843–868.
- [18] B. Štíbr, *Pure Appl. Chem.* 75 (2003) 1295–1304.
- [19] J. Holub, D.L. Ormsby, J.D. Kennedy, R. Greatrex, B. Štíbr, *Inorg. Chem. Commun.* 3 (2000) 178–181.
- [20] B. Štíbr, J. Holub, M. Bakardjiev, I. Pavlík, O.L. Tok, I. Čisařová, B. Wrackmeyer, M. Herberhold, *Chem. Eur. J.* (2003) 2239–2244.
- [21] B. Štíbr, J. Holub, M. Bakardjiev, I. Pavlík, O.L. Tok, B. Wrackmeyer, *Eur. J. Inorg. Chem.* 8 (2003) 2524–2528.
- [22] M. Bakardjiev, I. Holub, B. Štíbr, D. Hnyk, B. Wrackmeyer, *Inorg. Chem.* (in press).
- [23] M. Bakardjiev, J. Holub, M.J. Carr, J.D. Kennedy, B. Štíbr, *Dalton Trans.* (2005) 909–913.