Amino-Substituted Ferra-bis(tricarbollides) − Metallatricarbaboranes Designed for Linear Molecular Constructions

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Reactions between high purity $FeCl_2$ and the anion [*nido*-7-(*t*BuHN)-7,8,9-$C_3B_8H_{10}$)]$^-$ ($\mathbf{1}^-$) have been used for efficient syntheses of the twelve-vertex double-cluster metallatricarbollide complexes of the *para*,*para* (*p*,*p*) type [*closo*-9,9′-(RHN)$_2$-*commo*-2,2′-Fe^{II}-1,7,9-($C_3B_8H_{10}$)-1′,7′,9′-($C_3B_8H_{10}$)] (**2**) (**2a**, R = *t*Bu and **2b**, R = H) (yields 42–45% for **2a**). Compound **2b**, which contains two reactive amino substituents conveniently attached to the tricarbollide subclusters in *p*-positions with respect to the metal center, was prepared via facile cleavage of the *t*Bu substituent in **2a** either by $AlCl_3$ or by thermal means. The structure of **2b** constitutes a good setting for the synthesis of building blocks for constructing linear metallatricarbollide rods of high stability. Two isomeric compounds of the *para*,*meta* (*p*,*m*) type **3**, [*closo*-9,10′-(RHN)$_2$-*commo*-2,2′-Fe-1,7,9-($C_3B_8H_{10}$)-1′,7′,10′-($C_3B_8H_{10}$)] (where R = *t*Bu **3a** and/or H **3b**), were isolated in smaller yields from reactions of high purity $FeCl_2$ with $\mathbf{1}^-$ at higher temperatures. Also reported is the characterization of the *m*,*m*-type complex, [*closo*-10,10′-(*t*BuHN)$_2$-*commo*-2,2′-Fe^{II}-1,7,10-($C_3B_8H_{10}$)-1′,7′,10′-($C_3B_8H_{10}$)] (**4a**), and the two zwitterionic species of the new 7-L-7,8,10-$C_3B_8H_{10}$ type (**6**) [L = Me_3N **6a** and *t*Bu(Me)HN **6b**] isolated in moderate yields from the reaction of reagent grade $FeCl_2$ with $\mathbf{1}^-$. The molecular structures of **2b**, **3a**, and **6b** were determined by single-crystal X-ray diffraction studies. Multinuclear (^1H and ^{11}B), two-dimensional [^{11}B-^{11}B]-COSY, and $^1H\{^{11}B(\text{selective})\}$ magnetic resonance measurements enabled complete assignments of all resonances for all compounds and are in excellent agreement with the structures proposed.

Introduction

The first venture into the area of twelve-vertex metallatricarbollide chemistry was the synthesis of the mixed-sandwich cyclopentadienyl-ferratricarbollide analogues of ferrocene, the *closo* complexes [9-R-2-(η^5-C_5H_5)-2,1,7,9-$FeC_3B_8H_{10}$] [where R = H_2N, CH_3NH, $(CH_3)_2N$, *t*BuHN, and *t*BuCH_3N][1] and of the isomeric [10-R-2-(η^5-C_5H_5)-2,1,7,10-$FeC_3B_8H_{10}$] (where R = H_2N, CH_3NH, $(CH_3)_2N$, and *t*BuHN)[2] species. In contrast to double-cluster metal dicarbollide "full" sandwiches, which are quite common and easily available,[3] we have found that the corresponding metallatricarbollide counterparts cannot be prepared under comparable conditions. Finally it was recognized that such complexes could be synthesized only under forcing reaction conditions. In a preliminary communication[4] we reported a low-yield isolation of the first representatives of the double-cluster metallatricarbollide family, [*closo*-9,9′-(*t*BuHN)$_2$-*commo*-2,2′-M^{II}-1,7,9-($C_3B_8H_{10}$)-1′,7′,9′-($C_3B_8H_{10}$)], where M = Fe and Ru (yields 4% and 9%, respectively). In this paper we report full experimental details on substantially improved, simple and good yielding syntheses of the isomeric ferra-bis(tricarbollides) containing amine functionalities, (*t*BuHN or H_2N) in *m*- and *p*-positions with respect to the Fe center. Also reported are compounds of the still unknown 7-L-7,8,10-$C_3B_8H_{10}$ (L = amine) type which are formed by metal-promoted isomerization reactions. Structures are presented in a simplified manner: unmarked vertices in Schemes 1 and 2 stand for cluster BH units, while C denotes the CH vertex if no substituent is attached to it. General structures of individual types of compounds discussed in this work are in the Structures diagram.

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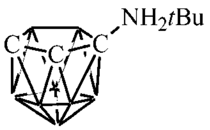

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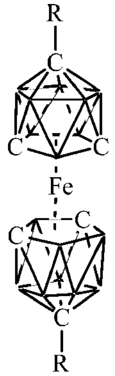
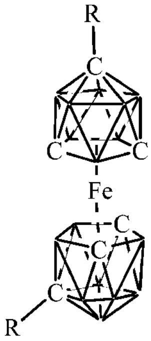


2 (R = NH*t*Bu, **2a**; H_2N, **2b**; NH*t*Bu and NH_2, **2c**)



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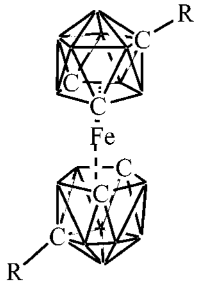

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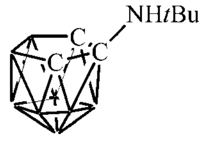
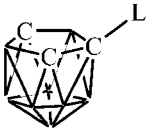


5$^-$



6 (L = Me_3N, **6a**; tBuMeHN, **6b**)

Results and Discussion

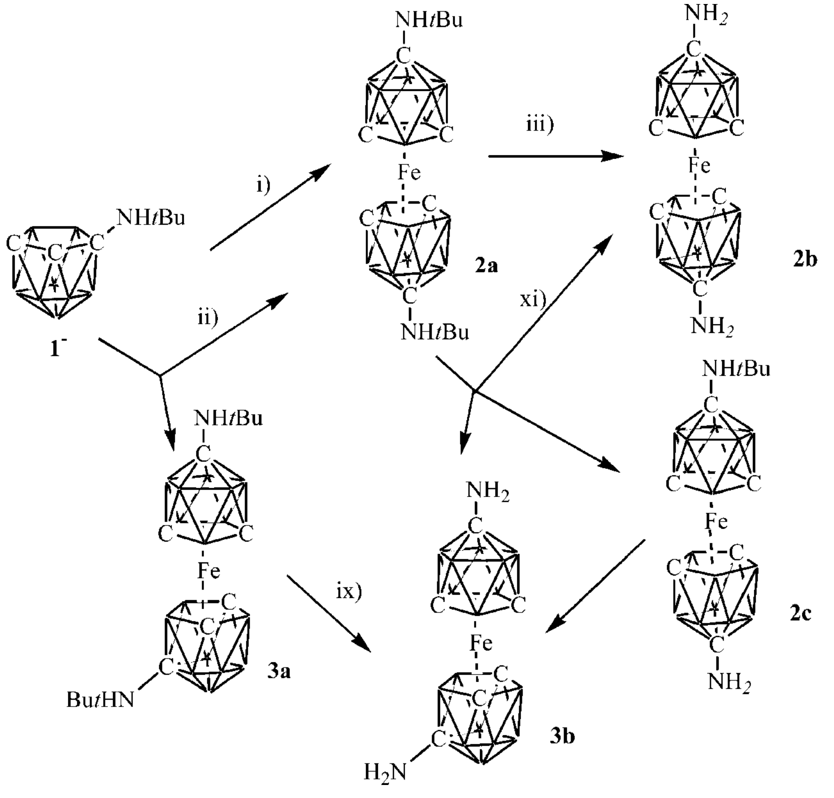
Syntheses

As shown in path i) of Scheme 1, the reaction between $Tl[7\text{-}(tBuHN)\text{-}7,8,9\text{-}C_3B_8H_{10}]$ $Tl(\mathbf{1}^-)$ and an excess of highly pure $FeCl_2$ (99.99%) in a diglyme-mesitylene mixture led to formation of [*closo*-9,9′-(*t*BuHN)$_2$-*commo*-2,2′-Fe^{II}-1,7,9-($C_3B_8H_{10}$)-1′,7′,9′-($C_3B_8H_{10}$)] (**2a**). Complex **2a** was isolated as a single metallacarborane product in a significantly improved yield (43%, cf. a 4% yield in the previous method).[4]

Higher overall yields of the ferra bis(tricarbollides) (up to 62%) have been obtained when $Na[7\text{-}(tBuH_2N)\text{-}7,8,9\text{-}C_3B_8H_{10}]^-$ $Na(\mathbf{1}^-)$ was heated to reflux in diglyme in the presence of an excess of high-purity $FeCl_2$ (path ii) of Scheme 1). In this case, however, the main product **2a** (yield 45%) was always accompanied by the isomeric compound [9,10′-(*t*BuHN)$_2$-*commo*-2,2′-Fe-*closo*-1,7,9-($C_3B_8H_{10}$)-1′,7′,10′-($C_3B_8H_{10}$)] (**3a**) (yield 17%). The advantage of the $Na(\mathbf{1}^-)$ reaction is the good total yield of the sandwich compounds, but the presence of **3a** substantially complicates the isolation of **2a** since the mixture of **2a** and **3a** must be then separated by preparative liquid chromatography. Attempts at carrying out the reaction in a mesitylene-diglyme mixture or decreasing the reaction temperature led to similar isomeric mixtures and also to a substantial decrease in the total yield of **2a** and **3a** (ca. 25%). On the other hand, if the process was directed to obtain products with bare NH_2 groups (**2b** and **3b**), the pre-purified mixture of **2a** and **3a** could be first conveniently treated to remove the butoxide function (see text below), and the resultant products could be separated more easily.

Complex **3a** apparently originates from *dsd* isomerization on one of the tricarbollide ligands of **2a** in the reaction mixture as the concentration of **3a** increases with the reaction time. This observation is consistent with the similarly anomalous $p \rightarrow m$ isomerization path reported for the mixed-sandwich metallatricarbollide series.[2]

Consistent with the previously reported findings[2] are the isobutylene elimination reactions leading to H_2N derivatives in the series of bis(tricarbollide) iron sandwiches reported in this work. The reactions of both **2a** and **3a** with anhydrous $AlCl_3$ in hexane at reflux removes the *t*Bu substituent to give the complexes [*closo*-9,9′-(H_2N)$_2$-*commo*-2,2′-Fe^{II}-1,7,9-($C_3B_8H_{10}$)-1′,7′,9′-($C_3B_8H_{10}$)] (**2b**) and [*closo*-9,9′-(H_2N)$_2$-*commo*-2,2′-Fe^{II}-1,7,9-($C_3B_8H_{10}$)-1′,7′,10′-($C_3B_8H_{10}$)] (**3b**), respectively (yields of 82% and 80%, respectively, see paths iii) and ix) of Scheme 1). For the preparation of **3b**, it was convenient to apply the $AlCl_3$ reaction on a mixture of **2a** and **3a** obtained from the complexation of $Na(\mathbf{1}^-)$ as outlined above, which resulted typically in a total yield of 79% of the H_2N- derivatives **2b** and **3b**. The advantage of this approach is that the mixture of compounds **2b** and **3b** could be easily separated by conventional column chromatography. Alternatively, the isobutylene elimination, giving **2b**, could be achieved by briefly heating **2a** at 210 °C in vacuo (see path xi) of Scheme 1). This thermal cleavage is, however, accompanied by simultaneous formation of the isomeric [*closo*-9,10′-(H_2N)$_2$-*commo*-2,2′-Fe^{II}-1,7,9-($C_3B_8H_{10}$)-1′,7′,10′-($C_3B_8H_{10}$)] (**3b**) which, depending on reaction time, accompanies the main



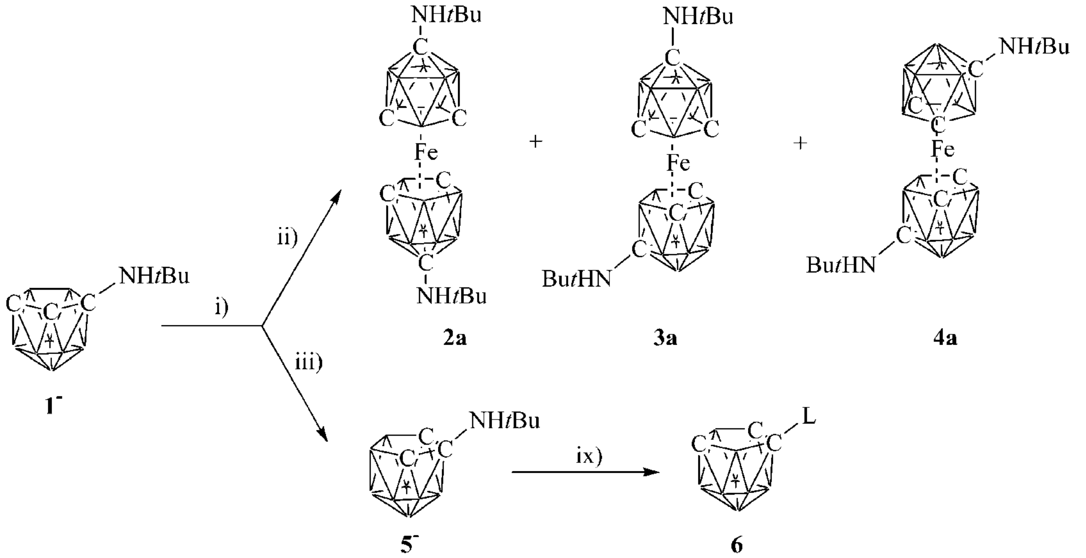
Scheme 1. Formation of ferratricarbollides, their thermal rearrangements and cleavage of their butyl groups. i) Tl(1^-), $FeCl_2$ (99.99%), diglyme/mesitylene (1:4), reflux. ii) Na(1^-), $FeCl_2$ (99.99%), diglyme, reflux. iii), ix) $AlCl_3$, hexane, reflux. xi) 210 °C, 15 min

product in small to moderate yields. Another by-product of this thermal cleavage is the linearly shaped [*closo*-9-(*t*BuHN),9′-(H_2N)-*commo*-2,2′-Fe^{II}-1,7,9-($C_3B_8H_{10}$)-1′,7′,10′-($C_3B_8H_{10}$)] (**2c**) (yield 20%). Complex **2c** evidently arises from one-side loss of a butyl group from **2a**. These side isobutylene-elimination reactions are the reason why **3a** cannot be obtained in good yields by thermal rearrangement of **2a**.

It should be noted that the iron complexation reactions outlined above are rather sensitive to the purity of the $FeCl_2$ employed since the reagent grade $FeCl_2$ used in the preliminary communication[4] provided completely different reaction products. This original reaction[4] has now been studied in more detail and has been found to be very complex. Based on multiple experiments, it was found that prolonged treatment of 7-(*t*BuH_2N)- *nido*-7,8,9-$C_3B_8H_{10}$ (**1**) with NaH and an excess of the reagent-grade $FeCl_2$ in diglyme at reflux (path i) of Scheme 2), followed by chromatographic separation, resulted in the isolation of complexes **2a** and **3a** in yields 4 and 6%, respectively. The reaction also gave trace amounts of the third *m,m*-substituted isomer, [*closo*-10,10′-(*t*BuHN)$_2$-*commo*-2,2′-Fe^{II}-(1,7,10-$C_3B_8H_{10}$)$_2$] (**4a**). Nevertheless, the formation of these three iron complexes represents only a side reaction mode (path ii) of Scheme 2). The main reaction mode (path iii) of Scheme 2) is, however, associated with the recently reported metal-promoted rearrangement of anion $\mathbf{1}^-$ giving at lower temperatures (DME at reflux) the [8-*t*BuNH-*nido*-7,8,9-$C_3B_8H_{10}$]$^-$ ($\mathbf{5}^-$) anion [and finally the neutral compound 8-*t*BuNH-*nido*-7,8,9-$C_3B_8H_{11}$ (**5**) upon protonation].[5] Under the reaction conditions now employed (diglyme at reflux) compound **5** was isolated in only trace amounts and the main reaction products were identified as 7-Me_3N-*nido*-7,8,10-$C_3B_8H_{10}$ (**6a**) and 7-*t*Bu(Me)HN-*nido*-7,8,10-$C_3B_8H_{10}$ (**6b**) (yields of 14 and 17%, respectively). These compounds are representatives of the zwitterionic 7-L-7,8,10-$C_3B_8H_{10}$ (**6**) family and it is reasonable to suppose that their formation is associated with further cage rearrangement of anion $\mathbf{5}^-$, followed by in situ *N*-methylation by the solvent methyl groups (diglyme) (path ix) of Scheme 2). The rearrangement is evidently associated with the migration of the unsubstituted cage carbon C7 in $\mathbf{5}^-$ into the C10 position. A similar rearrangement of the [7,8,9-$C_3B_8H_{11}$]$^-$ and 7-$(CH_3)_3$N-7,8,9-$C_3B_8H_{10}$ *nido*-tricarbollide compounds into their isomeric congeners, [7,8,10-$C_3B_8H_{11}$]$^-$ and 10-$(CH_3)_3$N-7,8,10-$C_3B_8H_{10}$, has already been subject of theoretical and experimental studies.[6,7]

X-ray Diffraction Studies

The structure of compound **2a** has already been determined by an X-ray diffraction study published in a preliminary communication.[4] The results of the X-ray diffraction analysis of the bis-tricarbollide complex [*closo*-9,9′-$(H_2N)_2$-*commo*-2,2′-Fe^{II}-1,7,9-($C_3B_8H_{10}$)-1′,7′,9′-$C_3B_8H_{10}$)] (**2b**) resulting from cleavage of the *t*Bu end groups is shown in Figure 1. As follows from the comparison of the crystallo-



(L = Me$_3$N, 6a; *t*BuMeHN, 6b)

Scheme 2. Reactions with reagent grade FeCl$_2$ (metal-promoted rearrangements) i) Na(**1**$^-$), FeCl$_2$ (98%), diglyme, reflux. ii) side formation of ferratricabollides. iii) main reaction mode, the formation of zwitterions of the 7-L-7,8,10-C$_3$B$_8$H$_{10}$ type (**6**) (L = Me$_3$N **6a** and *t*Bu(Me)HN **6b**)

graphically determined structures of **2a**[4] and the structurally similar **2b**, a change in the *t*BuHN substituent for the unsubstituted H$_2$N group has no significant effect either on the N−C9 or C9−B distances. In contrast to **2a**, however, the molecules of **2b** are symmetrical, with two independent molecules in the unit cell. The iron atoms in both molecules are situated at the center of symmetry and the mutual configuration of the C$_2$B$_3$ pentagons is therefore exactly staggered. This means the C$_2$B$_3$ pentagonal planes flanking the metal center are parallel and the arrangement of the C9, Fe, and C9^i atoms is linear in both molecules. An interesting feature is that the two molecules form dimeric assemblies via a weak hydrogen bond N1−H1A−N2 with the N1−N2 distance being 3.378(2) Å and the N1−H1A−N2 angle being 172°.

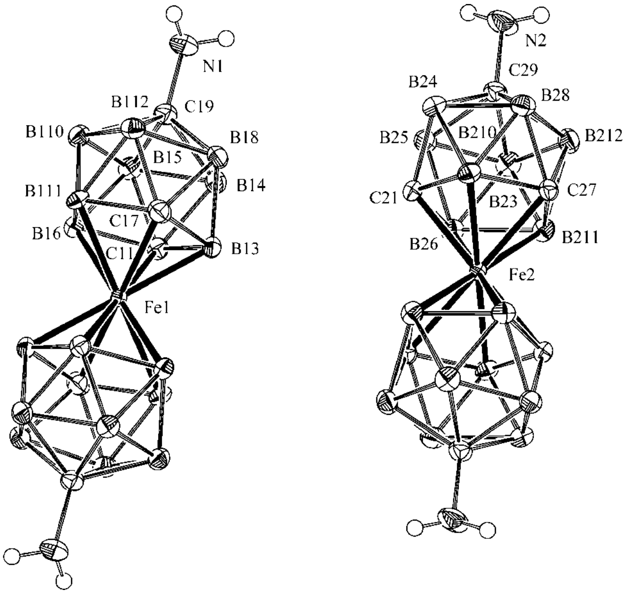


Figure 1. ORTEP representation of the molecular structure of **2b** with crystallographic numbering. Hydrogen positions omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Both molecules are situated on a center of symmetry; selected bond lengths (Å): Fe1−C(11) 2.064(2), Fe1−C(17) 2.061(2), Fe2−C(21) 2.060(2), Fe2−C(27) 2.072(2), Fe1−B(13) 2.054(2), Fe1−B(16) 2.075(2), Fe1−B(111) 2.075(2), Fe2−B(23) 2.047(2), Fe2−B(26) 2.075(2), Fe2−B(211) 2.080(2), N1−C(19) 1.431(2), N2−C(29) 1.432(2)

The results of the X-ray diffraction analysis of the bis(tricarbollide) complex [*closo*-9,10′-(*t*BuHN)$_2$-*commo*-2,2′-Fe-1,7,9-(C$_3$B$_8$H$_{10}$)-1′,7′,10′-(C$_3$B$_8$H$_{10}$)] (**3a**) are shown in Figure 2. The tricarbollide subclusters in **3a** are different and Figure 2 shows *p*-substitution in one of the tricarbollide subunits and *m*-substitution in the second. However, no marked differences can be seen in the corresponding bond parameters between the cages. The mutual configuration of the C$_2$B$_3$ pentagons is staggered and the torsion angles are very close to the ideal value of 36° for a perfectly staggered conformation. As expected, the mean C$_2$B$_3$ pentagonal planes flanking the metal center in **3a** are very close to parallel, the dihedral angle between the planes being 2.25(1)°, and the C9−Fe2−B9′ jack-knife angle at 179.02(1)° is essentially linear. The disposition of the C9, Fe2, and C10′ atoms is reflected by the C9−M2−C10′ angle of 154.83(1)°.

The structure of 7-*t*Bu(Me)HN-*nido*-7,8,10-C$_3$B$_8$H$_{10}$ (**6b**), shown in Figure 3, confirms the 7,8,10 arrangement of the cage carbon atoms and the C7 substitution by the *t*Bu(Me)HN group which causes the asymmetry of the molecule. However, upon comparing the bond parameters in **6b** with those found for the isomeric compound 7-*t*BuMeNH-*nido*-7,8,9-C$_3$B$_8$H$_{10}$ [6b] and the symmetrically substituted 10-Me$_3$N-*nido*-7,8,10-C$_3$B$_8$H$_{10}$,[6f] no significant conclusions could be drawn on the trends in the bond lengths

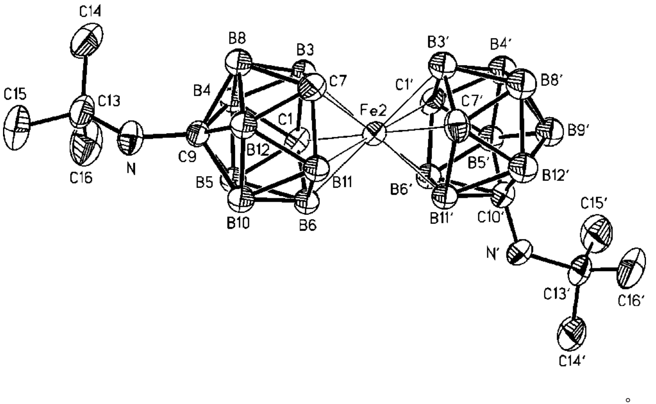


Figure 2. Molecular structure of **3a** with selected bond lengths (Å): Fe−C(1) 2.083(5), Fe−C(7) 2.067(5), Fe−C(1′) 2.078(4), Fe−C(7′) 2.064(5), Fe−B(3) 2.079(6), Fe−B(6) 2.084(6), Fe−B(11) 2.073(5), Fe−B(3′) 2.065(6), Fe−B(6′) 2.058(6), Fe−B(11′) 2.044(6), N−C(9) 1.433(5), N′−C(10) 1.424(6). Hydrogen positions omitted for clarity. Hydrogen atoms omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level

associated with the upper C_3B_2 pentagon brought by the substituent. The largest differences can be seen for the longer inter-atomic distances B9−C10 [1.673(6) Å] and C10−B11 [1.609(6) Å] found in the structure of the symmetrically substituted derivative 10-Me_3N-*nido*-7,8,10-$C_3B_8H_{10}$. There is, however, some uncertainty due to the disorder in this structure.[6f]

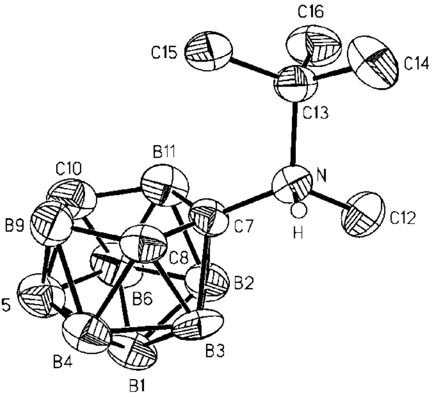


Figure 3. Molecular structure of **6b** with selected bond lengths (Å): N−C(7) 1.517(4), C(7)−C(8) 1.543(5), C(7)−B(11) 1.590(6), C(8)−B(9) 1.593(6), C(10)−B(9) 1.596(7), C(10)−B(11) 1.623(7). Hydrogen atoms omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level

NMR Spectroscopy

Figure 4 shows simplified stick diagrams comparing the ^{11}B chemical shifts for selected complexes of types **2** and **3** with those of the structurally related mixed-sandwich *closo* compounds [9-*t*BuHN-2-(η^5-C_5H_5)-2,1,7,9-$FeC_3B_8H_{10}$][1] and [10-*t*BuHN-2-(η^5-C_5H_5)-2,1,7,10-$FeC_3B_8H_{10}$].[2] The NMR spectroscopic data are also consistent with the structures for the *p, p* substituted complexes of type **2** determined crystallographically. The ^{11}B NMR spectra of compounds **2a**[4] and **2b** show very similar 4:2:4:2:4 patterns of doublets with only slight differences. The same intensity patterns apply to the corresponding BH resonances in the ^1H NMR spectra, in which one singlet resonance of intensity 4, assigned to the magnetically equivalent CH cage units, was also clearly found. As seen in Figure 4, the ^{11}B NMR spectra are very similar to that of [9- *t*BuHN-2-(η^5-C_5H_5)-*closo*-2,1,7,9-$FeC_3B_8H_{10}$][1] which exhibits a general upfield shift of the all resonances in comparison with those of compounds of type **2**.

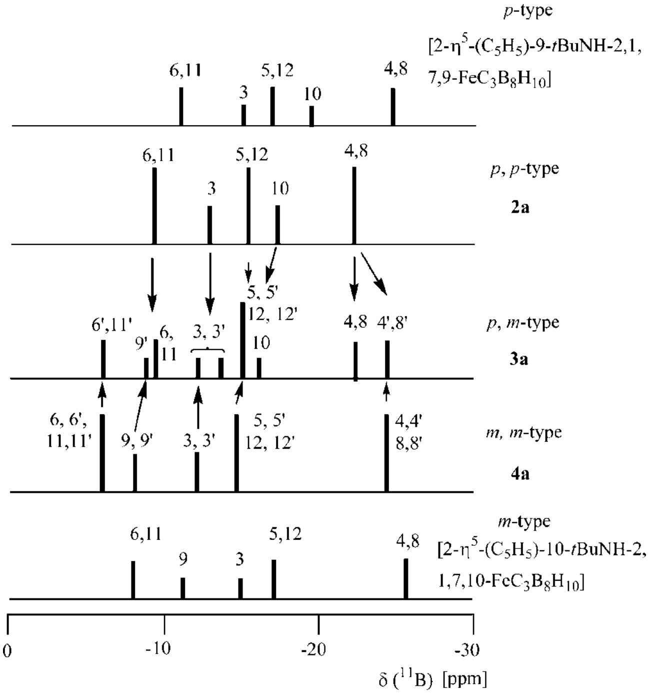


Figure 4. Stick representation and comparison of the ^{11}B NMR shifts for the *t*BuNH-substituted mixed sandwiches (data from ref.[1b,2]) and double-cluster ferratricarbollides **2a**, **3a**, and **4a**

Two sets of slightly shifted resonances with the same spectral patterns can be observed in the ^{11}B NMR spectrum of **2c**, those due to B10,10′ and B5,12,5′,12′ being coincidentally overlapping. The $^1H\{^{11}B\}$ NMR spectrum of **2c** contains two nonequivalent CH signals and also two related sets of resonances for each subcluster with coincidental overlaps for H6,11,6′,11′ and H3,3′. The ^{11}B NMR spectrum of **4a** (see Figure 4) with the *m,m* configuration of both ligands consists of 4:2:2:4:4 patterns of doublets as does the spectrum of the corresponding mixed-ligand complex [10-*t*BuHN-2-(η^5-C_5H_5)-*closo*-2,1,7,9-$FeC_3B_8H_{10}$].[2] The ^{11}B NMR spectra of the *p,m* type complexes **3a** and **3b** consist of two series of signals clearly attributable to those of the two nonequivalent tricarbollide ligands with *p*- and *m*- positioned substituents. The signals associated with the nonequivalent tricarbollide ligands can be clearly distinguished due to close similarities with the corresponding ^{11}B patterns found for **2b** and **4a**. The same similarities can be also found in the corresponding $^1H\{^{11}B\}$ NMR spectra of complexes **3a** and **3b**.

In accord with the absence of symmetry, the ^{11}B NMR spectra of the zwitterionic tricarbollide derivatives **6a** and **6b** consist of eight different signals with two coincidental overlaps found in the spectrum of **6b**. As shown in Figure 5, the ^{11}B NMR patterns show very close similarities with those of the structurally related anion [7-Me-*nido*-7,8,10-$C_3B_8H_{10}$]$^-$.[7] The ^{11}B NMR spectra of **6a** and **6b** themselves exhibit only slight differences in chemical shifts. Also eight singlets corresponding to BH signals were found in the $^1H\{^{11}B\}$ spectra of both compounds along with two different CH signals for each derivative. The respective ^1H NMR signals corresponding to Me_3N- and *t*Bu(Me)HN-substitution in **6a** and **6b** were clearly identified.

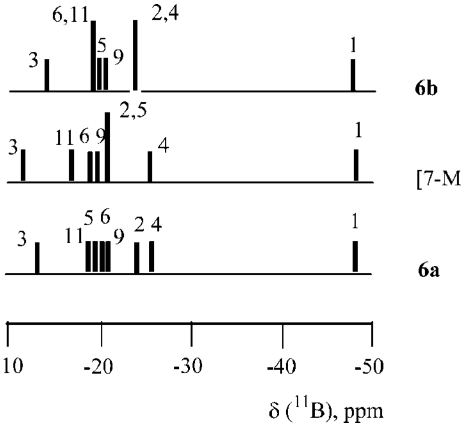


Figure 5. Stick representation and comparison of the ^{11}B NMR shifts for the zwitterions of the 7-L-7,8,10-$C_3B_8H_{10}$ type **6** (L = Me_3N **6a** and *t*Bu(Me)HN **6b**) with those for the [7-Me-*nido*-7,8,10-$C_3B_8H_{10}$]$^-$ anion (data from ref.[7])

Mass spectra of all the newly prepared compounds of types **2**, **3**, **4**, and **6** show theoretical cut-offs in their molecular-ion envelopes.

Conclusions

This work has opened up efficient preparative routes to the ferra bis(tricarbollides) of which compounds of type **2** with *p,p* orientation of the two reactive amino functionalities are the most important. These complexes are neutral and highly stable 26-cluster-electron *closo* complexes, perfect tricarbollide analogues of ferrocene. Optimization of the synthetic procedures has made these compounds generally feasible for their future synthetic use as metallacarborane building units for chemical constructions of linearly shaped oligomeric rod molecules. It was also demonstrated that cage isomerization of these compounds leads to *p,m* and *m,m* oriented shapes, which offers another modification in the area of structurally designed cluster chemistry. Moreover, it can be anticipated that the amine functions attached to the subclusters can be modified via analogous organic reactions, which should lead to other stable molecules with variable substituents. An important aspect of this work is that metal complexation reactions can be significantly affected by the purity of the metal reagent, which may significantly influence the nature of reaction products. This was documented by the metal-promoted isomerization reactions leading to new types of zwitterionic tricarbaborane compounds of type **6**. Aspects of this metallacarborane chemistry will be further developed and relevant experimental work in this area is in progress.

Experimental Section

General Procedures: All reactions were carried out with use of standard vacuum or inert-atmosphere techniques as described by Shriver[8] although some operations, such as preparative TLC, were carried out in air. The starting compound **1** was prepared according to the literature.[6g] Diethylene glycol dimethyl ether (diglyme) from Aldrich, 1,3,5-trimethylbenzene, benzene and hexane were dried with sodium wire and freshly distilled prior to use, the former being distilled at reduced pressure from sodium diphenylketyl. Dichloromethane was dried with CaH_2 and distilled before use. Aldrich anhydrous $FeCl_2$ of the three different purity grades 99.998% (H_2O < 10 ppm), 99.99% (H_2O < 100 ppm) and 98% was used. High-surface dry 96% NaH (prepared in this laboratory) was used. Other chemicals were reagent or analytical grade and were used as purchased. Preparative liquid chromatography was carried out using Aldrich silica gel (60−230 mesh) as the stationary phase under nitrogen. The mixtures of the isomeric derivatives **2a** and **3a** were separated by semi-preparative low-pressure chromatography on a pre-packed Merck Lobar® column LiChroprep® Si 60 (40−63μm), using hexane/CH_2Cl_2 (3:1, v/v) as the mobile phase, flow rate 7 mL/min, detection visual (the red bands) and by UV at 295 nm.

The purities of individual chromatographic fractions were checked by analytical TLC on Macherey−Nagel plates with UV indicator (silica gel on aluminium foil; detection by UV 254 nm followed by 2% aqueous $AgNO_3$ spray) and for the compounds of types **2** and **3** also by HPLC (see below). Melting points were measured in sealed capillaries and are uncorrected. Analyses were performed in the I.I.C. analytical laboratories using standard procedures. Low-resolution mass spectra were obtained using a Finnigan MAT MAGNUM ion trap quadrupole mass spectrometer equipped with a heated inlet option, as developed by Spectronex AG, Basle, Switzerland (70 eV, EI ionisation). Proton (^1H) and boron (^{11}B) NMR spectroscopy were performed at 11.75 Tesla with a Varian UNITY-500 instrument. The [^{11}B-^{11}B]-COSY[9] and $^1H\{^{11}B(\text{selective})\}$[10] NMR experiments were essentially as described in other related papers from our laboratories.[11] Chemical shifts are given in ppm to high-frequency (low field) of Ξ = 160 MHz (nominally $F_3B{\cdot}OEt_2$ in $CDCl_3$) for ^{11}B (quoted ± 0.5 ppm) and Ξ = 500 MHz ($SiMe_4$) for ^1H (quoted ± 0.05 ppm), Ξ being defined as in ref.[12] Residual solvent ^1H resonances were used as internal secondary standards. Coupling constants $^1J_{BH}$ are taken from resolution-enhanced ^{11}B spectra with a digital resolution of ± 1 Hz. Analytical HPLC was used for monitoring the ratio of **2a** and **3a** or **2b** and **3b**. The system consisted of a Merck−Hitachi 6200 Intelligent pump, D-6000 Interface, Rheodyne 7125 injection valve with a 20-μL sample loop and a L 7450 Diode Array detector with 7000 Manager Software 2.1. Chromatographic conditions: analytical separation on a 4 × 250 mm I.D. steel column (LiChrosorb SI 60 (10 μm), Merck Darmstadt, packed by Labio Ltd., Prague), detection by Diode Array 200−300 nm, sensitivity range 0−2.0 A.U.F.S. Chromatographic data for the separation of **2a** and **3a**: hexane/CH_2Cl_2 (75:25, v/v) as the mobile phase, flow rate 1.0 mL/min, capacity factors (k'), selectivity (α) and resolution (*Rs*) for analytical separations were: **2a:** $k_2' = 3.09$ **3a:** $k_{3'} = 4.25$, $\alpha = 1.38$, $Rs = 3.72$; chromatographic conditions for the separation of **2b** and **3b**: CH_2Cl_2/CH_3CN (97:3, v/v) as the mobile phase, flow rate 1.0 mL/min, capacity factors (k') $k_7' = 5.65$ $k_{8'} = 10.4$, $\alpha = 1.85$, $Rs = 5.3$.

[*closo*-9,9′-(tBuHN)$_2$-*commo*-2,2′-Fe^{II}-1,7,9-($C_3B_8H_{10}$)-1′,7′,9′-($C_3B_8H_{10}$)] (2a) and [*closo*-9,10′-(tBuHN)$_2$-*commo*-2,2′-Fe^{II}-1,7,9-($C_3B_8H_{10}$)-1′,7′,10′-($C_3B_8H_{10}$)] (3a): a) The starting salt Tl^{+}**1**$^{-}$ [1b] (2.50 g, 6.11 mmol) was stirred in a mesitylene/diglyme solvent mixture (40 mL, 25:75, v/v), $FeCl_2$ (99.99%, 1.60 g, 12.7 mmol) was then added and the mixture heated and stirred under gentle reflux for 8 h. After cooling to room temperature, water (2 mL) was added dropwise and the solvents were removed by rotary evaporation. The dark residue was digested with Et_2O (20 mL) and 1 M HCl (10 mL). The organic layer was then separated and the aqueous phase extracted with two additional portions of diethyl ether (20 mL). The combined organic extracts were evaporated and the reddish solid was treated with three portions of hexane (15 mL), filtered, and the combined red hexane extracts were evaporated. Crude complex **2a** (680 mg, 49% yield) was then isolated by repeated extraction of the solid residue with hexane, filtration of the combined extracts, and evaporation of the solvent. The compound was purified by flash chromatography on a silica gel column (2.5 × 35 cm) by elution with hexane/benzene (65:35, v.v.) to isolate 602 mg (43%) of **2a** as a red, semi-crystalline material. An analytical sample was crystallized from a concentrated petroleum ether solution at ca. 5 °C (red needles) and identified by NMR spectroscopy as reported earlier.[4] b) Compound **1** (1.01 g, 4.91 mmol) was stirred in diglyme (15 mL), dry NaH (0.22 g, 9.17 mmol) was added, and the slurry was stirred at room temperature for 1 h and then heated at 80 °C (bath temperature) for 30 min. After cooling, $FeCl_2$ (99.99%, 1.33 g, 10.49 mmol) was added and the reaction mixture heated under gentle reflux for 3 h with stirring. The mixture was then worked-up as in the preceding experiment giving a mixture of compounds **2a** and **3a**. This was separated by semi-preparative liquid chromatography on a pre-packed Merck Lobar® column (see above) to separate two red bands of R_f = 0.25 and 0.20 (TLC in 25% CH_2Cl_2 in hexane), from which compounds **2a** and **3a** were obtained in respective yields of 514 mg (45%) and 194 mg (17%) after evaporation. Compound **3a** was crystallized from a warm pentane solution by cooling to 5 °C. **3a:** R_f = 0.20 (CH_2Cl_2/hexane, 25: 75, v/v); m.p. 152−155 °C. ^{11}B NMR (160.4 MHz, 25 °C, $CDCl_3$): δ = −6.6 [d, ^1J(B,H) = 174 Hz, 2 B, B6′,11′], −8.3 (d, 1 B, B9′), −9.2 [d, ^1J(B,H) = 153 Hz, 2 B, B6,11], −12.3 [d, ^1J(B,H) = 170 Hz, 1 B, B3′], −13.4 [d, ^1J(B,H) = 168 Hz, 1 B, B3], −15.2 [d, ^1J(B,H) = 174 Hz, 4 B, B5,12,5′,12′] −16.9 [d, ^1J(B,H) = 177 Hz, 1 B, B10], −22.4 [d, ^1J(B,H) = 177 Hz, 2 B, B4,8], −24.05 [d, ^1J(B,H) = 161 Hz, 2 B, B4′,8′] ppm, all theoretical [^{11}B-^{11}B] cross-peaks observed. ^{1}H{^{11}B} NMR (500 MHz, 25 °C, $CDCl_3$): δ = 3.78 (s, 1 H, H 3′), 3.66 (s, 1 H, H3), 3.32 (s, 2 H, H6′,11′), 3.05 (s, 1 H, H9′) 2.98 (s, 2 H, H6,11], 2.49 (s, 4 H, H5,12,5′,12′), 2.35 (s, 2 H, H4,8), 2.30 (m, 1 H, N*H*-*t*Bu), 2.12 (s, 1 H, H10), 2.07 (s, 4 H, cage C*H*), 1.52 (s, 2 H, H4′,8′), 1.22 and 1.19 (s, 18 H, *t*Bu) ppm. IR (KBr): $\tilde{\nu}$ = 2534 (B−H) cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 468 (4) [M$^+$], 465 (100) [M$^+$ − 3H]. $C_{14}H_{30}B_{16}FeN_2$ (465.30): calcd. B 37.17, N 6.01; found B 36.86, N 5.94.

[*closo*-9,9′-(H_2N)$_2$-*commo*-2,2′-Fe^{II}-1,7,9-($C_3B_8H_{10}$)-1′,7′,9′-($C_3B_8H_{10}$)] (2b) and [*closo*-9,10′-(H_2N)$_2$-*commo*-2,2′-Fe^{II}-1,7,9-($C_3B_8H_{10}$)-1′,7′,10′-($C_3B_8H_{10}$)] (3b): Compound **2a** or **3a** (200 mg, 0.57 mmol) was dissolved in hexane (20 mL) and $AlCl_3$ (800 mg, 6.0 mmol) was then added in one portion. The reaction slurry was stirred under gentle reflux for 2 h. After cooling, the reaction slurry was treated with water (10 mL) and the solvents were evaporated. The solid residue was treated with 10% aqueous KOH (15 mL), extracted with CH_2Cl_2 (2 × 15 mL), the organic portion was separated, and the solvent evaporated to give 124 mg (82%) of **2b** or 121 mg (80%) of **3b**. For the preparation of **3b**, it is convenient to apply the $AlCl_3$ reaction on a mixture of **2a** and **3a** obtained in the preceding experiment, which results typically in a total yield of 79% of the H_2N- derivatives **2b** and **3b**. The isomers were then separated by chromatography on a silica gel column (1.5 × 25 cm), using a CH_2Cl_2/MeCN mixture (95:5, v/v) as the mobile phase.

2b: R_f = 0.24 (CH_2Cl_2); m.p. >360 °C. ^{11}B NMR (160.4 MHz, 25 °C, $CDCl_3$): δ = −8.6 [d, ^1J(B,H) = 154 Hz, 2 B, B6,11], −12.6 [d, ^1J(B,H) = 169 Hz, 1 B, B3], −15.6 [d, ^1J(B,H) = 170 Hz, 2 B, B5,12], −17.3 [d, ^1J(B,H) = 165 Hz, 1 B, B10], −22.7 [d, ^1J(B,H) = 177 Hz, 2 B, B4,8] ppm, all theoretical [^{11}B-^{11}B] cross-peaks observed. ^{1}H{^{11}B} NMR (500 MHz, 25 °C, $CDCl_3$): δ = 4.09 (s, 1 H, H3), 2.92 (s, 2 H, H6,11), 2.44 (br. s, 1 H, N*H*), 2.33 (s, 2 H, H5,12), 2.26 (s, 2 H, H4,8), 1.97 (s, 1 H, H10), 1.86 (s, 2 H, cage C*H*) ppm. IR (KBr): $\tilde{\nu}$ = 2572 (B−H) cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 356 (15) [M$^+$], 353 (100) [M$^+$ − 3H]. $C_6H_{24}B_{16}FeN_2$ (353.08): calcd. B 48.99; found B 48.71.

3b: R_f = 0.14 (CH_2Cl_2); m.p. 282 °C. ^{11}B NMR (160.4 MHz, 25 °C, $CDCl_3$): δ = −6.6 [d, ^1J(B,H) = 167 Hz, 2 B, B6′,11′], −8.0 (d, 1 B, B9′), −8.7 [d, ^1J(B,H) = 156 Hz, 2 B, B6,11], −13.2 (d, 2 B, B3,3′], −14.9 [d, ^1J(B,H) = 179 Hz, 4 B, B5,12,5′,12′], −17.0 (d, 1 B, B10), −22.7 [d, ^1J(B,H) = 174 Hz, 2 B, B4,8], −23.4 [d, ^1J(B,H) = 156 Hz, 2 B, B4′,8′] ppm, all theoretical [^{11}B-^{11}B] cross-peaks observed. ^{1}H{^{11}B} NMR (500 MHz, 25 °C, $CDCl_3$): δ = 3.58 and 3.79 (s, 2 H, H3,3′), 3.17 (s, 2 H, H6′,11′), 2.95 (H9′), 3.04 (s, 2 H, H6,11), 2. 49 (br. s, 1 H, N*H*), 2.49 and 2.47 (s, 4 H, H (5,12,5′,12′)], 2.31 (s, 2 H, H4,8), 2.02 (s, 1 H, H10), 2.24 and 2.165 (4 H, cage CH), 1.56 (s, 2 H, H4′,8′) ppm. IR (KBr): $\tilde{\nu}$ = 2575 (B−H) cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 356 (13) [M$^+$], 354 (100) [M$^+$ −2H]. $C_6H_{24}B_{16}FeN_2$ (353.08): calcd. B 48.99; found B 48.30.

Thermal Decomposition of [*closo*-9,9′-(tBu HN)$_2$-*commo*-2,2′-Fe^{II}-1,7,9-($C_3B_8H_{10}$)-1′,7′,9′-($C_3B_8H_{10}$)] (2a): Complex **2a** (100 mg, 0. 21 mmol) was sealed in a glass ampoule under vacuum and heated in a furnace for 15 min at 210 °C. The ampoule was then carefully opened, the residue dissolved in CH_2Cl_2 (3 mL) and mounted onto the top of a silica gel column (20 × 1.5 cm). Elution with a hexane/CH_2Cl_2 mixture (1: 1, v/v), followed by gradually increasing the content of CH_2Cl_2 to 100%, recovered a small amount of the starting compound (8 mg) and provided red compounds **2c** (18 mg, 20%) and **2b** (39 mg,51%). Subsequent elution with CH_2Cl_2/acetonitrile (9:1, v/v) eluted **3b** (10 mg, 13%), which was characterized as described above.

2c: R_f = 0.48 (CH_2Cl_2); m.p. 228−232 °C (dec. to **7** + **8**). ^{11}B NMR (160.4 MHz, 25 °C, $CDCl_3$): δ = −8.6 (d, 2 B, B6,11 or 6′,11′), −9.0 (d, 2 B, B6,11 or 6′,11′), −12.6 (d, 1 B, B3 or B3′), −13.0 (d, 1 B, B3 or B3′), −15.7 (d, 4 B, B5,12,5′,12′), −17.3 (d, 2 B, B10,10′), −22.7 (d, 2 B, B4,8 or 4′,8′), −22.8 (d, 2 B, B4,8 or 4′,8′) ppm. ^{1}H{^{11}B} NMR (500 MHz, 25 °C, $CDCl_3$): δ = 4,08 (s, 1 H, H3 or H3′), 4.05 (s, 1 H, H3 or H3′), 2.92 (s, 2 H, H6,11 or H6′,11′), 2.87 (s, 2 H, H6,11 or H6′,11′), 2.43 (br. s, 2 H, N*H*$_2$), 2.17 (br. s., 1 H, N*H*-*t*Bu), 2.372 (s, 2 H, H5,12 or H5′,12′), 2.32 (s, 2 H, H5,12 or H5′,12′), 2.09 (s, 1 H, H10 or H10′), 1.87 (s, 1 H, H10 or H10′), 2.31 (s, 2 H, H4,8 or H4′8′), 2.25 (s, 2 H, H4,8 or H4′8′), 1.87 (s, 2 H, cage C*H*), 1.73 (s, 2 H, cage C*H*), 1.19 (s, 9 H, *t*Bu) ppm. IR (KBr): $\tilde{\nu}$ = 2534 (B−H) cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 357 (1.4) [M$^+$], 354 (100) [M$^+$ − 3H].

[*closo*-10,10′-(tBuHN)$_2$-*commo*-2,2′-Fe^{II}-1,7,10-($C_3B_8H_{10}$)-1′,7′,10′-($C_3B_8H_{10}$)] (4a), 7-Me_3N-7,8,9-*nido*-$C_3B_8H_{10}$ (6a), and 7-*t*Bu(Me)HN-7,8,10-*nido*-$C_3B_8H_{10}$ (6b): To a stirred slurry of compound **1** (500 mg, 2.43 mmol) in diglyme (15 mL) was added dry NaH (120 mg, 5 mmol), the mixture was stirred at room temperature for 1 h, and then heated at 80 °C (bath) for 30 min. After

Table 1. Crystal data and structure refinement for compounds **2b**, **3a**, and **6b**

Empirical formula	$C_6H_{24}B_{16}FeN_2$	$C_{14}H_{40}B_{16}FeN_2$	$C_8H_{23}B_8N$
Habit and size, mm	prism, 0.3 × 0.3 × 0.25	plate, 0.3 × 0.26 × 0.24	prism, 0.2 × 0.12 × 0.12
Crystal system	triclinic	orthorhombic	monoclinic
Space group	$P\bar{1}$ (No, 2)	$P2_12_12_1$	$P2_1/n$ (No. 14)
a, Å	7.0260(1)	11.425(2)	8.534(4)
b, Å	11.6020(2)	33.2485(11)	12.820(4)
c, Å	11.7410(2)	6.7392(11)	12.932(5)
α, deg	65.5910(9)	90	90
β, deg	81.8160(9)	90	99.58(3)
γ, deg	87.4050(9)	90	90
Z	2	4	4
μ, mm^{-1}	0.862	0.597	0.051
Wavelength, Å	0.71073	0.71069	0.71069
θ range in deg, % completeness	1−27.5, 99.4	1.9−25.0, 99.8	2.2−22.5, 99.9
No. of reflections measured	13158	2609	1965
No. of unique reflections; $R_{int.}$ [a]	3944; 0.022	2609	1824, 0.0615
No. of observed ref. $[I > 2\sigma(I)]$	3545	2235	721
No. of parameters	229	230	192
GOF[b] all data	1.078	1.074	0.816
Final R[c] indices $[I > 2\sigma(I)]$	$R1 = 0.029$, $wR2 = 0.080$	$R1 = 0.0441$, $wR2 = 0.1063$	$R1 = 0.0609$, $wR2 = 0.1030$
R[c] indices (all data)	$R1 = 0.032$, $wR2 = 0.083$	$R1 = 0.0619$, $wR2 = 0.1141$	$R1 = 0.2244$, $wR2 = 0.1218$
w_1/w_2 [d]	0.0366/0.588	0.0494/1.8452	0.0356 /0.0000
max./min. Δρ, e·Å^{-3}	0.435/−0.381	0.259/−0.347	0.144/−0.142

[a] $R_{int} = \Sigma|F_o^2 - F_o^2(\text{mean})|/\Sigma F_o^2$ (summation is carried out only where more than one symmetry equivalent is averaged). [b] GOF = $[\Sigma[w(F_o^2 - F_c^2)^2]/(N_{reflns.} - N_{param.})]^{1/2}$. [c] $R(F) = \Sigma ||F_o| - ||F_c||/\Sigma |F_o|$, $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$. [d] Weighting scheme $w = [\sigma^2(F_o^2) + (w_1P) + w_2P]^{-1}$, $P = [\max(F_o^2,0) + 2F_c^2]/3$.

cooling, reagent grade $FeCl_2$ (98%, 1580 mg, 12.5 mmol) was added and the mixture gently heated to reflux for 24 h with stirring. After cooling to room temperature, water (5 mL) was added dropwise and the diglyme removed by rotary evaporation. The dark residue was digested with Et_2O (50 mL) and 1 M HCl (40 mL). The organic layer was separated and the aqueous phase extracted with two additional 20 mL portions of Et_2O. The combined organic extracts were evaporated, the reddish solid was treated with three 20 mL portions of hexane and the solution thus obtained was filtered and the solvents evaporated to give a mixture of compounds **2a** and **3a**. The mixture was separated by preparative liquid chromatography on a silica gel column (25 × 1.5 cm), using 25% CH_2Cl_2 in hexane as the mobile phase to separate the red bands of R_f (anal., 25% CH_2Cl_2 in hexane) 0.25, 0.20, and 0.15. The first fractions contained trace quantities of compound **5**, which was identified from its NMR spectra.[5] Complexes **2a** (22 mg, 4%), **3a** (26 mg, 5%), and **4a** (12 mg 2%) were then isolated from individual fractions and purified by crystallization from concentrated petroleum ether at ca. 0 °C. The pale brown solid residue after hexane extraction was dissolved in 5% MeCN in CH_2Cl_2 and chromatographed on a silica gel column (25 × 1.5 cm), using CH_2Cl_2 and finally a CH_2Cl_2/MeCN (4:1, v/v) mixture (TLC monitoring). Evaporation of the two last fractions resulted in the isolation of compounds **6a** (66 mg, 14%) and **6b** (92 mg, 17%), which were recrystallized from hot CH_2Cl_2.

4a: R_f (CH_2Cl_2/hexane, 25:75, v/v) 0.16. ^{11}B NMR (160.4 MHz, 25 °C, $CDCl_3$): δ = −6.5 [d, ^1J(B,H) = 153, 4 B, B6,11,6′,11′], −8.1 (d, 2 B, B9,9′), −12.2 [d, ^1J(B,H) = 165, 2 B, B3,3′], −14.7 [d, ^1J(B,H) = 174, 4 B, B5,12,5′,12′], −23.7 [d, ^1J(B,H) = 165, 4 B, B4,8,4′,8′] ppm, all theoretical [^{11}B-^{11}B] cross-peaks observed. $^1H\{^{11}B\}$ NMR (500 MHz, 25 °C, $CDCl_3$): δ = 3.56 (s, 2 H, H3,3′), 3.42 (s, 4 H, H6,11,6′,11′), 3.13 (s, 2 H, H9,9′), 2.61 (s, 2 H, N*H*), 2.59 (s, 4 H, H5,12,5′,12′), 2.27 (s, 4 H, cage C*H*), 1.57 s (s, 4 H, H4,8,4′,8′), 1.25 (s, 18 H, *t*Bu) ppm. MS (70 eV, EI): *m*/*z* (%) = 468 (18) [M$^+$], 466 (100) [M$^+$ − 2H].

6a: R_f (CH_2Cl_2) 0.25; m.p. 298−300 °C. ^{11}B NMR (160.4 MHz, 25 °C, CD_3CN): δ = −12.8 [d, ^1J(B,H) = 159 Hz, 1 B, B3], −17.9 (d, 1 B, B11), −18.5 (d, 1 B, B5), −19.3 (d, 1 B, B6), −20.0 [d, ^1J(B,H) = 137 Hz, 1 B, B9], −23.4 [d, ^1J(B,H) = 153 Hz, 1 B, B2], −25.7 [d, ^1J(B,H) = 150 Hz, 1 B, B4], −48.0 [d, ^1J(B,H) = 143 Hz, 1 B, B1] ppm, all theoretical [^{11}B-^{11}B] cross-peaks observed, except uncertain B5−B9, B6−B11. $^1H\{^{11}B\}$ NMR (500 MHz, 25 °C, CD_3CN): δ = 3.08 (m, 9 H, Me), 2.31 (s, 1 H, H3), 2.15 (s, 1 H, cage C*H*), 1.68 (s, 1 H, H11), 1.67 (s, 1 H, cage C*H*), 1.36 (s, 1 H, H5), 1.36 (s, 1 H, H6), 1.89 (s, 1 H, H9), 1.58 (s, 1 H, H2), 1.12 (s, 1 H, H4), 0.01 (s, 1 H, H1) ppm. IR (KBr): ṽ = 2556 (B−H) cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 193 (8) [M$^+$], 192 (18) [M$^+$ − H]. $C_6H_{19}B_8N$ (191.78): calcd. B 45.14; found B 44.25.

6b: R_f (CH_2Cl_2) 0.12; m.p. 194−196 °C. ^{11}B NMR (160.4 MHz, 25 °C, CD_3CN): δ = −13.8 [d, ^1J(B,H) = 156 Hz, 1 B, B3], −18.2 (d, 2 B, B6,11), −19.9 (d, 1 B, B5), −20.5 [d, ^1J(B,H) = 134 Hz, 1 B, B9], −23.7 [d, ^1J(B,H) 145 Hz, 2 B, B2,4] −48.0 [d, ^1J(B,H) = 137 Hz, 1 B, B1] ppm, all theoretical [^{11}B-^{11}B] cross-peaks observed. $^1H\{^{11}B\}$ NMR (500 MHz, 25 °C, CD_3CN): δ = 6.19 (br. s, 1 H, N*H*), 2.15 (m, 3 H, Me), 2.01 (s, 1 H, H3), 1.95 (s, 1 H, H9), 1.19 (s, 1 H, H2 or H4), 1.70 (s, 1 H, cage C*H*), 1.66 (s, 1 H, H6 or H11), 1.35 (s, 1 H, H6 or H11), 1.55 (s, 9 H, *t*Bu), 1.27 (s, 1 H, H5), 0.87 (s, 1 H, cage CH), 0.06 (s, 1 H, H1) ppm. IR (KBr): ṽ = 2534 (B−H) cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 221 (52) [M$^+$], 220 (100) [M$^+$ − H]. $C_8H_{23}B_8N$ (219.76): calcd. B 39.35; found B 37.99.

X-ray Crystallography

Crystallographic Data for 2b: A red crystal of **2b** of dimensions 0.3 × 0.3 × 0.25 mm was mounted on a glass fiber with epoxy cement and placed on a four-circle Nonius−KappaCCD diffractometer equipped with a CCD area detector at 150(2)K with Mo-K_α radiation. The crystallographic details are summarized in Table 1. The structure was solved by the direct methods (SIR97)[13] and refined by a full-matrix least-squares procedure based on F^2 (SHELXL-

97).[14] The hydrogen atoms were found on a difference Fourier map, but some of them behaved erroneously during refinement and were therefore fixed in idealized positions (riding model) and assigned temperature factors $H_{\mathrm{iso}}(H) = 1.2U_{\mathrm{eq}}$ (pivot atom). The final difference map displayed no peaks of chemical significance.

Crystallographic Data for 3a and 6b: A pale red crystal of **3a** and a colorless crystal of **6b** were analyzed at 294 K with a Rigaku AFC5S diffractometer with Mo-K_α radiation. The crystallographic details are summarized in Table 1. The structures were solved by the direct method and refined on F^2 with the SHELXL-97 program.[14] For **3a**, boron atoms were refined isotropically but the rest of the non-hydrogen atoms were refined with anisotropic thermal displacement parameters. Hydrogen atoms were placed in calculated positions and were treated as riding atoms using the SHELX97[14] default parameters. For **6b**, the reflection power of the crystal steeply dropped at high reflection angles and therefore the data collection was limited to $2\theta_{\mathrm{max.}} = 45°$. The non-hydrogen atoms were refined with anisotropic thermal displacement parameters. Hydrogen atoms of the carborane cage were found from a difference Fourier map and refined with fixed U. The hydrogen atoms of the methyl groups were placed in calculated positions and treated as riding atoms. The final difference maps of **3a** and **6b** displayed no peaks of chemical significance.

CCDC-215766, -215767 and -215768 contain the supplementary crystallographic data of the compounds **3a**, **6b** and **2a** for this paper. These data can be obtained free of charge at wwww.ccdc.cam.ac.uk/conts/retrieving.hmtl [or from Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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