Diferratricarbaboranes of the *subcloso*-[(η^5-C$_5$H$_5$)$_2$Fe$_2$C$_3$B$_8$H$_{11}$] Type, the First Representatives of the 13-Vertex Dimetallatricarbaborane Series

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Abstract: Treatment of the [2-Cp-9-*t*BuNH-*closo*-2,1,7,9-FeC$_3$B$_8$H$_{10}$] (**1**) ferratricarbollide (Cp = η^5-C$_5$H$_5^-$) with Na$^+$C$_{10}$H$_8^-$ in 1,2-dimethoxy-ethane (DME) at room temperature produced an air-sensitive transient anion with a tentatively identified *nido*-[*t*BuNH-CpFeC$_3$B$_8$H$_{10}$]$^{2-}$ constitution. In-situ reaction of this low-stability ion with [CpFe(CO)$_2$I] or [CpFe(CO)$_2$]$_2$ generated three violet diferratricarbaboranes identified as paramagnetic *subcloso* complexes [4,5-Cp$_2$-4,5,1,6,7-Fe$_2$C$_3$B$_8$H$_{11}$] (**2**; yield 2%),

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[4,5-Cp$_2$-4,5,1,7,12-Fe$_2$C$_3$B$_8$H$_{11}$] (**3**; yield 2%), and [7-*t*BuNH-4,5-Cp$_2$-4,5,1,7,12-Fe$_2$C$_3$B$_8$H$_{10}$] (**4**; yield 14%). These first representatives of the 13-vertex dimetallatricarbaborane family were characterized by EPR and IR spectroscopy, and mass spectrometry, and their structures were determined by X-ray diffraction analysis.

Introduction

In a theoretical context, the basic geometric arrangement for 13-vertex *closo*-borane cages is a docosahedral structure as has been predicted for the parent [B$_{13}$H$_{13}$]$^{2-}$ borane dianion, which is still unknown.[1] In contrast, the first 13-vertex dicarbaborane, [C$_6$H$_4$(CH$_2$)$_2$]-3-Ph-1,2-*closo*-1,2-C$_2$B$_{11}$H$_{10}$, with henicosahedral geometry, has been reported recently.[2] However, apart from this sole example of a nonmetallic 13-vertex carborane cluster, supraicosahedral boron-containing species are represented largely by 13-vertex metalladicarbaboranes. These compounds have docosahedral geometry and their stability may be attributed mostly to the stabilization effect of the cage metal units. The first 13-vertex *closo* monometalladicarbaboranes of the [MC$_2$B$_{10}$H$_{12}$] type were pre-pared in Hawthorne's laboratories,[3] in pioneering work that triggered much research elsewhere into varying the cluster metal vertex and the carborane ligand.[4–6] The 13-vertex dimetalladicarbaboranes are exemplified by the *hypercloso* compound (2n cage electron)[7] [(CpFe)$_2$C$_2$B$_9$H$_{11}$],[8] *closo*-[(CpCo)$_2$C$_2$B$_9$H$_{11}$],[9] and the mixed-metal *subcloso*-[CpCo(C$_2$B$_9$H$_{11}$)FeCp] complex.[9,10] Conjointly of great interest is the recently reported synthesis of the *hypercloso*-[(Cp*Ru)$_2$(C$_2$B$_9$H$_{11}$)] diruthenadicarbaborane, made by direct electrophilic insertion of a second ruthenium vertex into the *subcloso*-[Cp*RuC$_2$B$_9$H$_{11}$]$^-$ ion.[11] In addition to these supraicosahedral dicarbaborane species there is a series of carbon-rich 13-vertex metallatetracarbaboranes that have emerged from the advanced work of the Grimes group.[12] These include *nido*-[CpCo(CH$_3$)$_4$C$_4$B$_8$H$_8$], several isomers of *nido*-[(C$_6$H$_5$)$_2$PCH$_2$]$_2$Ni(CH$_3$)$_4$C$_4$B$_8$H$_8$], and the series of *nido*-[(CO)$_3$M-(CH$_3$)$_4$C$_4$B$_8$H$_8$] complexes (M = Mo and W). Due to the presence of four cage carbon units, these compounds are forced to adopt open-cage geometries different from those of the closed-structure species mentioned above. An interesting venture by Sneddon et al. into the area of the 13-vertex metallatricarbaboranes was the isolation of a complex containing the {Co$_3$C$_3$B$_7$}[13] cage as a minor product from metal incorporation into the 10-vertex tricarbaborane *arachno*-RC$_3$B$_7$H$_{12}$. Here we report on the successful synthesis and unambiguous structural characterization of a new 13-vertex *subcloso* family of paramagnetic diferratricarbaboranes of the [(CpFe)$_2$C$_3$B$_8$H$_{11}$] type. We also rationalize the occurrence of paramagnetic and diamagnetic types of cluster-borane compounds.

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Unmarked vertices in Scheme 1 stand for cluster BH units, C≡CH, and the numbering system used in this work for the 12- and 13-vertex *closo* cages is demonstrated in general structures **I** and **II**.
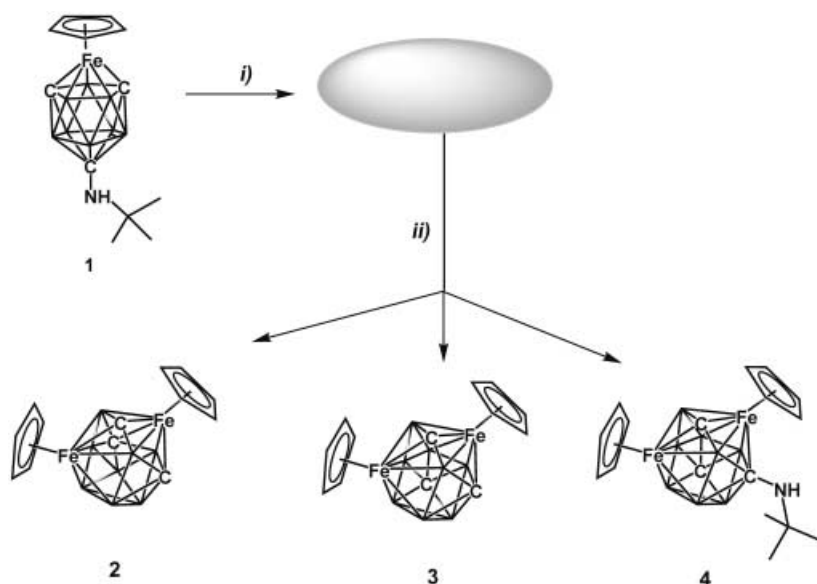
Scheme 1. Simplified scheme for the formation of the bimetallic complexes **2**, **3**, and **4**: *i*) Na, DME, RT, 8 h, reflux 4 h; *ii*) [CpFe(CO)₂I] or [{CpFe(CO)₂}₂], RT, 16 h, reflux 4 h.
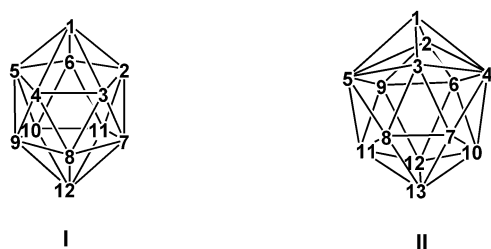
Results and Discussion

Syntheses: The neutral tricarbollide complex [2-Cp-9-*t*BuNH-*closo*-2,1,7,9-FeC₃B₈H₁₀] **1**[14] produces, upon reduction with Na⁺C₁₀H₈⁻ in 1,2-dimethoxyethane (DME) (room temperature, 8 h), a dark red, air-sensitive metallatricarbaborane anion (path *i* in Scheme 1), which was tentatively identified as the 12-vertex *nido*-[*t*BuNH-CpFeC₃B₈H₁₀]²⁻ ion on the basis of its NMR spectra. The presence of naphthalene seems essential for the stabilization of this transient anion in the solution; otherwise elimination of metallic Fe would be observed as the main reaction pathway.

The intermediate anion was not isolated; instead it was treated in situ with [CpFe(CO)₂I] or [CpFe(CO)₂]₂ and stirred for 16 h at ambient temperature, then heated at reflux for 4 h (path *ii* in Scheme 1). From the very complex reaction mixture, three 13-vertex diferratricarbaboranes have

been isolated in a pure state by preparative TLC chromatography and fully characterized. These violet complexes were identified unambiguously as *subcloso* compounds [4,5-Cp₂-4,5,1,6,7-Fe₂C₃B₈H₁₁] (**2**; yield 2%), [4,5-Cp₂-4,5,1,7,12-Fe₂C₃B₈H₁₁] (**3**; yield 2%), and [7-*t*BuNH-4,5-Cp₂-4,5,1,7,12-Fe₂C₃B₈H₁₀] (**4**; yield 14%). The isolated compounds are relatively stable in air, but their storage lifetimes are lengthened considerably if they are kept under anaerobic conditions. As Scheme 1 shows, the main reaction mode is suggested to be the insertion of one {CpFe} fragment into the assumed hexagonal open face of the intermediate anion upon rearrangement of the cluster carbon atoms. The result of this rearrangement is a movement of carbon atoms into positions of lowest coordination and maximum spatial separation. The absence of the amine functionality in species **2** and **3** is undoubtedly due to its cleavage from the cluster, probably attributable to the presence of excess sodium in the reaction mixture.

Structural studies: A more detailed structural characterization of the transient dark red anion was unfortunately impossible because of its extreme sensitivity to air. Nonetheless, the formation of this intermediate closely resembles the well-known formation of the [C₂B₁₀H₁₂]²⁻ ion by two-electron reduction of *o*-carborane.[15] This dianion has also been used as a transient intermediate in polyhedral expansion reactions leading to 13-vertex metalladicarbaboranes upon reaction with suitable metal reagents.[3–6] The intermediate anion is a diamagnetic species, the ¹¹B NMR spectrum of which exhibits eight doublets of equal intensities; however, the presence of a paramagnetic impurity precluded more detailed assignments based on [¹¹B–¹¹B] COSY measurements, because of the absence of distinct spectral cross-peaks. Nevertheless, it can reasonably be supposed that this intermediate [*t*BuNH-CpFeC₃B₈H₁₀]²⁻ ion adopts a 12-vertex *nido* structure.[15]

The paramagnetic nature of all three complexes of the *subcloso*-[(CpFe)₂C₃B₈H₁₁] type isolated as described above precluded their NMR characterization. The compounds exhibit theoretical cut-off peaks in the molecular envelopes of their mass spectra that correspond to the cationic masses consistent with their crystallographically defined constitutions. Suitable crystals for single-crystal X-ray diffraction analyses of all three compounds were grown, enabling their full structural determination. Crystal data and structure refinement parameters for compounds **2**, **3**, and **4** are collated in Table 1. The crystallographically determined structures of

Table 1. Crystal data and structure refinement for **2**, **3**, and **4**.

Compound	**2**	**3**	**4**
crystal size [mm]	$0.38 \times 0.24 \times 0.22$	$0.38 \times 0.32 \times 0.26$	$0.40 \times 0.35 \times 0.33$
empirical formula	$C_{13}H_{21}B_8Fe_2$	$C_{13}H_{21}B_8Fe_2$	$C_{17}H_{30}B_8Fe_2N$
M_r	375.48	375.48	446.60
T [K]	294(2)	294(2)	193(2)
crystal system	monoclinic	triclinic	monoclinic
space group	$P2_1/n$ (no. 14)	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)
a [Å]	10.3698(8)	10.3085(18)	12.025(2)
b [Å]	13.4997(9)	11.7963(14)	7.1380(10)
c [Å]	12.0211(12)	7.2831(10)	24.688(5)
α [°]	90	97.637(11)	90
β [°]	104.191(8)	109.582(11)	102.39(3)
γ [°]	90	85.931(12)	90
Z	4	2	4
V [Å^3]	1631.5(2)	826.7(2)	2069.7(6)
μ [mm^{-1}]	1.764	1.741	1.404
ρ_{calcd} [Mg m^{-3}]	1.529	1.508	1.433
λ [Å]	0.71069	0.71069	0.71073
$F(000)$	764	382	924
θ range [°]	2.31–25.01	2.10–24.99	2.98–25.02
h, k, l collected	$0 \le h \le 12$,	$0 \le h \le 11$,	$0 \le h \le 14$,
	$0 \le k \le 16$,	$-13 \le k \le 14$,	$0 \le k \le 8$,
	$-14 \le l \le 13$	$-8 \le l \le 8$	$-29 \le l \le 28$
no. of reflections measured	3044	2679	3554
R(int)	0.0201	0.0107	0.020
no. of unique reflections	2879	2504	3389
no. of parameters	208	200	250
GOF[a] all data	1.029	1.035	1.073
final R[a] indices [$I > 2\sigma(I)$]	R1 = 0.0309, wR2 = 0.0714	R1 = 0.0406, wR2 = 0.0966	R1 = 0.0486, wR2 = 0.1035
R[a] indices (all data)	R1 = 0.0467, wR2 = 0.0763	R1 = 0.0556, wR2 = 0.1037	R1 = 0.0597, wR2 = 0.1072
$\Delta\rho$ (max/min) [e Å^{-3}]	0.322/−0.252	0.537/−0.480	0.982/−0.503

[a] $R1 = \Sigma ||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

compounds **2**, **3**, and **4** are represented in Figures 1, 2, and 3, respectively.

Figures 1 and 2 suggest that complexes **2** and **3** are isomeric parent compounds that differ only in the positioning of the cage CH vertices, and that compound **4** is substituted at one of the pentacoordinate CH vertices of the cage adjacent to the Fe center. In all these exclusively docosahedral structures, one of the cage carbon atoms occupies the lowest-coordinate position, C1, which has connectivity four when one considers bonding to other skeletal atoms. This CH vertex resides, in all cases, between the two {CpFe} vertices. The remaining two carbon atoms occupy positions connected to five skeletal atoms. All three cage carbon atoms are separated by at least one boron vertex and the two {CpFe} moieties occupy positions with connectivity six. The carbon positions of both Cp rings in compound **3** are disordered into two orientations and a similar disorder of the Cp ring at Fe5 was observed in compound **4**.

Inspection of interatomic distances and angles of **2**–**4** suggests that, for all the compounds isolated, the Fe–C distances to the four-coordinate C1 vertex (range 1.983–1.999 Å) are considerably shorter than those to the five-coordinate carbon vertices (range 2.123–2.169 Å). The mean Fe–C$_{Cp}$ separations (range 2.080–2.107 Å) fall between these values. The Fe–C$_{Cp}$ (mean plane centroid) distances (range 1.703–1.742 Å) are much longer than the Fe–C (mean hexagonal plane centroid) separations (range 1.300–1.352 Å). As expected, the Fe–B distances are generally longer than the comparable Fe–C separations, those to the B2 and B3 (range 2.194–2.253 Å) vertices being generally longer than others (range 2.081–2.150 Å). The
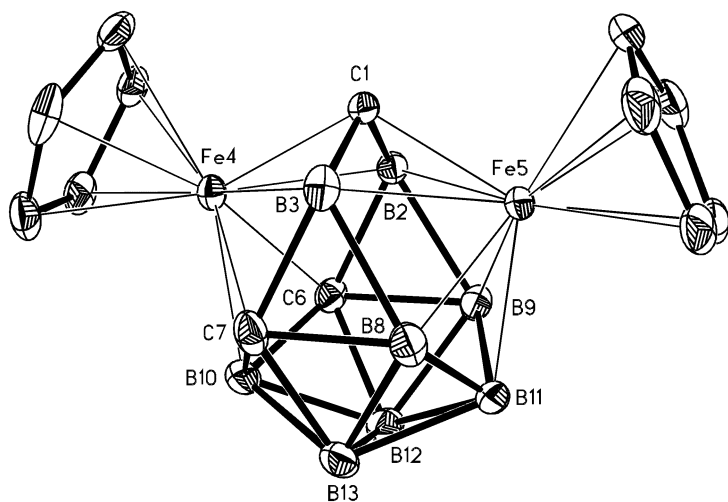

Figure 1. The structure of [4,5-Cp$_2$-*closo*-4,5,1,6,7-Fe$_2$C$_3$B$_8$H$_{11}$] (**2**), with 20% ellipsoids. Selected interatomic distances [Å] and angles [°]: Fe4–C1 1.998(3), Fe4–B2 2.194(3), Fe4–B3 2.195(3), Fe4–C6 2.131(3), Fe4–C7 2.123(3), Fe4–B10 2.091(4), Fe5–C1 1.983(3), Fe5–B2 2.253(3), Fe5–B3 2.241(3), Fe5–B8 2.147(4), Fe5–B9 2.130(3), Fe5–B11 2.117(4), C1–B2 1.553(4), C1–B3 1.561(5), C6–B2 1.691(4), C6–B10 1.684(5), C7–B3 1.704(5), C7–B10 1.684(5), B2–B9 1.829(5), B3–B8 1.813(5), B8–B11 1.765(6), B9–B11 1.771(5), Fe4–C$_{Cp}$ (mean) 2.080, Fe5–C$_{Cp}$ (mean) 2.094; C1-Fe4-B10 109.02(13), C1-Fe4-C7 84.81(12), B10-Fe4-C7 47.10(14), C1-Fe4-C6 84.18(11), B10-Fe4-C6 47.02(14), B10-Fe4-B2 87.84(14), C7-Fe4-B2 96.90(12), C6-Fe4-B2 46.01(12), C1-Fe4-B3 43.40(12), B10-Fe4-B3 88.05(14), C7-Fe4-B3 46.43(13), C6-Fe4-B3 96.52(12), B2-Fe4-B3 76.91(13), C1-Fe5-B11 112.34(12), C1-Fe5-B9 88.60(12), B11-Fe5-B9 49.28(14), C1-Fe5-B8 88.49(13), B11-Fe5-B8 48.89(15), B9-Fe5-B8 88.06(15), C1-Fe5-B3 42.85(12), B11-Fe5-B3 89.86(14), B9-Fe5-B3 100.92(13), B8-Fe5-B3 48.74(14), C1-Fe5-B2 42.43(12), B11-Fe5-B2 90.41(13), B9-Fe5-B2 49.23(12), B8-Fe5-B2 100.76(13), B3-Fe5-B2 74.80(12).
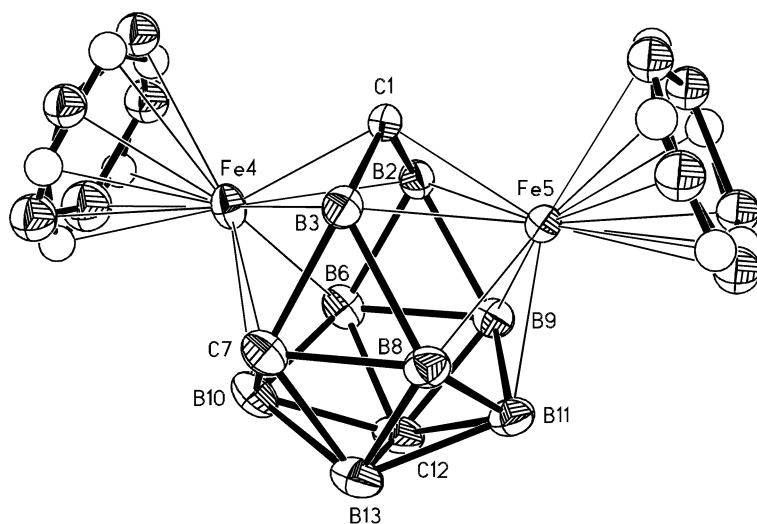
Figure 2. The structure of $[4,5\text{-}Cp_2\text{-}closo\text{-}4,5,1,7,12\text{-}Fe_2C_3B_8H_{11}]$ (**3**), with 20% ellipsoids. The disordered Cp rings at Fe4 and Fe5 with minor occupancies have been drawn as open circles. Selected interatomic distances [Å] and angles [°]: Fe4–C1 1.999(4), Fe4–B2 2.243(5), Fe4–B3 2.199(5), Fe4–B6 2.149(6), Fe4–C7 2.123(4), Fe4–B10 2.081(6), Fe4–C_{Cp} (mean) 2.101, Fe5–C1 1.994(4), Fe5–B2 2.250(5), Fe5–B3 2.236(5), Fe5–B8 2.127(5), Fe5–B9 2.150(5), Fe5–B11 2.089(5), Fe5–C_{Cp} (mean) 2.107, C1–B2 1.563(6), C1–B3 1.570(6), C7–B3 1.715(6), C7–B10 1.692(7), B2–B6 1.762(7), B2–B9 1.793(7), B3–B8 1.795(7), B6–B10 1.775(8), B8–B11 1.749(7), B9–B11 1.773(7), C12–B13 1.656(8), C12–B6 1.701(7), C12–B9 1.703(7), C12–B10 1.714(8), C12–B11 1.725(8); C1–Fe4–B10 110.3(2), C1-Fe4-C7 85.69(17), B10-Fe4-C7 47.5(2), C1-Fe5-B11 111.8(2), C1-Fe5-B8 88.18(18), B11-Fe5-B8 49.0(2), B2-C1-B3 123.4(4), B2-C1-Fe5 77.5(2), B3-C1-Fe5 76.7(2), B2-C1-Fe4 77.0(2), B3-C1-Fe4 75.0(2), Fe5-C1-Fe4 121.2(2), B13-C7-B10 63.2(3), B13-C7-B3 118.4(4), B10-C7-B3 122.6(4), B13-C7-B8 60.6(3), B10-C7-B8 112.4(4), B3-C7-B8 62.9(3), B13-C7-Fe4 119.6(3), B10-C7-Fe4 65.0(3), B3-C7-Fe4 69.0(2), B8-C7-Fe4 117.5(3), B13-C12-B6 116.9(4), B13-C12-B9 116.4(4), B6-C12-B9 62.9(3), B13-C12-B10 63.4(3), B6-C12-B10 62.6(3), B9-C12-B10 114.3(4), B13-C12-B11 63.1(3), B6-C12-B11 114.2(4), B9-C12-B11 62.3(3), B10-C12-B11 113.4(4).

C–C (Cp ring) distances, for instance in **3**, are within the expected limits (range 1.379–1.424 Å); this applies generally to all the compounds. The C1–B2 and C1–B3 bond lengths (range 1.553–1.570 Å) are shorter than other C–B separations (range 1.656–1.735 Å). The B–B distances are within the expected limits (range 1.720–1.829 Å).

Figures 4 and 5 show the EPR spectra of the unsubstituted species **3** and the substituted complex **4**; the spectrum of compound **2** is almost identical to that of compound **3**. The spectrum of **3** exhibits a broad signal ($g = 2.0911$) while that of **4** consists of two main signals at $g = 2.0019$ and 2.0253 with hyperfine splitting more pronounced than in **3** due to electronuclear interaction with the ^1H, ^{11}B, and ^{14}N nuclei associated with the carborane cluster. Nevertheless, both spectra exhibit EPR signals which are characteristic of an $S = \frac{1}{2}$ system. The shape of both spectra is more typical of a free-radical system[16] (see also ref. [17], for example) in which the free electron is dissipated over the carborane ligand,[18] rather than of low-spin iron(III) complexes.[16,19] The shape of the complexes **2** and **3**, and **4** resembles that of the diamagnetic bimetallic dicarbaborane *hypercloso* compounds $[(CpFe)_2C_2B_9H_{11}]$[8] and $[(Cp*Ru)_2C_2B_9H_{11}]$,[11] and *closo* $[(CpCo)_2C_2B_9H_{11}]$,[9] respectively. Taking these analogies and electron counting rules into account, the paramagnetic tricarbaboranes **2** and **3**, and **4** of the $[(CpFe)_2C_3B_8H_{11}]$ type belong to the 13-vertex 27-electron ($2n+1$ cage electrons) family, for which we suggest using a prefix *subcloso*[10] in their nomenclature. This potentially broad class of compounds has been exemplified so far only by the long-known $[CpFe(C_2B_9H_{11})CoCp]$ member of the dicarbaborane series.[9] The $[(CpFe)_2C_3B_8H_{11}]$-type complexes described in this work and the recently reported[20] 12-vertex $[(CpFe)_2 MePCB_8H_9]$ compound can also be envisaged as complexes of the *subarachno* ($2n+5$ cage electron)[10] $\eta^6,\eta^6\text{-}C_3B_8H_{11}^{2-}$ and $\eta^6\text{-}MePCB_8H_{11}^{2-}$ ligands, respectively, charge-compensated by two $\{CpFe^{II}\}^+$ fragments. In contrast, the complexing ligand in the isoelectronic bimetalladicarbaborane *subcloso* species $[CpFe(C_2B_9H_{11})CoCp]$[9] is *arachno*-$\eta^6,\eta^6\text{-}C_2B_9H_{11}^{4-}$, which is capped by $\{CpFe^{III}\}^{2+}$ and $\{CpCo^{III}\}^{2+}$ vertices. The surmise that the paramagnetism of both $[(CpFe)_2C_3B_8H_{11}]$ and $[CpFe(C_2B_9H_{11})CoCp]$ is a consequence of the odd number ($2n+1$) of cage electrons is further supported by the diamagnetism of $[(CpFe)_2C_2B_9H_{11}]$[8] and $[(Cp*Ru)_2C_2B_9H_{11})]$,[11] which evidently contain two paramagnetic Fe^{III} and Ru^{III} centers, respectively,[11] although their molecules as a whole have an even ($2n$) electron count, which is the reason for the observed diamagnetism. Conversely, the $[(CpFe)_2C_3B_8H_{11}]$-type and $[(CpFe)_2MePCB_8H_9]$[20] complexes have two diamagnetic Fe^{II} centers, but the odd electron count causes the molecule as a whole to be paramagnetic. Moreover, the $2n+1$ electron count seems to be a very stable configuration for the 13-vertex bimetallic tricarbaborane systems: all our attempts so far to synthesize the 28-cage electron *closo* congeners, $[CpFe(C_3B_8H_{11})CoCp]$ and $[CpFe(C_3B_8H_{11})RhCp*]$, by conventional metal insertion into the same open-cage intermediate anion, have failed because of the low stability of the resulting complexes.

Conclusion

The work presented here demonstrates that the 12-vertex *closo* tricarbollide complex **1**[14] undergoes a two-electron reduction to generate a transient anion that, upon subsequent cluster expansion, generates bimetallic complexes of general constitution *subcloso*-$[(CpFe)_2C_3B_8H_{11}]$. The three paramagnetic compounds **2**, **3**, and **4** isolated as described in this work are the first representatives of the 13-vertex dimetallatricarbaborane series. Further syntheses based on the intermediate anion *nido*-$[t\text{BuNH-CpFeC}_3B_8H_{10}]^{2-}$ and investiga-

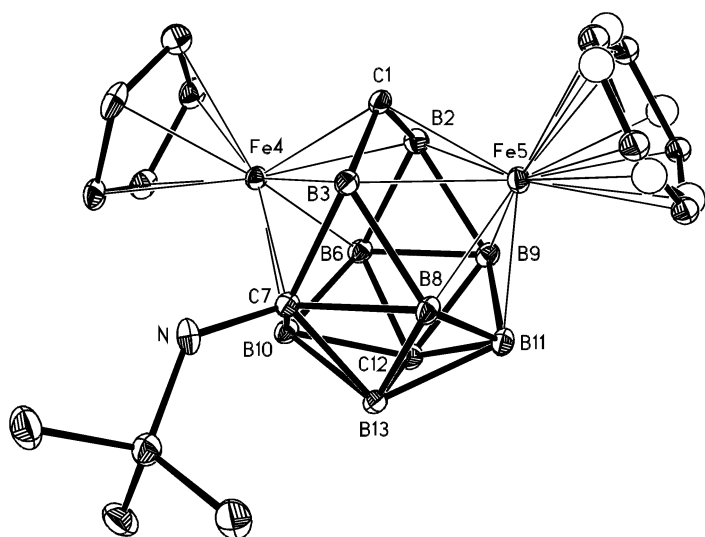Figure 3. The structure of [7-*t*BuNH-4,5-Cp₂-*closo*-4,5,1,7,12-Fe₂C₃B₈H₁₁] (**4**), with 20% ellipsoids. The disordered Cp rings at Fe5 with minor occupancy have been drawn as open circles. Selected interatomic distances [Å] and angles [°]: Fe4–C1 1.994(4), Fe4–B2 2.234(5), Fe4–B3 2.223(5), Fe4–C7 2.169(4), Fe4–B6 2.112(5), Fe4–B10 2.046(5), Fe4–C$_{Cp}$ (mean) 2.087, Fe5–C1 1.994(4), Fe5–B2 2.243(5), Fe5–B3 2.216(5), Fe5–B9 2.147(5), Fe5–B8 2.124(5), Fe5–B11 2.089(5), Fe5–C$_{Cp}$ (mean) 2.099, N–C7 1.444(5), C1–B2 1.566(6), C1–B3 1.566(6), C7–B3 1.709(6), C7–B10 1.703(6), B2–B9 1.791(7), B2–B6 1.777(7), B3–B8 1.800(6), B6–B10 1.784(7), B8–B11 1.747(7), B9–B11 1.781(6), C12–B13 1.656(6), C12–B6 1.698(6), C12–B9 1.702(6), C12–B10 1.704(6), C1-Fe4-B10 110.63(17), C1-Fe4-B6 87.32(18), B10-Fe4-B6 50.78(19), C1-Fe4-C7 85.31(15), B10-Fe4-C7 47.55(16), B6-Fe4-C7 86.86(17), C1-Fe4-B3 43.15(16), B10-Fe4-B3 87.30(18), B6-Fe4-B3 99.98(18), C7-Fe4-B3 45.76(15), C1-Fe4-B2 42.99(17), B10-Fe4-B2 90.95(18), B6-Fe4-B2 48.17(18), C7-Fe4-B2 99.18(16), B3-Fe4-B2 76.27(17), C1-Fe5-B11 111.81(17), B3-C1-B2 123.1(4), B3-C1-Fe4 76.2(2), B2-C1-Fe4 76.7(2), B3-C1-Fe5 75.9(2), B2-C1-Fe5 77.1(2), Fe4-C1-Fe5 121.3(2), N-C7-B10 118.5(3), N-C7-B3 111.7(3), B10-C7-B3 119.7(3), N-C7-B13 119.5(3), B10-C7-B13 63.9(3), B3-C7-B13 116.0(3), N-C7-B8 121.1(3), B10-C7-B8 111.9(3), B3-C7-B8 61.8(2), B13-C7-B8 60.1(2), N-C7-Fe4 113.1(3), B10-C7-Fe4 62.4(2), B3-C7-Fe4 68.8(2), B13-C7-Fe4 117.3(3), B8-C7-Fe4 116.1(3), B13-C12-B6 119.7(3), B13-C12-B9 117.5(3), B6-C12-B9 63.5(3), B13-C12-B10 65.1(3), B6-C12-B10 63.2(3), B9-C12-B10 115.2(3), B13-C12-B11 63.1(3), B6-C12-B11 115.6(3), B9-C12-B11 62.4(3), B10-C12-B11 114.6(3).
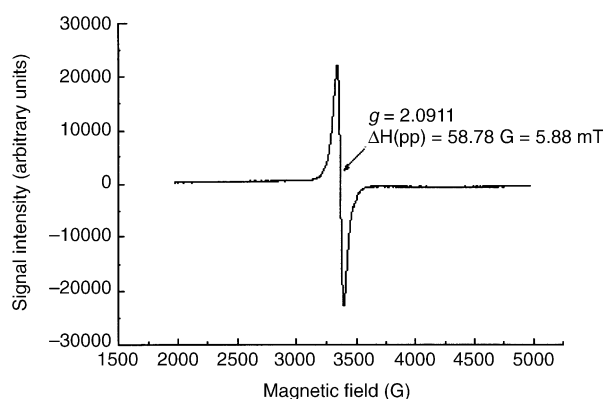

Figure 4. X-band EPR spectra of [4,5-Cp₂-*closo*-4,5,1,7,12-Fe₂C₃B₈H₁₁] (**3**).

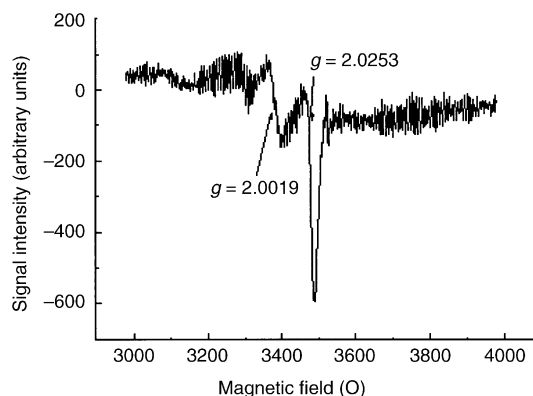tions in the area of supraicosahedral metallacarboranes are currently in progress in our laboratories.

Figure 5. X-band EPR spectra of [7-*t*BuNH-4,5-Cp₂-*closo*-4,5,1,7,12,-Fe₂C₃B₈H₁₀] (**4**).

Experimental Section

General: All reactions were carried out under argon with standard vacuum or inert-atmosphere techniques as described by Shriver and Drezdon,[21] although some operations, such as preparative TLC, were performed in air. The starting compound **1** was prepared according to the literature method.[14] Ethylene glycol dimethyl ether (DME; Aldrich) was dried over sodium wire and freshly distilled from sodium diphenylketyl before use. Hexane, benzene, and CH₂Cl₂ were dried over CaH₂ and freshly distilled before use. Other chemicals were reagent or analytical grade and were used as purchased. Preparative TLC was carried out using silica gel G with a fluorescent indicator (Aldrich, type UV 254) as the stationary phase on 200 × 200 × 1 mm³ plates, made on glass formers from aqueous slurries which were then dried in air at 80 °C. The purity of individual chromatographic fractions was checked by analytical TLC on Machery Nagel plates with a UV indicator (silica gel on aluminum foil; detection by 254 nm UV light and 2% aqueous AgNO₃ spray). 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, Basel, Switzerland (70 eV, EI ionization). IR spectra were obtained on a EU 9512 Pye–Unicam Fourier transform spectrometer. ¹H and ¹¹B NMR spectra were measured on a Varian Mercury+ spectrometer. Residual solvent ¹H resonances were used as internal secondary standards. Chemical shifts are referenced to F₃B·OEt₂ for ¹¹B and (SiMe₄) for ¹H. The X-band EPR spectra were recorded on an E-540 Elexsys spectrometer (Bruker Biospin, Germany) in the solid state at room temperature.

[*nido*-CpFeC₃B₈H₁₀*t*BuNH]²⁻ intermediate anion: A solution of **1** (20 mg, 61.3 μmol) in [D₈]THF (2 mL) under an argon atmosphere in an Aldrich Safe Seal NMR tube was treated with naphthalene (3 mg) and small pieces of sodium metal (20 mg). The mixture was shaken vigorously for 8 h at ambient temperature, while the supernatant solution slowly turned dark red. At this point, the NMR spectra of the mixture were measured to partially characterize the open-cage intermediate anion. ¹¹B{¹H} NMR (128 MHz, [D₈]THF, 25 °C): δ = 4.9 (s, 1B), −0.23 (s, 1B), −6.4 (s, 1B), −10.4 (s, 1B), −12.1 (s, 1B), −16.8 (s, 1B), −20.6 (s, 1B), −24.4 ppm (s, 1B) (no diagnostic [¹¹B-¹¹B]-COSY cross-peaks observed, because of a paramagnetic impurity). ¹H NMR (400 MHz, [D₈]THF, 25 °C): δ = 5.84 (s, 5H, Cp), 3.67 (s, 1H, cage CH), 2.41 (s, 1H, cage CH), 1.202 ppm (s, 9H, *t*Bu).

Compounds of the [(CpFe)₂C₃B₈H₁₀X] type (X = H, *t*BuNH) 2, 3, and 4: *Method A*: A solution of **1** (220 mg, 0.675 mmol) in DME (15 mL) was treated with naphthalene (30 mg) and small pieces of sodium metal (0.20 g). The slurry was stirred for 8 h at ambient temperature and the mixture slowly turned dark red. At this point, the original TLC spot of **1** disappeared and a new, dark red and rapidly AgNO₃-reducing spot, R_f(CH₂Cl₂) = 0.55, belonging to the intermediate red anion, appeared. The supernatant solution was transferred by cannula into a separate flask containing C₅H₅Fe(CO)₂I (230 mg, 0.757 mmol), then the reaction mixture was stirred for 16 h at room temperature and then refluxed gently

for 4 h. (Reactions carried out without heating, at low ($-33\,^\circ$C) or ambient temperatures, provided metal insertion products only in trace quantities). After the solution had been cooled, the solvent was evaporated and the resulting complex mixture of compounds was separated by repeated chromatography on a silica gel column (2×20 cm^2) with hexane–CH$_2$Cl$_2$ (1:1 to 1:4, v/v) and hexane–benzene (2:1 to 1:1, v/v) mixtures as mobile phases. The purity of individual fractions was checked by analytical TLC; pure fractions were evaporated to dryness to isolate three products of R_f (benzene–hexane, 1:2) 0.51 (yield 43 mg, 14%, recrystallized from hot pentane), 0.24 (yield 6 mg, 2%, recrystallized from CH$_2$Cl$_2$–heptane), and 0.17 (yield 6 mg, 2%, recrystallized from CH$_2$Cl$_2$–heptane), which were characterized as **4**, **3**, and **2**, respectively.

Compound **2**: m.p. 192–193$\,^\circ$C; IR (KBr): $\tilde{\nu} = 2509$ (BH), 2858, 2924, 3439 cm^{-1} (CH); MS (70 eV): m/z (%): 377 (55) [M^+], 376 (88) [M^+-H]; 375 (100) [M^+-2H]; elemental analysis: calcd (%) for C$_{13}$H$_{21}$B$_8$Fe$_2$ (375.56): C 41.57, H 5.64; found: C 40.02, H 5.32.

Compound **3**: m.p. 205–207$\,^\circ$C; IR (KBr): $\tilde{\nu} = 2518$ (BH), 2929, 3438 cm^{-1} (CH); MS (70 eV): m/z (%): 377 (55) [M^+], 376 (90) [M^+-H]; 375 (100) [M^+-2H]; elemental analysis: calcd (%) for C$_{13}$H$_{21}$B$_8$Fe$_2$ (375.56): C 41.57, H 5.64; found: C 39.81, H 5.28.

Compound **4**: m.p. 130–132$\,^\circ$C; elemental analysis: calcd. (%) for C$_{17}$H$_{30}$B$_8$Fe$_2$N (446.68): C 45.72, H 6.77; found: C 45.31, H 6.52; IR (KBr): $\tilde{\nu} = 2506$ (BH), 2920, 3439 cm^{-1} (CH); MS (70 eV): m/z (%): 448 (67) [M^+], 447 (100) [M^+-H].

Impure fractions were also isolated, containing non-boron Fe compounds and unidentified compounds, probably of the [(CpFe)$_2$C$_3$B$_8$H$_{10}$NHtBu] and [CpFeC$_3$B$_7$H$_9$NHtBu] types, that could not be separated further.

Method B: Complex **1** (500 mg, 1.53 mmol) was dissolved in DME (20 mL) and then treated with naphthalene (50 mg) and sodium metal (500 mg) as in Method A. The dark red solution was transferred by cannula into a flask containing [CpFe(CO)$_2$]$_2$ (400 mg, 1.65 mmol); the reaction mixture was stirred for 48 h at room temperature, refluxed gently for an additional 48 h, then worked up. The products were separated by column chromatography essentially in the same manner as in Method A, to isolate **4** (yield 36 mg, 5%), **3** (yield 9 mg, 2%), and **2** (yield 14 mg, 5%).

X-ray crystallography: Data were collected for violet crystals of **2** and **3** mounted at room temperature on a Rigaku AFC5S diffractometer using graphite monochromatized Mo$_{K\alpha}$ and for a violet crystal of **4** at $-80\,^\circ$C on a Rigaku AFC7S diffractometer. All data were collected in $\omega/2\theta$ scan mode up to $2\theta_\mathrm{max} = 50.0^\circ$ and corrected for absorption (psi scans). The crystallographic details are summarized in Table 1. The structures were solved by direct methods and refined on F^2 by the SHELXL97 program.[22] For **3**, both Cp rings are disordered into two orientations mutually rotated by 31° and 27°. For **4**, the Cp ring coordinated to Fe5 is disordered into two orientations mutually rotated by about 22°. For each structure, the disordered Cp rings were refined as rigid groups and with isotropic thermal displacement parameters for the carbon atoms. Non-hydrogen atoms, except for the carbon atoms of the disordered Cp rings, were refined with anisotropic displacement parameters and hydrogen atoms were treated as riding atoms using the SHELX97 default parameters. For each structure, carbon and boron atoms could be distinguished reliably. The final difference maps had no peaks of chemical significance. CCDC-202045 (**2**), CCDC-202046 (**3**), and CCDC-202047 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

Acknowledgement

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do (for x = 3), and *subarachno* (for x = 5), for compounds with an odd number of cage electrons.

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