Organometallics **2005,** *24,* 4387−4392 4387

Ferra- and Ruthenatricarbollides $CpFeC_3B_8H_{11}$ and $Cp^*RuC_3B_8H_{11}$

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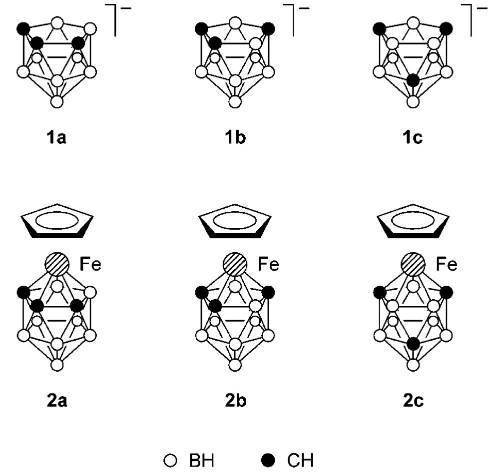
Received February 25, 2005

The room-temperature photochemical reaction of the tricarbollide anion [*nido*-7,8,9-$C_3B_8H_{11}$]$^-$ (**1a**) with [$CpFe(C_6H_6)$]$^+$ proceeds without cluster rearrangement to form the 12-vertex *closo*-ferratricarbollide 1-Cp-1,2,3,4-$FeC_3B_8H_{11}$ (**2a**, the metal atom is assigned number 1). **2a** rearranges to the isomeric complex 1-Cp-1,2,3,5-$FeC_3B_8H_{11}$ (**2b**) at 110 °C and further to 1-Cp-1,2,4,10-$FeC_3B_8H_{11}$ (**2c**) at 165 °C. The reaction of **1a** with [Cp^*RuCl]$_4$ is accompanied by polyhedral rearrangement giving 1-Cp*-1,2,3,5-$RuC_3B_8H_{11}$ (**3b**). Its further isomerization occurs slowly at room temperature and rapidly at 65 °C to give complex 1-Cp*-1,2,4,10-$RuC_3B_8H_{11}$ (**3c**). Similar reactions of [*nido*-7,8,10-$C_3B_8H_{11}$]$^-$ (**1b**) with [$CpFe(C_6H_6)$]$^+$ and [Cp^*RuCl]$_4$ afford **2b** and **3b**, respectively. A diamond-square-diamond mechanism for the **2a** → **2b** → **2c** rearrangement sequence is proposed. The relative stability of isomers **2a**−**c** was estimated by DFT calculations. The constitution of the compounds prepared was determined by multinuclear NMR spectroscopy and mass spectrometry. The structures of **2a**, **2b**, and **3c** were established by X-ray diffraction.

Introduction

Due to the presence of the pentagonal open face and single negative charge, the known 11-vertex *nido*-tricarbaborane (tricarbollide) anions [*nido*-7,8,9-$C_3B_8H_{11}$]$^-$ (**1a**) and [*nido*-7,8,10-$C_3B_8H_{11}$]$^-$ (**1b**) along with their hypothetical congener [*nido*-2,8,10-$C_3B_8H_{11}$]$^-$ (**1c**) can be considered as close analogues of the Cp^- anion, thus making tricarbollide complexes similar to metallocenes.[1,2] However, in contrast to the series of amino-substituted tricarbollide complexes, e.g., 12-vertex *closo*-ferratricarbollides 1-Cp-12-NR_2-1,2,4,12-$FeC_3B_8H_{10}$[3,4] and 1-Cp-10-NR_2-1,2,4,10-$FeC_3B_8H_{10}$,[5] little is known about the unsubstituted compounds of the $CpFeC_3B_8H_{11}$ type. A single preliminary note reports on the reaction between **1a** and $CpFe(CO)_2I$ in refluxing toluene giving two complexes formulated as 1-Cp-1,2,3,4-$FeC_3B_8H_{11}$ (**2a**) and 1-Cp-1,2,4,10-$FeC_3B_8H_{11}$ (**2c**).[6] However, the present study revealed that the product previously assigned the structure **2a** (as a result of wrong interpretation of the [$^{11}B-^{11}B$]-COSY NMR data) is in fact complex 1-Cp-1,2,3,5-$FeC_3B_8H_{11}$ (**2b**). Herein we describe syntheses and rearrangements of three isomeric $CpFeC_3B_8H_{11}$ compounds, **2a**−**c**, which are derivatives of anions **1a**−**c**, respectively. The related ruthenium complexes $Cp^*RuC_3B_8H_{11}$ are also reported. For these compounds we use a numbering system in which the metal vertex bears number 1. This system removes the disadvantages of the original "C" numbering[7] and has been already used for the structurally related phosphadicarbollide complexes *closo*-$CpFePC_2B_8H_{10}$.[8]

Chart 1



1a **1b** **1c**

2a **2b** **2c**

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[†] Russian Academy of Sciences.

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[1] Štíbr, B. *J. Organomet. Chem.* **2005**, *690*, 2694.

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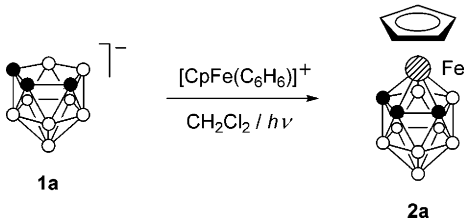
[6] Štíbr, B.; Holub, J.; Teixidor, F.; Viñas, C. *Collect. Czech. Chem. Commun.* **1995**, *60*, 2023.

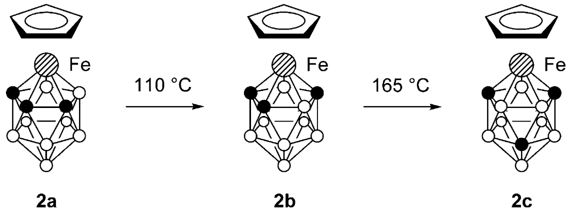
[7] Casey, J. B.; Evans, W. J.; Powell, W. H. *Inorg. Chem.* **1981**, *20*, 1333, and references therein. The main disadvantage of the "C" numbering system for metallacarboranes consists of changing the numbering order for the whole framework in the case of cluster rearrangement.

10.1021/om050139o CCC: $30.25

Scheme 1



Scheme 2



Results and Discussion

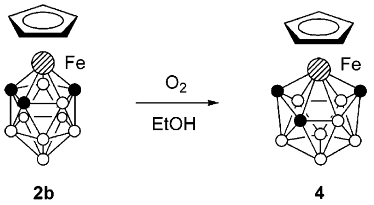
Synthesis. We have found earlier that the $[CpFe(C_6H_6)]^+$ cation can be used for the incorporation of the $[CpFe]^+$ fragment into carborane cages.[9] The photochemical reaction of **1a** with $[CpFe(C_6H_6)]^+$ in CH_2Cl_2 at room temperature gives red complex **2a** in 60% yield (Scheme 1). **2a** undergoes cluster rearrangement in refluxing toluene to give the isomeric dark red compound **2b** in 71% yield (Scheme 2). Further rearrangement is achieved by heating **2b** in refluxing mesitylene, resulting in almost quantitative formation of the orange isomer **2c**.

Revision of the data reported previously[6] allows us to conclude that the reaction of **1a** with $CpFe(CO)_2I$ in refluxing toluene gives complexes **2b** and **2c**. We found that the mixture of **2b** (15%) and **2c** (35%) is also formed by reaction of the neutral tricarbaborane *nido*-7,8,9-$C_3B_8H_{12}$ (H[**1a**]) with $[CpFe(CO)_2]_2$ in refluxing diglyme.

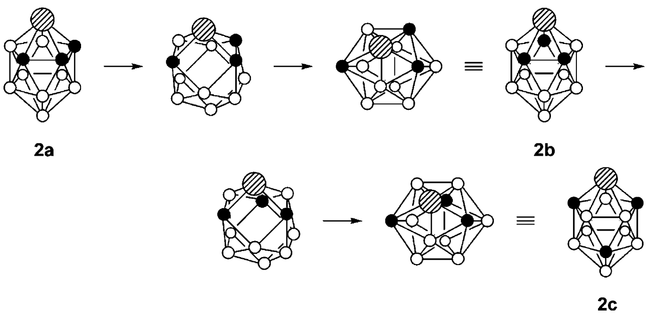
Although compounds **2a**−**c** are stable in the solid state, **2a** and **2b** are less so in solution. Complex **2a** slowly disproportionates in polar solvents ($MeNO_2$, THF, CH_2Cl_2) to give ferrocene, H[**1a**] (both identified by NMR spectroscopy), and an uncharacterized orange Fe-containing precipitate. The disproportionation is facilitated by increasing the temperature and polarity of the solvent. Complex **2b**, though stable in solution in inert atmosphere, undergoes boron elimination upon air oxidation in ethanol to produce the previously reported[6] 11-vertex ferracarborane 1-Cp-1,2,3,4-*closo*-$FeC_3B_7H_{10}$ (**4**) in 45% yield (Scheme 3). Derivatives of **4** have been studied in detail by Sneddon and coworkers.[10]

The formation of ferratricarbollides **2b**,**c** via thermal isomerization of **2a** is associated with progressive space separation of the CH vertexes that is consistent with a diamond-square-diamond mechanism[11] outlined in Scheme 4. The rearrangement starts with the breaking of the unfavorable C−C connectivity in **2a**, leading to the **2b** isomer via a cubooctahedral intermediate. Breakage of the second C−C connectivity in the next step leads to **2c**, a framework with maximum separation of the cage carbon atoms.

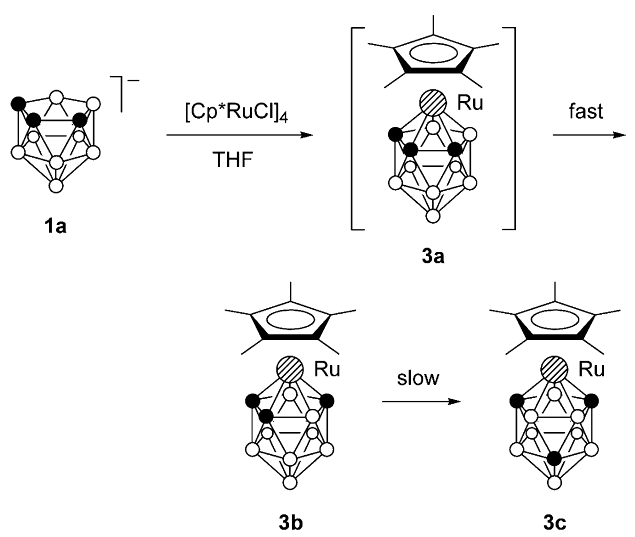
Scheme 3



Scheme 4



Scheme 5



A different reaction scenario was observed for the analogous ruthenatricarbollide compounds $Cp^*RuC_3B_8H_{11}$. Thus, a room-temperature reaction between **1a** and $[Cp^*RuCl]_4$ in THF for 2 h affords the rearranged light yellow complex 1-Cp*-1,2,3,5-$RuC_3B_8H_{11}$ (**3b**) (58%) instead of the expected **3a** (Scheme 5). This indicates a lower barrier for the isomerization of the ruthenium compounds in comparison with that for the iron analogues. It is further confirmed by the quantitative conversion of **3b** into the isomeric 1-Cp*-1,2,4,10-$RuC_3B_8H_{11}$ (**3c**) compound upon prolonged standing at room temperature in solution. More surprisingly, this rearrangement also proceeds in the solid state although

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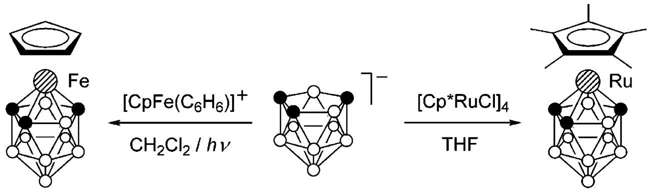
(8) (a) Štíbr, B.; Holub, J.; Bakardjiev, M.; Pavlík, I.; Tok, O. L.; Císařová, I.; Wrackmeyer, B.; Herberhold, M. *Chem. Eur. J.* **2003**, *9*, 2239. (b) Štíbr, B.; Holub, J.; Bakardjiev, M.; Hnyk, D.; Tok, O. L.; Milius, W.; Wrackmeyer, B. *Eur. J. Inorg. Chem.* **2002**, 2320.

(9) Earlier, using this cation we have prepared, 1-Cp-4-SMe_2-1,2,3-*closo*-$FeC_2B_9H_{10}$: Kudinov, A. R.; Meshcheryakov, V. I.; Petrovskii, P. V.; Rybinskaya, M. I. *Izv. Akad. Nauk, Ser. Khim.* **1999**, 177; *Russ. Chem. Bull.* **1999**, *48*, 176 (Engl. Transl.).

(10) (a) Plumb, C. A.; Carroll, P. J.; Sneddon, L. G. *Organometallics* **1992**, *11*, 1665. (b) Wasczcak, M. D.; Lee, C. C.; Hall, I. H.; Carroll, P. J.; Sneddon, L. G. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2228. (c) Barnum, B. A.; Carroll, P. J.; Sneddon, L. G. *Inorg. Chem.* **1997**, *36*, 1327. (d) Ramachandran, B. M.; Trupia, S. M.; Geiger, W. E.; Carroll, P. J.; Sneddon, L. G. *Organometallics* **2002**, *21*, 5078.

(11) Lipscomb, W. N. *Science* **1966**, *153*, 373.

Scheme 6



2b **1b** **3b**

much slower. Complex **3c** can also be obtained directly from **1a** and $[Cp^*RuCl]_4$ by extending the reaction time to 4 days.

Nothing was known previously about the coordinating ability of the tricarbollide anion **1b**. We found that this anion reacts easily with $[CpFe(C_6H_6)]^+$ (*hν*, 20 °C, 5 h) and $[Cp^*RuCl]_4$ (20 °C, 2 h) to give the corresponding metallatricarbollides **2b** and **3b** (Scheme 6). No rearrangement was observed during these reactions.

NMR Study. The NMR spectra for all the compounds isolated, except **2a**,[12] have been completely assigned using $[^{11}B-^{11}B]$-COSY[13] and $^1H\{^{11}B(selective)\}$[14] NMR techniques. Simplified stick diagrams in Figure 1 show graphical intercomparison of the ^{11}B NMR shifts for all four isomers of $CpFeC_3B_8H_{11}$ thus far known (**2a**−**c**, and the recently reported 1-Cp-1,2,8,10-$FeC_3B_8H_{11}$ (**2d**)[15]) and for two isomers of $Cp^*RuC_3B_8H_{11}$ (**3b** and **3c**). Generally, iron and ruthenium complexes with identical positions of the cage carbon atoms display very similar spectral patterns. The spectrum of the 1,2,3,4-isomer **2a** shows a 2:1:1:2:2 pattern of doublets, while the spectra of the 1,2,3,5-isomers **2b** and **3b** exhibit 1:2:2:1:2 behavior. The spectra of the isostructural pair **2c** and **3c** of the 1,2,4,10-constitution display 1:2:1:2:2 patterns, while the spectrum of isomer **2d** shows a 2:2:1:1:2 pattern.

The most characteristic feature of the ^1H NMR spectra of the compounds isolated is the resonances of the cage CH units. In this respect, the 1,2,3,5-isomers **2b** and **3b** exhibit 2:1 patterns, while the 1,2,4,10-isomers display 1:2 behavior (reading upfield). Similarly, the ^{13}C NMR spectra of the 12-vertex ruthenatricarbollides **3b** and **3c** show 2:1 and 1:2 patterns for the cage C units, respectively.

X-ray Diffraction Study. The structures of compounds **2a**, **2b**, and **3c** were determined by a single-crystal X-ray diffraction study. The structure of ferratricarbollide **2a** (Figure 2) represents the first 12-vertex metallacarborane having three adjacent carbon atoms. Despite such heteroatom crowding, C−C, C−B, and B−B cage connectivities are within the usual length range. The distance from the iron atom to the middle cage carbon atom (2.003 Å) is significantly shorter than to the outer ones (av 2.037 Å). Accordingly, the C_3B_2 face is slightly nonplanar (mean deviation 0.016 Å), with the C3 atom being deviated from the C2−C4−B5−B6 plane by 0.059 Å toward the iron atom. The Cp ring is disordered over two positions. The Fe⋯Cp distance (av 1.675 Å) is only slightly longer than that in ferrocene (1.660 Å),[16] indicating similar bonding strength.

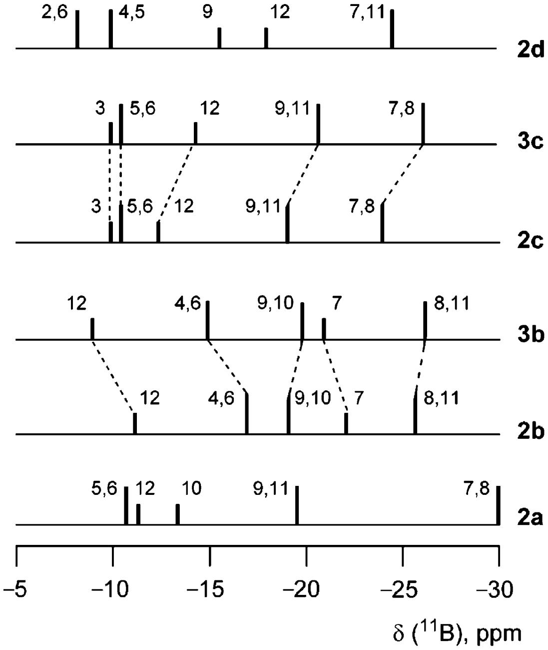


Figure 1. Simplified stick representation of the ^{11}B NMR shifts of all known isomers of $CpFeC_3B_8H_{11}$ (compounds **2a**−**d**) and $Cp^*RuC_3B_8H_{11}$ (compounds **3b** and **3c**).

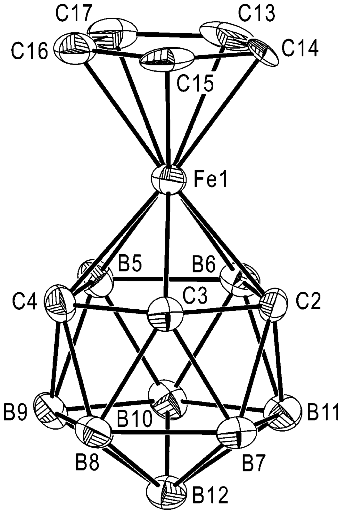


Figure 2. Molecular structure of **2a** with 50% thermal ellipsoids. The second conformation of the disordered Cp-ring and the hydrogen atoms are omitted for clarity. Selected interatomic distances (Å): Fe1−C2 2.028(2), Fe1−C3 2.003(2), Fe1−C4 2.045(2), Fe1−B5 2.092(4), Fe1−B6 2.077(4), Fe1−C13 2.030(4), Fe1−C14 2.057(4), Fe1−C15 2.082(4), Fe1−C16 2.075(4), Fe1−C17 2.047(4), C2−C3 1.619(3), C3−C4 1.613(3), C4−B5 1.691(4), B5−B6 1.779(4), B6−C2 1.700(4).

In the case of the isomeric compound **2b** (Figure 3), the Fe−C5 distance (2.067 Å) is longer than two other Fe−C(cage) distances (av 2.022 Å). The C_3B_2 face is more distorted than in **2a**, the C5 atom being deviated from the C2−C3−B4−B6 plane by 0.133 Å away from

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[12] Unfortunately, the decomposition of **2a** in solution with the formation of paramagnetic species does not allow performing the $^1H\{^{11}B(selective)\}$ NMR experiments.

[13] See, for example: (a) Kennedy, J. D. In *Multinuclear N. M. R.*; Mason, J., Ed.; Plenum Press: New York, 1987; p 221. (b) Hutton, W. C.; Venable, T. L.; Grimes, R. N. *J. Am. Chem. Soc.* **1984**, *106*, 29. (c) Schraml, J.; Bellama, J. M. *Two-Dimensional NMR Spectroscopy*; Wiley: New York, 1982, and references therein.

[14] Fontaine, X. L. R.; Kennedy, J. D. *J. Chem. Soc., Dalton Trans.* **1987**, 1573.

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[16] Haaland, A.; Nilsson, J. E. *Acta Chem. Scan.* **1968**, *23*, 2653.

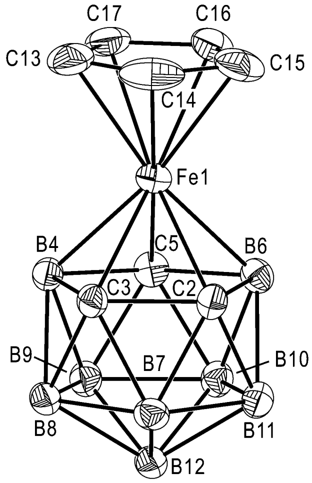

Figure 3. Molecular structure of **2b** with 50% thermal ellipsoids. The hydrogen atoms are omitted for clarity. Selected interatomic distances (Å): Fe1−C2 2.018(2), Fe1−C3 2.025(2), Fe1−B4 2.059(3), Fe1−C5 2.067(2), Fe1−B6 2.051(3), Fe1−C13 2.049(2), Fe1−C14 2.048(2), Fe1−C15 2.050(2), Fe1−C16 2.048(2), Fe1−C17 2.054(2), C2−C3 1.614(2), C3−B4 1.699(3), B4−C5 1.681(3), C5−B6 1.700(3), B6−C2 1.707(3).

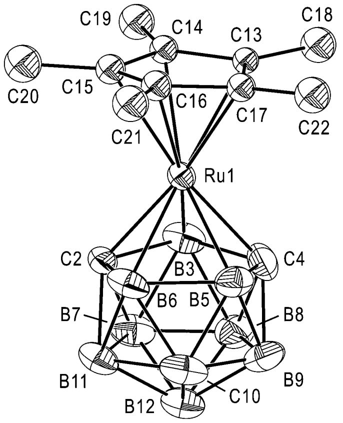

Figure 4. Molecular structure of **3c** with 50% thermal ellipsoids. The second conformation of the disordered Cp* ring and the hydrogen atoms are omitted for clarity. Selected interatomic distances (Å): Ru1−C2 2.168(5), Ru1−B3 2.118(7), Ru1−C4 2.156(7), Ru1−B5 2.109(7), Ru1−B6 2.124(7), Ru1−C13 2.221(12), Ru1−C14 2.228(12), Ru1−C15 2.194(15), Ru1−C16 2.196(12), Ru1−C17 2.178(12), C2−B3 1.665(10), B3−C4 1.693(10), C4−B5 1.690(10), B5−B6 1.771(11), B6−C2 1.756(10).

the iron atom. Similar to **2a**, the Fe···Cp distance (1.662 Å) is very close to that in ferrocene.

In the structure of ruthenatricarbollide **3c** (Figure 4), one of three cage carbon atoms is located in the *m*-position with respect to the metal atom and to two other carbon atoms lying on the C_2B_3 face. The overall geometry is significantly distorted from the expected C_s symmetry. The C_2B_3 face is twisted, so that the C4 and B3 vertexes are deviated by 0.096 Å from the C2−B6−B5 plane up and down, respectively. The Cp* ring is disordered over two positions. The Ru···Cp* distance in **3c** (av 1.818 Å) is close to that found in the related dicarbollide complex $[1\text{-Cp}^*\text{-}1,2,3\text{-RuC}_2B_9H_{11}]^-$ (1.819 Å),[17] but is noticeably longer than in pentamethylruthenocene (1.793 Å).[18]

DFT Calculations. The geometries of three $CpFeC_3B_8H_{11}$ isomers (**2a**−**c**) were optimized at the B3LYP/6-31G* level. The calculated structures of **2a** (disregarding the conformation of the Cp ring) and **2b** agree well with experimental data (deviations for **2a**: max 0.022, av 0.008 Å; for **2b**: max 0.021, av 0.014 Å), providing reliability of the calculation results. Isomer **2c** was found to be more stable than **2b** (by 8.53 kcal/mol) and **2a** (by 25.48 kcal/mol). Thus, the experimentally observed **2a** → **2b** → **2c** isomerization sequence shown in Scheme 2 correlates well with the calculated order of thermodynamic stabilities.

As shown in Table 1, the ^{11}B NMR chemical shifts, calculated using the GIAO method, are in a very good agreement with experimental values. For example, in the case of **2a** the deviation of the calculated chemical shifts from the experimental ones (max 1.9 ppm, av 0.9 ppm) is comparable to the difference between chemical shifts measured in different solvents, $CDCl_3$ and toluene-d_8 (max 1.5, av 1.2 ppm). This makes possible the assignment of NMR signals even in the absence of $[^{11}B-^{11}B]$-COSY correlations.

To estimate the strength of the Fe−tricarbollide bond, we calculated the enthalpies of reactions of the $[CpFe]^+$ fragment with **1a** and Cp^- anions leading to **2a** and ferrocene, respectively. The formation of ferrocene was found to be 58.58 kcal/mol more favorable than the formation of **2a**. This result correlates with the observed disproportionation of **2a** in polar solvents (vide supra).

Conclusion

We have developed simple and effective routes to the isomeric $CpFeC_3B_8H_{11}$ and $Cp^*RuC_3B_8H_{11}$ complexes that can be considered as tricarbollide analogues of ferrocene and ruthenocene. The compounds obtained are the first representatives of the unsubstituted metallatricarbollide series. The rearrangement of initially formed 1,2,3,4-isomers (**2a** and **3a**) is compatible with the diamond-square-diamond mechanism successively giving 1,2,3,5- (**2b** and **3b**) and 1,2,4,10-isomers (**2c** and **3c**) in accordance with progressive separation of the carbon atoms. In contrast to aminosubstituted metallatricarbollides,[3] the 1,2,4,12-isomer was neither isolated nor detected in the unsubstituted series, indicating that the complexation and rearrangement reactions are strongly influenced by the electronic and steric effects of a substituent.

Experimental Section

General Remarks. All reactions were carried out under argon in anhydrous solvents, which were purified and dried using standard procedures. The isolation of products was conducted in air unless otherwise stated. The starting materials $[Cp^*RuCl]_4$,[19] $[Cp^*RuCl_2]_2$,[20] $[CpFe(C_6H_6)]PF_6$,[21] H[**1a**], Tl-

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(21) (a) Nesmeyanov, A. N.; Vol'kenau, N. A.; Bolesova, I. N. *Tetrahedron Lett.* **1963**, *4*, 1725. (b) Nesmeyanov, A. N.; Vol'kenau, N. A.; Bolesova, I. N.; Polkovnikova, L. S. *Koord. Khim.* **1975**, *1*, 1252.

Table 1. Calculated and Experimental ^{11}B NMR Chemical Shifts for 2a−d

compound		^{11}B NMR shifts (assignment)				
2a	in $CDCl_3$	−9.8 (B5,6)	−10.9 (B12)	−12.3 (B10)	−18.0 (B9,11)	−28.9 (B7,8)
	in toluene-d_8	−8.6	−9.7	−10.8	−16.7	−28.0
	calculated	−9.4	−11.2	−13.3	−18.2	−30.8
2b	in $CDCl_3$	−11.0 (B12)	−16.0 (B4,6)	−17.2 (B9,10)	−21.0 (B7)	−25.0 (B8,11)
	calculated	−13.3	−15.7	−17.3	−21.5	−26.2
2c	in $CDCl_3$	−9.3 (B3)	−10.2 (B5,6)	−12.3 (B12)	−18.4 (B9,11)	−23.7 (B7,8)
	calculated	−9.1	−10.4	−16.3	−19.5	−25.0
2d	in $CDCl_3$[15]	−7.0 (B2,6)	−9.1 (B4,5)	−15.4 (B9)	−17.8 (B12)	−24.3 (B7,11)
	calculated	−4.9	−7.8	−17.4	−18.9	−25.2

[**1a**], Me_4N[**1a**], and Ph_4P[**1b**][2] were prepared as described in the literature. Visible light irradiation was performed by a high-pressure mercury vapor lamp with a phosphor-coated bulb (400 W). The ^{1}H, ^{11}B, and ^{13}C NMR spectra were recorded with Bruker AMX-400, Varian XL-500, and Varian MERCURY 400 instruments. The [^{11}B−^{11}B]-COSY and ^{1}H{^{11}B(selective)} NMR experiments were performed essentially as described previously.[22] Chemical shifts are given in ppm relative to internal $SiMe_4$ (^{1}H, ^{13}C) or external $BF_3{\cdot}OEt_2$ (^{11}B); the $J(^{11}B-^1H)$ constants are given in Hz. Unless otherwise stated, measurements were made at room temperature from $CDCl_3$ solutions.

1-Cp-1,2,3,4-FeC$_3$B$_8$H$_{11}$ (2a). A mixture of Me_4N[**1a**] (83 mg, 0.4 mmol) and $[CpFe(C_6H_6)]PF_6$ (138 mg, 0.4 mmol) in 15 mL of CH_2Cl_2 was irradiated with stirring at room temperature for 2 h, resulting in a color change from yellow to orange-red. Since **2a** is rather unstable in solution in air, the isolation of the product was carried out under argon atmosphere. The mixture was eluted through a short (3 cm) layer of silica gel and evaporated to dryness. The resulting red crystals were washed with petroleum ether to remove traces of ferrocene and dried in a vacuum to give 41 mg (40%) of **2a**. Alternatively, a solution of Me_4N[**1a**] (124 mg, 0.6 mmol) and $[CpFe(C_6H_6)]PF_6$ (206 mg, 0.6 mmol) in acetone (ca. 10 mL) was stirred for 0.5 h in order to induce ion metathesis, and the solvent was removed in a vacuum. The residue was dissolved in CH_2Cl_2 (20 mL) and irradiated as described above to give **2a** (92 mg, 60%). ^{1}H NMR (400 MHz, toluene-d_8): δ 4.61 (s, 1H, H3), 4.31 (s, 5H, Cp), 2.69 (s, 2H, H2,4). [^{11}B−^{11}B]-COSY NMR (128 MHz): all cross-peaks were observed. MS (70 eV, EI), *m/z* (%): 256 (42) [M]$^+$, 255 (60) [M − H]$^+$. Anal. Calcd for $C_8H_{16}B_8Fe$: C, 37.75; H, 6.34; B, 33.98. Found: C, 37.40; H, 6.27; B, 33.81.

1-Cp-1,2,3,5-FeC$_3$B$_8$H$_{11}$ (2b). Method A (by rearrangement of 2a). A solution of **2a** (40 mg, 0.16 mmol) in toluene (4 mL) was refluxed for 5 h. The solvent was evaporated in a vacuum, and the residue was dissolved in a CH_2Cl_2/petroleum ether mixture (2:1) and filtered. The evaporation of the resulting solution gave 28 mg (71%) of **2b**. Analytically pure sample was obtained by recrystallization from a concentrated hexane solution at 0 °C. ^{1}H NMR (500 MHz): δ 4.79 (s, 5H, Cp), 3.70 (s, 2H, H4,6), 3,49 (s, 1H, H5), 2.45 (s, 1H, H12), 1.38 (s, 4H, H2,3/H9,10), 1.35 (s, 1H, H7), 1.18 (s, 2H, H8,11). [^{11}B−^{11}B]-COSY NMR (128 MHz): all cross-peaks were observed. MS (70 eV, EI), *m/z* (%): 256 (35) [M]$^+$, 255 (70) [M − H]$^+$. Anal. Calcd for $C_8H_{16}B_8Fe$: C, 37.75; H, 6.34; B, 33.98. Found: C, 38.01; H, 6.87; B, 34.02.

Method B (by reaction of anion 1b with [CpFe(C$_6$H$_6$)]$^+$). A mixture of Ph_4P[**1b**] (142 mg, 0.3 mmol) and $[CpFe(C_6H_6)]PF_6$ (103 mg, 0.3 mmol) in 15 mL of CH_2Cl_2 was irradiated under stirring at room temperature for 5 h, resulting in a color change from yellow to dark red. The resulting mixture was evaporated to dryness, and the residue was dissolved in a CH_2Cl_2/petroleum ether mixture (2:1). The solution was eluted through a short (3 cm) layer of silica gel, and the solvent was removed in a vacuum to give 47 mg (62%) of **2b**.

1-Cp-1,2,4,10-FeC$_3$B$_8$H$_{11}$ (2c). A solution of compound **2b** (154 mg, 0.6 mmol) in mesitylene (8 mL) was refluxed for 12 h and then evaporated to dryness in a vacuum. The residue was dissolved in petroleum ether and eluted through a short (3 cm) layer of silica gel. The filtrate was evaporated to dryness, and the crude product was recrystallized from pentane at −78 °C to give pure **2c** (128 mg, 80%) identified by NMR spectroscopy.[6] Alternatively, compound **2b** (50 mg, 0.2 mmol) was sealed in a glass ampule under argon and heated at ca. 200 °C for 12 h. The ampule was opened at −78 °C, the contents were removed quantitatively by CH_2Cl_2, and the solvent was evaporated. Sublimation of the residue at ca. 120 °C in oil-pump vacuum gave 48 mg (96%) of pure **2c**.

Reaction of H[1a] with [CpFe(CO)$_2$]$_2$. A solution of H[**1a**] (100 mg, 0.74 mmol) and $[CpFe(CO)_2]_2$ (177 mg, 0.5 mmol) in diglyme (10 mL) was refluxed for 12 h. The solvent was removed in a vacuum, the residue was dissolved in CH_2Cl_2 (5 mL), and the solution was placed onto the top of a silica gel column (30 × 1.5 cm). Elution with 5% CH_2Cl_2/hexane under argon gave red-orange and yellow bands, from which compounds **2b** (28 mg, 15%) and **2c** (65 mg, 35%) were respectively isolated and identified by NMR spectroscopy.

1-Cp*-1,2,3,5-RuC$_3$B$_8$H$_{11}$ (3b). Method A (by reaction of anion 1a with [Cp*RuCl]$_4$). A mixture of $[Cp^*RuCl]_4$ (41 mg, 0.038 mmol) and Me_4N[**1a**] (33 mg, 0.16 mmol) in THF (3 mL) was stirred for 2 h. The resulting red solution was filtered and evaporated to dryness in a vacuum at room temperature. The residue was extracted by CH_2Cl_2/petroleum ether (1:1) and eluted through a short (3 cm) layer of silica gel. Evaporation of the solvent and recrystallization from petroleum ether gave 32 mg (58%) of **3b**. ^{1}H NMR (400 MHz): δ 2.92 (s, 1H, H5), 2.63 (s, 2H, H4,6), 2.20 (s, 1H, H12), 1.94 (s, 15H, Cp*), 1.69 (s, 1H, H7), 1.59 (s, 4H, H2,3/H9,10), 1.34 (s, 2H, H8,11). ^{11}B NMR (128 MHz): δ −8.0 (d (147), 1B, B12), −14.8 (d (165), 2B, B4,6), −19.4 (d (159), 2B, B9,10), −21.8 (d (160), 1B, B7), −26.9 (d (159), 2B, B8,11); all [^{11}B−^{11}B]-COSY cross-peaks were observed except for B7−B12. ^{13}C{^{1}H} NMR (100.6 MHz): 90.1 (s, 5C, *C*$_5$Me$_5$), 43.1 (br s, 1C, C5), 41.1 (br s, 2C, C2,3), 10.5 (s, 5C, C$_5$*Me*$_5$). MS (70 eV, EI), *m/z* (%): 371 (40) [M]$^+$, 370 (100) [M − H]$^+$. Anal. Calcd for $C_{13}H_{26}B_8Ru$: C, 42.21; H, 7.08; B, 23.38. Found: C, 42.44; H, 7.30; B, 23.21.

Method B (by reaction of anion 1b with [Cp*RuCl]$_4$). A mixture of $[Cp^*RuCl]_4$ (54 mg, 0.05 mmol) and Ph_4P[**1b**] (94 mg, 0.2 mmol) in THF (5 mL) was stirred for 2 h, and the solvent was removed in a vacuum at room temperature. The residue was dissolved in CH_2Cl_2, eluted through a short (3 cm) layer of silica gel, and evaporated to give 56 mg (76%) of **3b**.

1-Cp*-1,2,4,10-RuC$_3$B$_8$H$_{11}$ (3c). Method A (by rearrangement of 3b). A solution of **3b** (55 mg, 0.15 mmol) in THF (4 mL) was left for 4 days or refluxed for 2 h. The solvent was evaporated in a vacuum, and the residue was dissolved in a mixture of petroleum ether and CH_2Cl_2 (2:1) and eluted through a short (3 cm) layer of silica gel. The evaporation of the resulting solution gave 53 mg (97%) of **3c**. ^{1}H NMR (400 MHz): δ 3.14 (s, 1H, H12), 2.87 (s, 1H, H3), 2.72 (bs, 2H, H2,4), 2.16 (s, 2H, H5,6), 2.08 (s, 2H, H9,11), 2.05 (bs, 1H, H10), 1.94 (s, 15H, Cp*), 1.47 (s, 2H, H4.8). ^{11}B NMR (128 MHz): δ −8.7 (d (∼165), 1B, B3), −10.1 (d (180), 2B, B5,6), −13.7 (d (156), 1B, B12), −21.1 (d (171), 2B, B9,11), −26.9 (d (156), 2B, B7,8); all [^{11}B−^{11}B]-COSY cross-peaks were observed except for B3−

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B7,8. $^{13}C\{^1H\}$ NMR (100.6 MHz): 93.3 (s, 5C, C_5Me$_5$), 39.8 (br s, 2C, C2,4), 31.9 (br s, 1C, C10), 10.5 (s, 5C, C$_5$*Me*$_5$). MS (70 eV, EI), *m/z* (%): 371 (41) $[M]^+$, 370 (100) $[M - H]^+$. Anal. Calcd. for $C_{13}H_{26}B_8Ru$: C, 42.21; H, 7.08; B, 23.38. Found: C, 42.26; H, 7.41; B, 23.13.

Method B (by direct reaction of anion 1a with [Cp*RuCl]$_4$). A mixture of [Cp*RuCl]$_4$ (82 mg, 0.075 mmol) and Tl[**1a**] (101 mg, 0.3 mmol) or Me$_4$N[**1a**] (62 mg, 0.3 mmol) in THF (5 mL) was stirred at room temperature for 4 days or refluxed for 5 h. Alternatively, [Cp*RuCl]$_4$ was generated by stirring [Cp*RuCl$_2$]$_2$ (92 mg, 0.15 mmol) and Zn dust (100 mg, excess) in THF for 1 h followed by addition of Tl[**1a**]. The resulting light yellow solution was filtered and evaporated to dryness at room temperature. The residue was extracted by a CH_2Cl_2/petroleum ether (1:1) mixture and eluted through a thin layer (3 cm) of silica gel. The filtrate was evaporated to give small light yellow crystals of **3c** (88 mg, 80%). In the case where the product was oily, the elution through silica gel was repeated.

1-Cp-1,2,3,4-FeC$_3$B$_7$H$_{10}$ (4). A solution of **2b** (40 mg, 0.16 mmol) in ethanol (10 mL) was stirred in air for 12 h at room temperature. The solvent was evaporated and the residue was purified by preparative TLC chromatography on silica gel, using hexane as a mobile phase. The violet band with R_f 0.30 was extracted by CH_2Cl_2, evaporated, and sublimated at ca. 100 °C (oil-pump vacuum) to give 18 mg (45%) of **4** (identified by ^{1}H and ^{11}B NMR spectroscopy[6]).

Computational Details. All calculations were performed using Gaussian 98 (Revision A.7) software[23] at the B3LYP/6-31G* level. The structures of **2a**−**d**, Cp$_2$Fe, $[CpFe]^+$, $[1,2,3,4\text{-}FeC_3B_8H_{11}]^+$, Cp^-, and $[7,8,9\text{-}C_3B_8H_{11}]^-$ were optimized using tightened convergence criteria (options Opt = Tight, SCF = Tight). The frequency calculations were performed to confirm the global minimum and include ZPE corrections to the energy. The ^{11}B NMR shifts were calculated using the GIAO method by subtraction of calculated isotropic shielding values from those of B_2H_6 (93.50 at B3LYP/6-31G*). The experimental chemical shift of B_2H_6 was assigned 16.6 ppm.[24]

X-ray Crystallography. Crystals of **2a**, **2b**, and **3c** suitable for X-ray diffraction were grown by slow evaporation of CH_2Cl_2 solutions of the complexes. X-ray diffraction experiments were carried out with a Bruker SMART 1000 CCD area detector, using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å, ω-scans with a 0.3° step in ω and 10 s per frame exposure) at 120 K. Low temperature of the crystals was maintained with a Cryostream (Oxford Cryosystems) open-flow N$_2$ gas cryostat. Reflection intensities were integrated using SAINT software,[25] and absorption correction was applied semiempirically using the SADABS program.[26] The structures were solved by direct methods and refined by full-matrix least-squares against F^2 in anisotropic approximation for non-hydrogen atoms. The analyses of the Fourier density synthesis have revealed that the Cp and Cp* ligands in **2a** and **3c** are disordered by two positions with equal populations. All polyhedron hydrogen atoms were located from the Fourier density synthesis and refined in isotropic approximation. All calculations were performed using the SHELXTL software.[27] Crystal data and structure refinement parameters for **2a**, **2b**, and **3c** are given in Table 2.

Table 2. Crystal Data and Structure Refinement Parameters for 2a, 2b, and 3c

property	**2a**	**2b**	**3c**
molecular formula	$C_8H_{16}B_8Fe$	$C_8H_{16}B_8Fe$	$C_{13}H_{26}B_8Ru$
fw	254.54	254.54	369.89
cryst color, habit	red prism	red prism	yellow prism
cryst syst	orthorhombic	monoclinic	orthorhombic
space group	$P2_12_12_1$	$P2_1/c$	*Pbca*
temperature (K)	120(2)	120(2)	120(2)
a (Å)	6.472(1)	6.797(1)	10.141(4)
b (Å)	10.300(2)	9.929(2)	14.429(4)
c (Å)	17.749(4)	17.569(3)	24.061(7)
β (deg)		91.420(4)	
V (Å^3)	1183.3(5)	1185.4(4)	3520.7(19)
Z(*Z*′)	4(1)	4 (1)	8 (1)
F(000)	520	520	1504
ρ_{calc} (g cm^{-1})	1.429	1.426	1.396
μ (cm^{-1})	13.22	12.30	8.77
T_{min}/T_{max}	0.730/0.781	0.742/0.780	0.811/0.839
θ range (deg)	2.29−29.09	2.20−28.42	2.20−26.23
measd reflns (R_{int})	5495 (0.0378)	10 892 (0.0563)	9069 (0.0704)
unique reflns	2991	3423	4057
obsd reflns ($I > 2\sigma(I)$)	2661	2301	2113
parameters	219	194	210
R_1 (on *F* for obsd reflns)	0.0415	0.0425	0.0608
wR_2 (on F^2 for all reflns)	0.0922	0.0750	0.1251
GOF	1.069	0.935	1.020
ρ_{max}/ρ_{min} (e Å^{-3})	0.972/−0.603	0.849/−0.530	1.239/−0.635

The crystallographic data have been deposited with the Cambridge Crystallographic Data Center, CCDC 264297 for **2a**, CCDC 264298 for **2b**, and CCDC 264299 for **3c**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Acknowledgment. This work was supported by the Grant Agency of the Czech Republic (Project No. 203/05/2646) and by the Division of General Chemistry and Material Sciences of Russian Academy of Sciences (Grant No. 05-07). D.S.P. gratefully acknowledges INTAS for Young Scientist Fellowship (Grant No. 04-83-3848).

Supporting Information Available: Details of crystallographic experiments for compounds **2a**, **2b**, and **3c** (tables of crystal data collection, refinement parameters, atomic coordinates, anisotropic displacement parameters, bond distances, and bond angles) and calculation details for compounds **2a**−**d**, Cp$_2$Fe, and fragments $[CpFe]^+$, $[1,2,3,4\text{-}FeC_3B_8H_{11}]^+$, Cp^-, and $[C_3B_8H_{11}]^-$ (atomic coordinates for optimized geometry, energy data, summary of natural population analysis, and GIAO NMR shielding parameters). This material is available free of charge via the Internet at http://pubs.acs.org.

OM050139O

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