

Communication

New approaches to cluster modification in the 12-vertex metallatricarbollide series [☆]

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Received 17 September 2004; accepted 26 January 2005

Available online 11 March 2005

Abstract

Cluster opening of [2-Cp-9-^tBuNH-*closo*-2,1,7,9-FeC₃B₈H₁₀] (**1**) (Cp = η⁵-C₅H₅⁻), followed by oxidation, generates complexes [2-Cp-8-^tBuNH-*closo*-2,1,8,10-FeC₃B₈H₁₀] (**2**), [2-Cp-4-^tBuNH-*closo*-2,1,4,12-FeC₃B₈H₁₀] (**3**), [2-Cp-1-^tBuNH-*closo*-2,1,7,10-FeC₃B₈H₁₀] (**4**), and [1-Cp-10-^tBuNH-*closo*-1,2,3,10-FeC₃B₇H₉] (**5**). Another variation of the syntheses led to compounds [2-Cp-*closo*-2,1,8,10-FeC₃B₈H₁₁] (**6**), [4-Cp-1-^tBuNH-*closo*-4,1,6,8-FeC₃B₉H₁₁] (**7**) and to two isomeric, not yet fully characterized, 13-vertex compounds of general *nido* structure [^tBuNH-Cp-FeC₃B₉H₁₂] (**8** and **9**).

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Keywords: Boranes; Carboranes; Metallatricarbollides; Metallatricarbaboranes

We have recently reported [1] that the neutral tricarbollide complex [2-Cp-9-^tBuNH-*closo*-2,1,7,9-FeC₃B₈H₁₀] (**1**) [2] (Cp = η⁵-C₅H₅⁻) produces, upon reduction with Na⁺C₁₀H₈⁻ in 1,2-dimethoxyethane (DME), an air sensitive metallatricarbaborane dianion, which was tentatively identified as a 12-vertex [*nido*-Cp-^tBuNH-FeC₃B₈H₁₀]²⁻ compound (**1**²⁻) on the basis of NMR spectroscopy. Treatment of this dianion in situ with [CpFe(CO)₂I] or [CpFe(CO)₂]₂ produced three 13-vertex diferratricarbaboranes of the 27-electron [*subcloso*-(Cp₂-X-(Fe)₂C₃B₈H₁₀)] type (where X = H and ^tBuNH). Herein, we present in a preliminary fashion further useful extensions of the chemistry of **1**²⁻ that lead to a new type of cluster isomerisation, expansion and contraction reactions.

[☆] Presented at the EUROBORON 3 meeting, Průhonice-by-Prague, the Czech Republic, September 12–16, 2004.

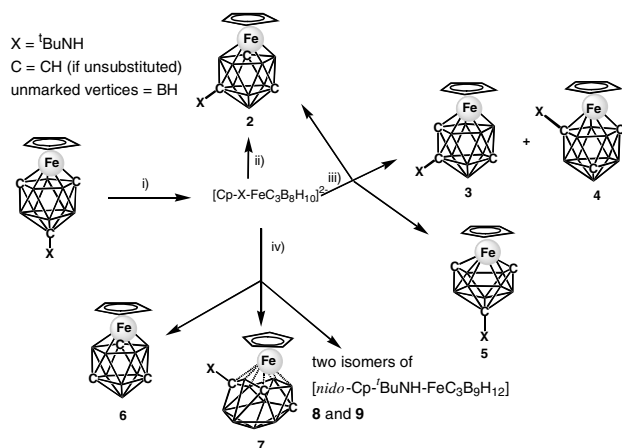
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New syntheses from dianion **1**²⁻ are outlined in Scheme 1. The wine-red **1**²⁻ (generated in situ in path (i)) can be converted via oxidation into three 12-vertex mixed-sandwich ferratricarbollide complexes, depending on reaction conditions. Thus, the oxidation by CuCl₂ (path (ii)) leads to cage closure and results in the isolation of [2-Cp-8-^tBuNH-*closo*-2,1,8,10-FeC₃B₈H₁₀] (**2**) (yellow, yield 82%).

Compound **2** (yield 32%) was also generated via air oxidation (path iii), but in this case was accompanied by other two isomers, [2-Cp-1-^tBuNH-*closo*-2,1,4,12-FeC₃B₈H₁₀] (**3**) (yellow, yield 8%) and [2-Cp-1-^tBuNH-*closo*-2,1,7,10-FeC₃B₈H₁₀] (**4**) (yellow-orange, yield 2%), and the 11-vertex species [1-Cp-10-^tBuNH-*closo*-1,2,3,10-FeC₃B₇H₉] (**5**) (violet, yield 9%).

Another variation of the syntheses based on anion **1**²⁻ emerges from its reaction with Me₂S · BH₃ (THF, 60 °C, see path iv). The reaction generated complexes [2-Cp-*closo*-2,1,8,10-FeC₃B₈H₁₁] (**6**) (yellow, yield 6%) and [4-Cp-1-^tBuNH-*closo*-4,1,6,8-FeC₃B₉H₁₁] (**7**) (orange, yield 11%) along with two isomeric 13-vertex



Scheme 1. Conversions of the $[nido-Cp-{}^tBuNH-FeC_3B_8H_{10}]^{2-}$ dianion (**1**²⁻) (i) Na, THF; (ii) CuCl₂, THF, r.t. (yield 82%); (iii) O₂ (air), THF, r.t.; (iv) Me₂S·BH₃, THF, 60 °C.

compounds of general *nido* structure $[Cp-{}^tBuNH-FeC_3B_9H_{12}]$ (yellow compounds **8** and **9**, (yields 13% and 27%, respectively).

Compound **2** and **3** are new cage isomers of the aminosubstituted 12-vertex *closo* ferratricarbollide family [3], so far single compounds containing only one cage carbon vertex next to the Fe-centre, while complex **4** is a

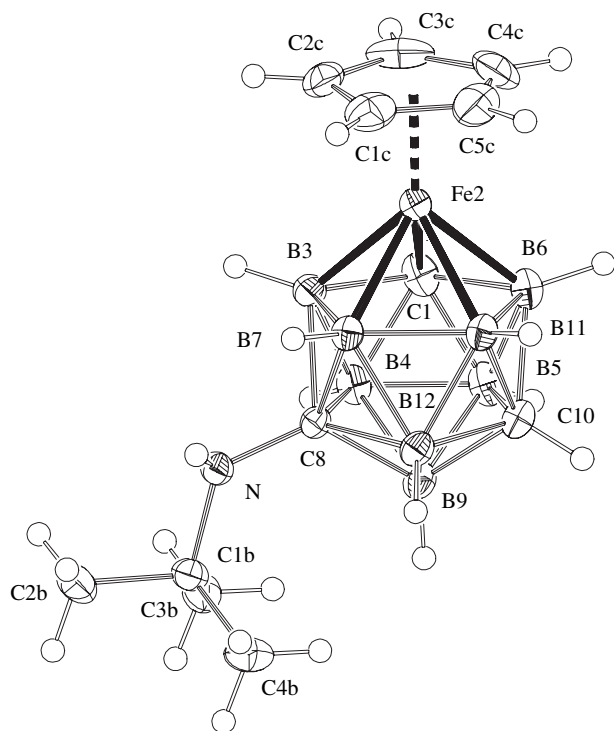


Fig. 1. ORTEP representation of the molecular structure of $[2-Cp-8-{}^tBuNH-2,1,8,10-FeC_3B_8H_{10}]$ (**2**), thermal ellipsoids are drawn with 50% probability level. Selected interatomic distances (Å) and angles (°): Fe2–C1 2.0305(15); Fe2–B3 2.0147(18); Fe2–B6 2.0142(19); Fe2–B7 2.0450(16); Fe2–B11 2.0415(16); B3–C1–B6 112.35(10); C8–B9–C10 102.68(11).

positional isomer of the earlier reported complexes of structure $[2-Cp-10-X-closo-2,1,7,10-FeC_3B_8H_{10}]$ [4]. Complex **5** contains a *closo* 11-vertex cage which is isomeric to that reported for the parent $[1-Cp-1,2,3,4-FeC_3B_7H_{10}]$ compound [5]. Compound **6** is another, so far unreported, symmetrical isomer of the parent $[CpFeC_3B_8H_{11}]$ series³ that normally results upon abstraction of {^tBuNH} moiety from complex **2**. Complex **7** is the first representative of the 13-vertex *closo* metallatricarbaborane family.

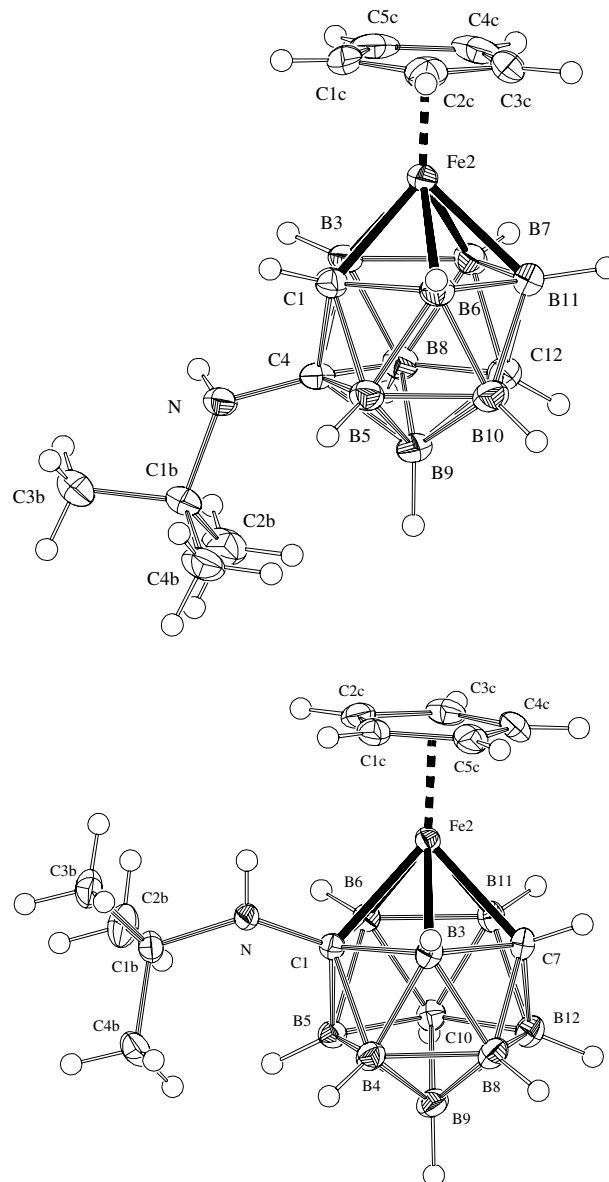


Fig. 2. ORTEP representation of the molecular structures of two minor isomers $[2-Cp-4-{}^tBuNH-2,1,4,12-FeC_3B_8H_{10}]$ (**3**) (top) and $[2-Cp-1-{}^tBuNH-2,1,7,10-FeC_3B_8H_{10}]$ (**4**) (bottom), thermal ellipsoids are drawn with 50% probability level. Selected interatomic distances (Å) and angles (°) for **3**: C1–Fe2 1.985(3); C4–B8 1.729(5); C4–B5 1.7042; B3–C1–B6 113.7(1); B6–B11–B7 107.4(1); B8–C12–B10 114.5(9); C1–N–C4 125.6(5); for **4**: C1–Fe2 2.0687(13); C7–Fe2 2.032(1); C1–Fe2–C7 83.94(6); B3–C1–B6; C1–B3–C7 105.19(10).

As shown in Figs. 1–4, the structures of complexes 2–7 were determined by an X-ray diffraction study [6] and all compounds discussed above were characterized by NMR and mass spectroscopy (for selected NMR characteristics see [7], full data sets will be published in a full paper). More detailed structural studies on the *nido*-13-vertex complexes 8 and 9 are in progress. We are aware of the fact that the work may raise some cluster-numbering problems [8].

We have demonstrated that new synthetic strategies based on reductive opening of *closo* skeletons may be a multipurpose tool in the hands of a chemist. The open-structured transient intermediate (see compound 1^{2-} in this case) can be “zipped down” again via oxidation to generate new cage isomers that are otherwise unavailable by conventional methods. This is evidently a consequence of total reorganization of cluster carbons within the cluster core in the intermediate. Isolation of ferratricarbaborane cages larger and smaller than 12-vertices via cage expansion and contraction in the

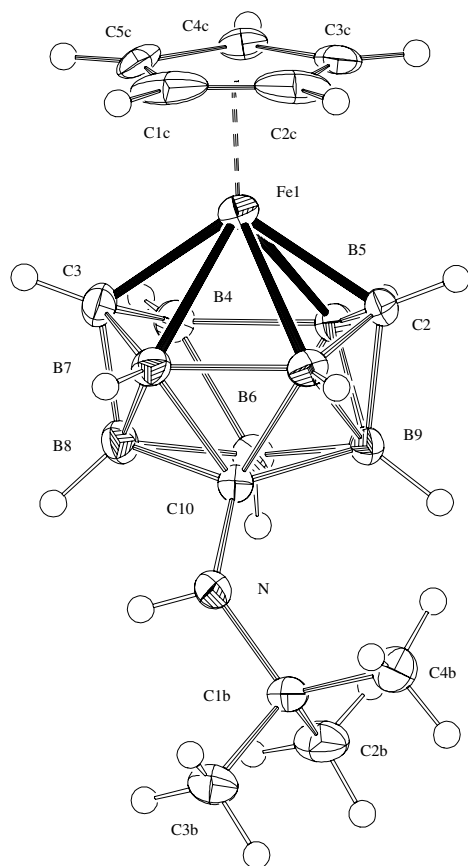


Fig. 3. ORTEP representation of the molecular structure of the 11 vertex [1-Cp-10-*t*BuHN-1,2,3,10-FeC₃B₇H₉] (**5**), thermal ellipsoids are drawn with 50% probability level. Selected interatomic distances (Å) and angles (°): Fe1–C2 1.9776(18); Fe1–C3 1.970(2); Fe1–B4 2.255(2); Fe1–B5 2.261(2); Fe1–B6 2.236(2); Fe1–B7 2.216(2); C10–B9 1.689(3); C10–B11 1.829(3); C10–B6 1.785(3); C2–Fe1–C3 111.65(8); B8–C10–B9 114.49(14).

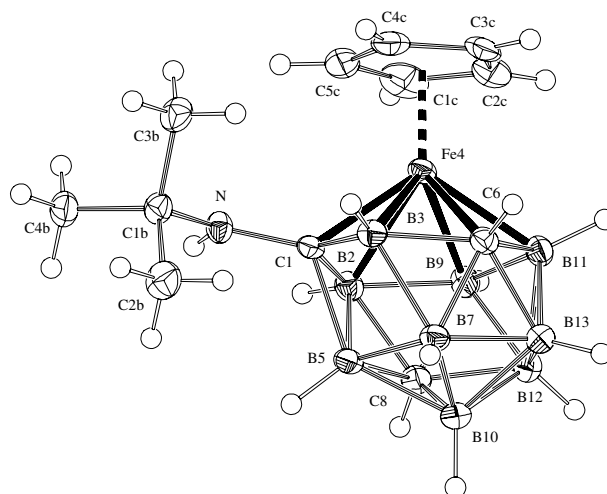


Fig. 4. ORTEP representation of the molecular structure of the 13-vertex [4-Cp-1-*t*BuNH-4,1,6,8,-FeC₃B₉H₁₁] (**7**), thermal ellipsoids are drawn with 50% probability level. Selected interatomic distances (Å) and angles (°): Fe4–C1 2.0893(15); Fe4–B2 2.1702(16); Fe4–C6 2.1011(15); C1–B2 1.572(2); C1–B3 1.534(2); C1–B5 1.809(2); B2–B5 1.964(3); B3–B7 1.847(2); B5–B7 1.850(2); B5–C8 1.777(2); C1–Fe4–B11 109.77(6); B2–C1–B3 120.50(12); B2–B9–B11 116.95(12), Fe4–C_{CP} (mean plane centroid) 1.6795(4), Fe4–(mean hexagonal plane centroid) 1.6775(3). Square open face distances: C1–B7 2.768(2); B3–B5 2.152(2).

transient 1^{2-} demonstrates further utility of these synthetic approaches. More detailed investigations around this type of chemistry are in progress in our laboratories.

Acknowledgements

We thank to Dr. Z. Plzák for mass spectra from the Institute of Inorganic Chemistry for mass spectra and Prof. A.R. Kudinov from N. Nesmeyanov Institute of Organoelement Compounds, R.A.S., Moscow, Russian Federation for his help with assignment of ¹¹B NMR shifts of **6**. The work was supported by the Ministry of Education of the Czech Republic (Project LC523) by GA ČR (Grant No. 203/05/2646).

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- [6] Crystallographic data for the structural analyses have been deposited in the Cambridge Crystallographic Data Centre, CCDC 252879, 260054, 252881, 252880, and 252883 for compounds **2**, **3**, **4**,

5, and **7**, respectively. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge CB2 1EY, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

- [7] $^{11}\text{B}\{^1\text{H}\}$ NMR (CDCl_3): **2**: $\delta = -3.1$ (B6), -4.0 (B11), -11.3 (B3,7), -14.6 (B9,12), -22.9 (B5), -25.7 (174) (B4); **3**: $\delta = -6.5$ (B11), -8.7 (B3), -12.7 (B7), -15.2 (B9), -16.0 (B6), -19.7 (B5), -23.1 (B8), -23.4 (B10); **4**: $\delta = -7.4$ (B3), -9.0 (B6), -14.0 (B11), -16.2 (B9), -18.6 (B5), -21.7 (B4), -24.8 (B12), -25.1 (B8); **5**: $\delta = -1.1$ (B8,9), -18.1 (B4,5,6,7), -22.3 (B11); **6**: $\delta = -7.0$ (B3,6), -9.1 (B7,11), -15.4 (B9), -17.8 (B12), -24.3 (B4,5); **7**: $\delta = 0.6$, -11.0 , -12.7 (2B), -13.9 , -15.6 (2B), -21.0 , -27.8 (still unassigned); **8**: $\delta = -5.2$, -7.1 (2B), ca. -8.5 (1B), -13.5 , -16.1 , -18.5 , -22.3 , -23.3 , -24.9 (still unassigned); **9**: $\delta = -4.9$, -7.2 (4B), -10.2 (2B), -18.9 , -21.6 , -44.0 (still unassigned). ^1H NMR (CDCl_3): **2**: $\delta = 4.6$ (5H, Cp), 2.0 (2H, cage CH), 1.14 (9H, ^tBu); **3**: $\delta = 4.59$ (5H, Cp), 3.4 (1H, cage CH), 2.69 (1H, cage CH), 1.14 (9H, ^tBu); **4**: $\delta = 4.63$ (5H, Cp), 2.04 (1H, cage CH), 1.91 (1H, cage CH), 1.14 (9H, ^tBu); **5**: $\delta = 4.50$ (5H, Cp), 2.49 (2H, cage CH), 0.96 (9H, ^tBu); **6**: $\delta = 4.64$ (5H, Cp), 1.94 (2H, cage CH), 1.25 (1H, cage CH); **7**: $\delta = 4.60$ (5H, Cp), 2.0 (2H, cage CH), 1.14 (9H, ^tBu); **8**:

$\delta = 4.60$ (5H, Cp), 2.21 (1H, cage CH), 1.25 (1H, cage CH), 1.14 (9H, ^tBu), -0.34 (1H, μH); **9**: $\delta = 4.34$ (5H, Cp), 1.60 (1H, cage CH), 1.45 (9H, ^tBu), 1.41 (1H, cage CH), -6.29 (1H, $\mu\text{Fe-H-B}$). MS (70 eV, EI): **2**: $m/z = 327$ (55%) $[\text{M}]^+$, 326 (95%) $[\text{M}^+ - \text{H}]$, 311 (100%) $[\text{M}^+ - \text{CH}_3]$ $[\text{M}]^+$, **3**: $m/z = (55\%)$ $[\text{M}]^+$, 326 (98%) $[\text{M}^+ - \text{H}]$, 311 (100%) $[\text{M}^+ - \text{CH}_3]$ $[\text{M}]^+$, 255 (65%) $[\text{M}^+ - \text{NHC}_4\text{H}_9 - \text{H}]$, **4**: $m/z = 327$ (62%) $[\text{M}]^+$, 326 (92%) $[\text{M}^+ - \text{H}]$, 311 (100%) $[\text{M}^+ - \text{CH}_3]$, 255 (22%) $[\text{M}^+ - \text{NHC}_4\text{H}_9 - \text{H}]$, **5**: $m/z = 316$ (10%) $[\text{M}]^+$, 314 (100%) $[\text{M}^+ - 2\text{H}]$, **6**: $m/z = 256$ (57%) $[\text{M}]^+$, 255 (100%) $[\text{M}^+ - \text{H}]$, **7**: $m/z = 340$ (23) $[\text{M}]^+$, 339 (56%) $[\text{M}^+ - \text{H}]$, 323 (100%) $[\text{M}^+ - \text{CH}_3 - \text{H}]$, **8**: $m/z = 341$ (20%) $[\text{M}]^+$, 283 (65%) $[\text{M}^+ - \text{C}_4\text{H}_9 - \text{H}]$, 282 (65%) $[\text{M}^+ - \text{C}_4\text{H}_9 - 2\text{H}]$.

- [8] For the numbering of the 12- and 13-vertex *closo* cages encountered in this work, the original, rather inconvenient IUPAC “C-numbering system”, was still employed (see [2]). More transparent appears to be the “Fe-numbering” (see [3]), according to which some compounds should be formulated as follows: [1-Cp-12- $^t\text{BuNH-closo-1,2,4,12-FeC}_3\text{B}_8\text{H}_{10}$] (**1**), [1-Cp-7- $^t\text{BuNH-closo-1,2,7,9-FeC}_3\text{B}_8\text{H}_{10}$] (**2**), [1-Cp-8- $^t\text{BuNH-closo-1,2,8,10-FeC}_3\text{B}_8\text{H}_{10}$] (**3**), [1-Cp-2- $^t\text{BuNH-closo-1,2,4,10-FeC}_3\text{B}_8\text{H}_{10}$] (**4**), [1-Cp-*closo-1,2,7,9-FeC}_3\text{B}_8\text{H}_{11}] (**6**), and [1-Cp-2- $^t\text{BuNH-closo-1,2,6,9-FeC}_3\text{B}_9\text{H}_{11}$] (**7**).*