

Communication

8-Dioxane ferra(III) bis(dicarbollide): A paramagnetic functional molecule as versatile building block for introduction of a Fe(III) centre into organic molecules

Jaromír Plešek^a, Bohumír Grüner^{a,*}, Jan Macháček^{a,b,c}, Ivana Císařová^b, Josef Čáslavský^c

^a Institute of Inorganic Chemistry, v.v.i., Academy of Sciences of the Czech Republic, Area of Research Institutes, Husinec-Řež 1001, 25068 Řež, Czech Republic

^b Department of Inorganic Chemistry, Faculty of Natural Sciences of Charles University, Hlavova 2030, 128 42, Prague 2, Czech Republic

^c Institute of Chemistry and Technology of Environmental Protection, Technical University, Brno, Purkyňova 118, 612 00 Brno, Czech Republic

Received 8 June 2007; received in revised form 17 July 2007; accepted 18 July 2007

Available online 27 July 2007

Abstract

The synthesis of a new, paramagnetic *closo*-[(8-(-CH₂CH₂O)₂-1,2-C₂B₉H₁₀)(1',2'-C₂B₉H₁₁)-3,3'-Fe]⁰ (**3**) is reported. This compound can serve as a versatile building block for construction of both anionic and zwitterionic derivatives, as exemplified by the synthesis of a series of compounds of general formula *closo*-[(8-X-(CH₂CH₂O)₂-1,2-C₂B₉H₁₀)(1',2'-C₂B₉H₁₁)-3,3'-Fe], bearing organic end groups (X = NC₅H₅ (**4**), (C₆H₅)₃P (**5**), OH (**6**), and 2-O(1-CH₃O-C₆H₄) (**7**)) attached to the cluster by a diethyleneglycol spacer. Molecular structures of **3**, **4**, **5** and **7** were determined by single-crystal X-ray diffraction analysis and by the long-time neglected method of paramagnetic, high field NMR (¹H, ¹³C and ¹¹B) spectroscopy.

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Keywords: Boranes; Carboranes; Dicarbollides; X-ray diffraction; NMR

Since their discovery by Hawthorne and Andrews [1] four decades ago, iron (**1**) and cobalt (**2**) bis(dicarbollide)(1-) anions [(1,2-C₂B₉H₁₁)₂-3-M(III)]⁻ have received considerable interest due to their close similarities to metallocenes, ionic character, high thermal, chemical and radiolytical stability [2,3]. However, only little attention has so far been paid to synthetic approaches leading to their modification by reactive groups that allow for their easy introduction as building blocks into larger molecules and materials. This applies especially to the iron sandwich anion **1** [2], particularly due to the rather underestimated possibility of the reliably characterization of such compounds by NMR spectroscopic techniques. Several years ago, we reported on the dioxane-**2** derivative [4]. One unique feature of this compound is the readiness of ring cleavage by a variety of nucleophiles [5–7]. This compound

proved to serve as the most versatile reagent in the chemistry of the diamagnetic complex **2** and opened up synthetically feasible routes to designed ionic molecules for many particular applications, such as efficient extraction agents for lanthanides and actinides [7–10] additives to conducting polymers [11], use in biomedicine as HIV protease inhibitors [12], labelling of DNA fragments [13], UV, IR and electrochemical, UV and IR markers [14], etc. Herein, we report in a preliminary fashion further a useful extension of this chemistry leading to the derivatization of the sandwich **1**, together with a notice on the possibility of convenient characterization of products by paramagnetic ¹¹B and ¹H NMR spectroscopy.

Heating of the Cs⁺ salt of anion **1** in an excess of dioxane, and in the presence of 2.05 molar equivalents of dimethyl sulphate as activator, leads to a dark violet zwitterionic compound *closo*-[(8-(-CH₂CH₂O)₂-1,2-C₂B₉H₁₀)(1',2'-C₂B₉H₁₁)-3,3'-Fe]⁰ (**3**). Compound **3** is formed as the single neutral product and can be easily isolated from

* Corresponding author. Tel.: +420 2 6617 3120; fax: +420 2 2094 0161.
E-mail address: gruner@iic.cas.cz (B. Grüner).

the mixture of ionic side products in an average yield of 60%. Compound **3**, characterized by melting points, mass spectrometry [15], HPLC [16] and X-ray crystallography [17] (see Fig. 1 and the Supplementary material), can be used to introduce easily the very stable paramagnetic, iron (III)-centred anion **1** into various organic molecules. In general, ring-cleavage reactions of **3** with uncharged N or P-nucleophiles (see Scheme 1) result in the formation of betain-type zwitterions. If the ring opener is an anion (*O,S*-nucleophiles), ionic species are produced. Thus, dioxane ring cleavage by amines and phosphines in toluene/DME solutions give rise to the corresponding ammonium or phosphonium derivatives (see Scheme 1 and the Supplementary material). As an example we report here two structurally characterized compounds with pyridinium (**4**) and triphenyl phosphonium (**5**) end groups obtained in essentially quantitative yields 96% and 93%, respectively. The crystallographically determined molecular structures [17] of **4** and **5** are presented in Figs. 2 and 3. In both structures, the cage carbon atoms, which are in pentagonal planes adjacent to the iron atom, adopt a staggered (*transoid*) conformation, whereas the arrangement in the starting compound **3** is closer to being eclipsed (*cisoid*).

Further useful applications of the chemistry of **3** consist in the use of alcoholates or phenolates as nucleophiles (see also Scheme 1 and the Supplementary material). Thus, the hydroxy derivative (Na**6**) can be prepared in 68% yield, by reaction in excess dioxane of **3** with a 10% aqueous solution of NaOH followed by dilution with water, dioxane evaporation, acidification, extraction into ether and chromatography. A representative of a phenoxy end group derivative, a guaiacolyl derivative (Na**7**), was obtained in 81% yield. The molecular structure of the sodium salt of

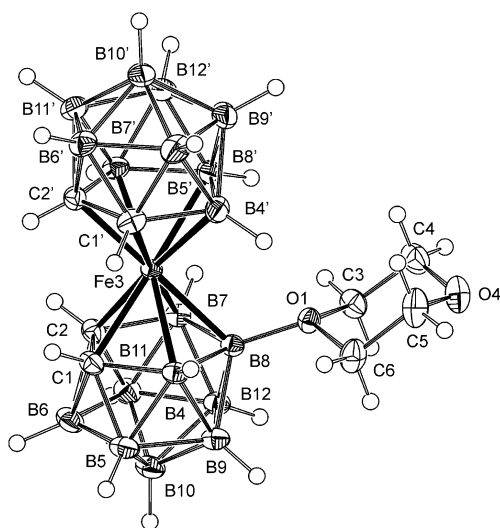
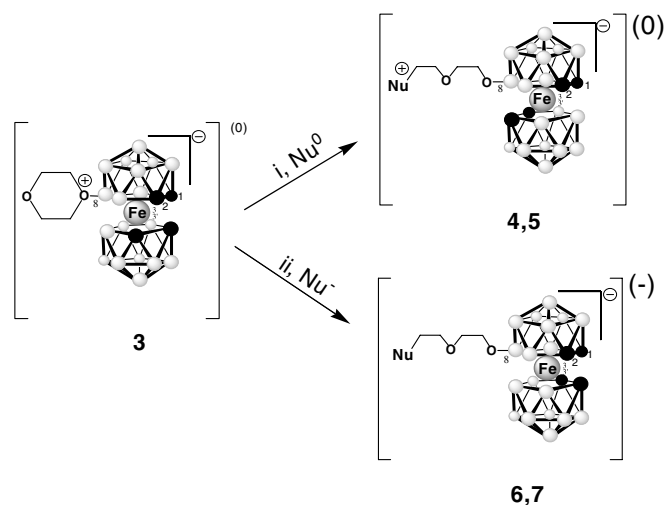


Fig. 1. ORTEP representation of the molecular structure of (**3**), thermal ellipsoids are drawn with 50% probability level. Selected interatomic distances (Å) and angles (°): Fe(3)–C(1) 2.0828(14); Fe(3)–C(2) 2.0888(15); Fe(3)–B(4) 2.1342(17); Fe(3)–B(7) 2.1449(15); Fe(3)–B(8) 2.1457(15); C(1)–C(2) 1.613(2); O(1)–B(8) 1.5199(18); O(1)–B(8)–B(4) 123.64(11); O(1)–B(8)–B(7) 122.58(11); Fe(3)–B(8)–O(1) 115.17(9).



Scheme 1. Conversions of the zwitterion (**3**) (i) toluene-DME, 80 °C (yields 96% and 93%); (ii) NaH, toluene-DME (yields 68% and 81%).

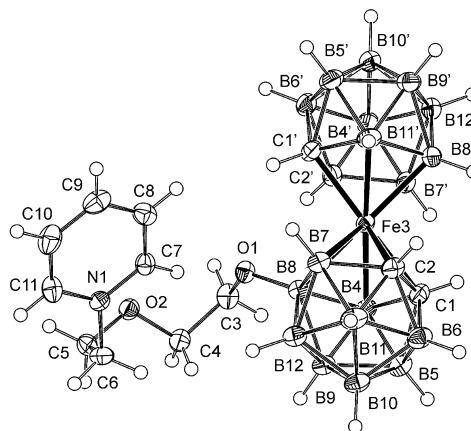


Fig. 2. ORTEP representation of the molecular structure pyridinium derivative **4** thermal ellipsoids are drawn with 50% probability level. Selected interatomic distances (Å) and angles (°): Fe(3)–C(1) 2.0705(14); Fe(3)–C(2) 2.0670(15); Fe(3)–B(4) 2.1347(15); Fe(3)–B(7) 2.1285(18); Fe(3)–B(8) 2.1675(17); B(8)–O(1) 1.4163(19); B(4)–B(8)–O(1) 127.76(12); B(7)–B(8)–O(1) 120.19(12).

7, determined by single-crystal X-ray diffraction [17], is presented in Fig. 4. An interesting feature is the tight coordination by oxygen atoms of the diethyleneglycol and guaiacol moiety towards the Na⁺ cation, and the B–H → Na interaction. The coordination sphere is completed by water molecule into shape of pentagonal pyramid. Probably due to the presence of the B–H → Na interaction, the position of cage carbon atoms is eclipsed (*cisoid*) in this structure. Compounds **4–7** are new *exo*-skeletal derivatives of the ferra dicarbollide family [2] containing end groups bonded to the cluster *via* a longer spacer.

The first characterization of the parent ion **1** by ¹¹B NMR spectroscopy was reported as early as in 1974 [18]. Apart from a few exceptions, solely the ¹¹B NMR data are presented [19,20], and there is almost no mention of the use of ¹H and ¹³C spectroscopy in the paramagnetic

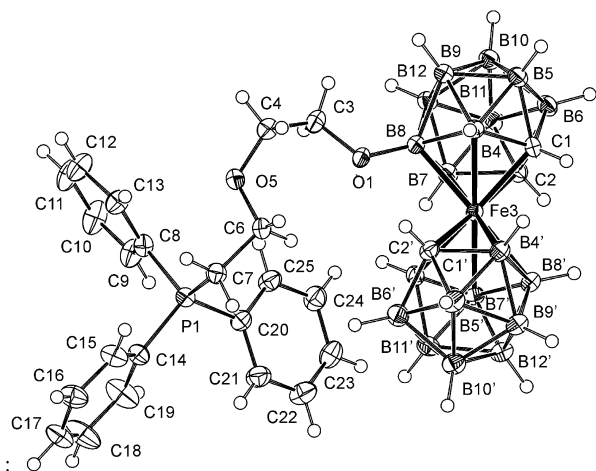


Fig. 3. ORTEP representation of the molecular structure of **5**, thermal ellipsoids are drawn with 50 % probability level. Selected interatomic distances (Å) and angles (°): Fe(3)–C(1) 2.0775(17); Fe(3)–C(2) 2.0794(17); Fe(3)–B(4) 2.1214(19); Fe(3)–B(7) 2.1269(19); Fe(3)–B(8) 2.1481(19); O(1)–B(8) 1.417(2); B(4)–B(8)–O(1) 123.02(14); B(7)–B(8)–O(1) 124.92(14).

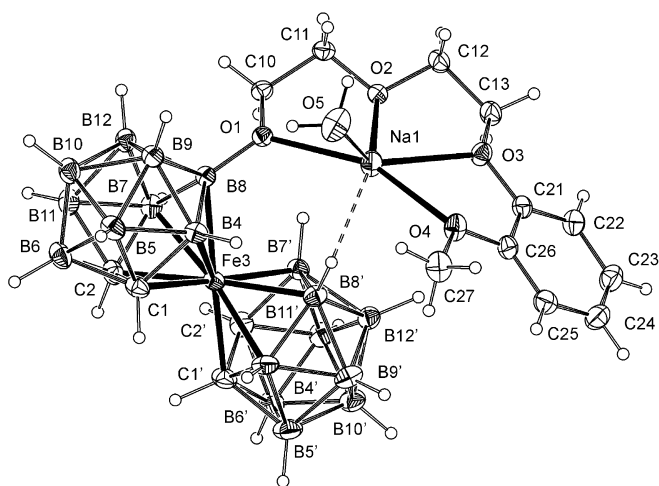


Fig. 4. ORTEP representation of the molecular structure of the Na⁺ complex of Na7, thermal ellipsoids are drawn with 50 % probability level. Selected interatomic distances (Å) and angles (°): Na(1)–O(1) 2.3982(17); Na(1)–O(2) 2.3819(15); Na(1)–O(3) 2.4157(17); Na(1)–O(4) 2.4403(18); Na(1)–O(5) 2.346(3); Na(1)–H(8') 2.1900; O(1)–Na(1)–H(8') 84.00; O(4)–Na(1)–H(8') 74.00; O(5)–Na(1)–H(8') 95.00; O(1)–Na(1)–O(5) 83.64(9); O(2)–Na(1)–O(5) 122.15(9); O(3)–Na(1)–O(5) 125.46(10); O(4)–Na(1)–O(5) 88.83(9); O(1)–Na(1)–O(4) 155.70(6).

ferra bis(dicarbollide) derivative series. Now, we have found that the $^{11}\text{B}\{^1\text{H}\}$, ^{13}C and ^1H NMR spectra of compounds **3–7** can be easily measured (taking precautions about extensive spectral spans) and can be used for NMR characterization similarly as in the corresponding diamagnetic ion **2** series (for data and the assignments see the [Supplementary material](#)). For assignment of the $^{11}\text{B}\{^1\text{H}\}$ NMR resonances, the published scheme for the parent ion **1** [18] was used. This is further supported by the evident broadening of all the extremely high-field B(8,8') and B(4,7,4',7') resonances, belonging to atoms

adjacent to the iron(III) centre. These signals and those of B(6,6') in the lowest field are strongly temperature dependent, which further helps the assignment and seems to confirm previous considerations [18]. Unfortunately, no cross-peaks were observed in ^{11}B – ^{11}B COSY experiments, apparently due to fast relaxation times of all ^{11}B nuclei. The spectra of substituted derivatives **3–7** show symmetry splitting of each signal present in parent ion **1** into two peaks due to presence of two symmetrically inequivalent dicarbollide ligands (see Fig. 5). Noteworthy is the extreme upfield shift of the B(8) resonance in **3** (approx. 175 ppm as compared to **1**), caused by shielding due to B(8)–O⁽⁺⁾ oxonium atom. In contrast, for all other substituted derivatives **4–7**, a downfield shift of this signal is observed. The ^1H NMR spectra of compounds **3–7** exhibit appreciable paramagnetic shifts of all signals; most pronounced being the temperature dependent broad signal of CH protons found in the range of approx. 68 and 35 ppm. No apparent ^1H – ^1H coupling could be seen, probably as a consequence of decoupling by the unpaired electron and fast relaxation times. This complicates the assignment that could be made only tentatively by inter-comparison of a larger series of simple compounds differing only in end groups and upon the elimination of the BH signals using $^1\text{H}\{^{11}\text{B}\}$ and $^1\text{H}\{^{11}\text{B}(\text{selective})\}$ experiments. In contrast, the ^{13}C signals could be easily assigned, taking into account the extreme high-field CH-carborane shift (–442.8 for parent ion **1** and ranging from –323 to –535 ppm for compounds **3–7**). A more detailed assignment based on comparison with the results of chemical calculations will appear in a subsequent full paper.

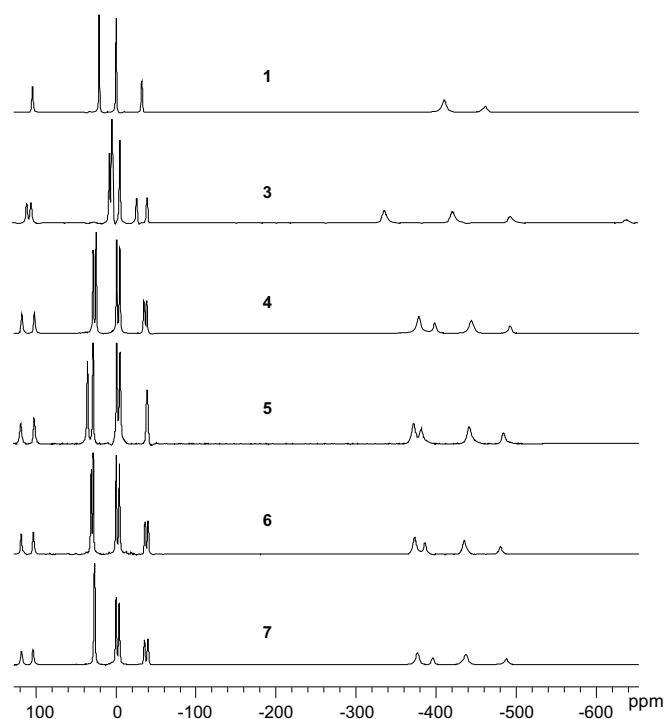


Fig. 5. $^{11}\text{B}\{^1\text{H}\}$ NMR spectra of the parent ion **1** and the derivatives **3–7**. Measured at 128 MHz in Acetone- d_6 at 295 K.

We can conclude that synthetic strategies based on ring-opening reactions of **3** may be a multi-purpose tool in the hands of a chemist. This exceptionally clean reaction opens the routes to a variety of more sophisticated products than just compounds **4–7** presented here, and could be used to generate novel, iron containing compounds otherwise unavailable by other conventional methods. In addition, we have shown that even the Fe(III) boron cluster sandwich derivatives can be easily investigated by NMR methods, which removes the main objections towards further more rapid developments in this area. More detailed studies of NMR properties are currently under investigation in our laboratories along with experiments leading to design and synthesis of new target compounds for applications in extraction science and biomedicine.

Acknowledgements

We thank to Prof. Z.J. Lesnikowski from Center of Medical Biology, Polish Academy of Sciences for promoting paramagnetic NMR measurements and helpful discussion and Dr. J. Fusek from the Institute of Inorganic Chemistry for NMR parameters. The work was partly supported by the Ministry of Education of the Czech Republic (Project LC 523 and Research Plans AV0Z40320502 and MSM0021620857), and Grant Agency of the Academy of Sciences of the Czech Republic (No. IAA400310613).

Appendix A. Supplementary material

CCDC 647876, 647877, 647878 and 647879 contain the supplementary crystallographic data for **3**, **4**, **5** and **7**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.07.026.

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- [15] Mp's (sealed capillaries, Koeffler stage) **3**: 180–183 °C, **4**: 181–182 °C, **5**: 197–199 °C, Na **6**: >360 °C, Na **7**: 234–236 °C; MS (ESI, negative): **3**: $m/z = 411.2$ (20%) $[M]^-$, 428 (100%) $[M + OH]^-$, **4**: $m/z = 490.2$ (100%) $[M]^-$, **5**: $m/z = 673.5$ (100%) $[M]^-$, Na **6**: $m/z = 428.1$ (100%) $[M]^-$, Na **7**: $m/z = 534.2$ (100%) $[M]^-$.
- [16] HPLC k' : (Separon SGX 4 × 250 mm ID, 3 mM Hexylamine Acetate in 58% aqueous CH₃CN, pH 6.0, 1 mL/min, detection DAD at 272 and 312 nm): **1**: 1.41, **3**: 8.99, **4**: 5.42, **5**: 23.13, Na **6**: 0.90, Na **7**: 2.32.
- [17] **Crystals structures**: The crystals of compounds of **3**, **4**, **5**, and Na **7** were measured on KappaCCD diffractometer with CCD area detector at 150(2)K, Mo K α radiation. Solutions: direct methods (SIR92) [21], refinements by full-matrix least squares based on F^2 (SHELXL97) the absorption was neglected. The hydrogen atoms were recalculated into idealised positions (riding model) and assigned temperature factors $\text{Hiso(H)} = 1.2\text{--}1.5 \text{ Ueq}(\text{pivot atom})$. The identification of C atoms in carborane cages were based on comparison of interatomic distances. The water molecule in Na **7** is disordered over two neighbouring (1.324 Å) positions, only this occupied by 70% is used for discussion. Crystal data for **3**: C₈H₂₉B₁₈FeO₂, monoclinic, space group $P2_1/c$; $a = 13.6840(3)$, $b = 10.2530(2)$, $c = 14.8720(2)$ Å, $\beta = 94.3540(11)^\circ$; $V = 2080.55(7)$ Å³; $Z = 4$; $\rho_{\text{calc}} = 1.302 \text{ Mg m}^{-3}$; $\mu = 0.728 \text{ mm}^{-1}$; 29458 diffractions, 4754 independent ($R_{\text{int}} = 0.029$), 278 parameters, $R_1 = 0.029$, wR_2 (all data) = 0.083, min./max. residual electron density $-0.30/0.270 \text{ eÅ}^{-3}$. Crystal data for **4**: C₁₃H₃₄B₁₈FeNO₂, triclinic, space group $P\bar{1}$; $a = 7.3330(2)$, $b = 12.8530(3)$, $c = 14.9820(3)$ Å, $\alpha = 68.7650(12)$, $\beta = 77.3950(14)$, $\gamma = 78.7530(13)^\circ$; $V = 1273.98(5)$ Å³; $Z = 2$; $\rho_{\text{calc}} = 1.269 \text{ Mg m}^{-3}$; $\mu = 0.607 \text{ mm}^{-1}$; 20378 diffractions, 5841 independent ($R_{\text{int}} = 0.026$), 332 parameters, $R_1 = 0.031$, wR_2 (all data) = 0.0917, min./max. residual electron density $-0.42/0.40 \text{ eÅ}^{-3}$. Crystal data for **5**: C₂₆H₄₄B₁₈FeO₂P, orthorhombic, space group $P2_12_12_1$; $a = 10.0060(1)$, $b = 16.7430(2)$, $c = 21.0080(2)$ Å; $V = 3519.48(6)$ Å³; $Z = 4$; $\rho_{\text{calc}} = 1.265 \text{ Mg m}^{-3}$; $\mu = 0.501 \text{ mm}^{-1}$; 64584 diffractions, 8054 independent ($R_{\text{int}} = 0.040$), 449 parameters, $R_1 = 0.0289$, wR_2 (all data) = 0.0779, min./max. residual electron density $-0.25/0.43 \text{ eÅ}^{-3}$. Crystal data for Na **7**: C₁₅H₃₈B₁₈FeNaO₅, monoclinic, space group $P2_1/c$; $a = 11.3720(2)$, $b = 26.0120(5)$, $c = 10.2470(2)$ Å, $\beta = 104.9460(12)^\circ$; $V = 2928.60(10)$ Å³; $Z = 4$; $\rho_{\text{calc}} = 1.297 \text{ Mg m}^{-3}$; $\mu = 0.558 \text{ mm}^{-1}$; 41006 diffractions, 5760 independent ($R_{\text{int}} = 0.046$), 371 parameters, $R_1 = 0.0376$, wR_2 (all data) = 0.1035, min./max. residual electron density $-0.29/0.31 \text{ eÅ}^{-3}$.
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