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03 May 2024

Accepted Manuscript

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Sergey A. Anufriev, Svetlana A. Erokhina, Kyrill Yu Suponitsky, Aleksei A. Anisimov, Julia N. Laskova, Ivan A. Godovikov, Fabrizia Fabrizi de Biani, Maddalena Corsini, Igor B. Sivaev, Vladimir I. Bregadze

Synthesis and Structure of Bis(Methylsulfanyl) Derivatives of Iron Bis(Dicarbollide)[1]

Sergey A. Anufriev,[1] Svetlana A. Erokhina,[1] Kyrill Yu. Suponitsky,[1] Aleksei A. Anisimov,[2] Julia N. Laskova,[1] Ivan A. Godovikov,[1] Fabrizia Fabrizi de Biani,[3] Maddalena Corsini,[3] Igor B. Sivaev,[1] Vladimir I. Bregadze[1]

[1] A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,

28 Vavilov Str., 119991, Moscow, Russia

[2] D.I. Mendeleev Russian Chemical Technological University,

9 Miusskaya Sq., 125047, Moscow, Russia

[3] Dipartimento di Biotecnologie, Chimica e Farmacia, Università degli Studi di Siena,

Via A. Moro 2, 53100 Siena, Italy

Abstract. Bis(methylsulfanyl) derivatives of iron(II) bis(dicarbollide) $[8,8'\text{-(MeS)}_2\text{-}3,3'\text{-Fe}(1,2\text{-}C_2B_9H_{10})_2]^{2-}$ ($\mathbf{4^{2-}}$), $[4,4'\text{-(MeS)}_2\text{-}3,3'\text{-Fe}(1,2\text{-}C_2B_9H_{10})_2]^{2-}$ ($\mathbf{5^{2-}}$), and $[4,7'\text{-(MeS)}_2\text{-}3,3'\text{-Fe}(1,2\text{-}C_2B_9H_{10})_2]^{2-}$ ($\mathbf{6^{2-}}$) were prepared by the treatment of the corresponding dimethylsulfonium derivatives **1**-**3** with potassium butylthiolate. Their oxidation by air in aqueous solution results in the corresponding derivatives of iron(III) bis(dicarbollide) $[8,8'\text{-(MeS)}_2\text{-}3,3'\text{-Fe}(1,2\text{-}C_2B_9H_{10})_2]^{-}$ ($\mathbf{7^{-}}$), $[4,4'\text{-(MeS)}_2\text{-}3,3'\text{-Fe}(1,2\text{-}C_2B_9H_{10})_2]^{-}$ ($\mathbf{8^{-}}$) and $[4,7'\text{-(MeS)}_2\text{-}3,3'\text{-Fe}(1,2\text{-}C_2B_9H_{10})_2]^{-}$ ($\mathbf{9^{-}}$). The structures of $(Bu_4N)_2[8,8'\text{-(MeS)}_2\text{-}3,3'\text{-Fe}(1,2\text{-}C_2B_9H_{10})_2]$ and $(Me_4N)[4,7'\text{-(MeS)}_2\text{-}3,3'\text{-Fe}(1,2\text{-}C_2B_9H_{10})_2]$ were determined through single-crystal X-ray diffraction. In the solid state, the rotation of the dicarbollide ligands with respect to each other is hampered due to formation of weak intramolecular CH···S(Me) hydrogen bonds between the ligands resulting in stabilization of *transoid*-conformation in the case of 8,8′-isomer and *gauche*-conformation in the case of 4,4'-

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and 4,7′-isomers. The synthesized bis(methylsulfanyl) derivatives of iron bis(dicarbollide) can be considered as a versatile platform for design of molecular switches.

1. Introduction

The decision of the Royal Swedish Academy of Sciences to award Jean-Pierre Sauvage, Sir James Fraser Stoddart and Bernard (Ben) L. Feringa the Nobel Prize in Chemistry 2016 "for the design and synthesis of molecular machines" was natural recognition of foremost importance of this area of research [1]. Moreover, this award brought none of the familiar controversies regarding whether the discovery honored was really chemistry (or, rather, biology or physics) because synthetic molecular machines are completely the creation of chemists which demonstrated imagination and considerable skill in the design and construction of synthetic (supra)molecular systems capable of performing mechanical movements in response to specific stimuli [2-6]. Based on the type of motion, molecular machines can be divided into two main types, that is, molecular motors and molecular switches. Molecular motors are molecular machines that are capable of unidirectional rotation motion by 360º powered by external energy input, whereas molecular switches are molecules or supramolecular complexes that can exist in two or more stable forms that differ in the mutual orientation of their components and can be converted from one state to another by various external stimuli such as heat, light, and chemical reagents, etc. [7]. Molecular switches are the main structural element of any molecular electronics devices, particularly molecular logic gates, where the combination of two or more molecular switches allows molecule to behavior like that of electronic logic gates, suggesting a basis for future nanosize computing devices [8].

Despite the significant progress in the synthesis and study of molecular switches, there are some problems caused by relatively low stability of many organic materials to atmospheric oxygen and moisture that stimulates the search for new types of compounds that can be used as

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versatile platforms in design of effective molecular switches. Therefore, there is growing interest in stable molecular switches based on metallocene complexes such as ferrocene or transition metal bis(dicarbollides) $[3,3'-M(1,2-C_2B_9H_{11})_2]^{n-}$ [9-12]. Unlike the cyclopentadienyl ligands, the dicarbollide ligands contain two carbon atoms and three boron atoms in its open pentagonal face that results in nonequivalence in energy of different rotamers. Preferability of varying conformations depends on the nature of the metal and its oxidation state. For examples, the *transoid* conformation with two pairs of carbon vertices reflected through a center of symmetry is the most preferable for nickel(III) bis(dicarbollide), whereas nickel(IV) bis(dicarbollide) prefers *cisoid* conformation (rotation angle 36°) [13]. The interconversion of the *transoid-* and *cisoid-* geometries via controlled the change of the nickel oxidation state provides the basis for the controlled rotation of the dicarbollide ligands and makes the nickel bis(dicarbollide) moiety a promising module for design of rotation molecular switchers [10,11]. However, rather low rotation barrier (~ 8 kJ/mol) between the *transoid-* and *gauche-*rotamers reduces the efficiency of the redox molecular switches based on the nickel bis(dicarbollide) moiety [14,15]. Therefore, an additional stabilization of individual rotamers of transition metal bis(dicarbollide) complexes is very important. Such stabilization can be achieved through the introduction of substituents which are able to form intramolecular hydrogen bonds between the dicarbollide ligands. It was found that the effective stabilization of the *transoid* conformation due to formation of the intramolecular hydrogen bonds $C_{carb}H\cdots XB$ (X = Cl, Br, I) between the ligands, can be achieved by introduction of halogen atoms at positions 8 and 8' of cobalt [16-18] and iron [19-20] bis(dicarbollides). Recently we demonstrated that stabilization of definite rotamers of cobalt bis(dicarbollides) can be reached via introduction of the methylsulfanyl substituents that results in formation of the intramolecular $C_{carb}H\cdots S(Me)B$ hydrogen bonds [21]. The addition of an external complexing metal M* results in the rupture of the weak hydrogen bonds in favor of formation of stronger $M^*\cdots S(Me)B$ coordination bonds leading to the turn of the dicarbollide

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ligands [22]. Therefore, the methylsulfanyl derivatives of cobalt bis(dicarbollide) can be considered as a versatile platform for design of molecular switches.

In this contribution we report synthesis of a series of the *B*-methylsulfanyl derivatives of iron bis(dicarbollide) $[X,Y'-(MeS)_2-3,3'-Fe(1,2-C_2B_9H_{10})_2]^{n-}$.

2. Results and Discussion

In contrast cobalt bis(dicarbollide) [21], our attempt to prepare methylsulfanyl derivatives of iron bis(dicarbollide) by direct reactions of iron salts with the corresponding deprotonated methylsulfanyl derivatives of *nido*-carborane were unsuccessful. Therefore, we proposed another synthetic scheme based on demethylation of known dimethylsulfonium derivatives of iron(II) bis(dicarbollide) (Figure 1).
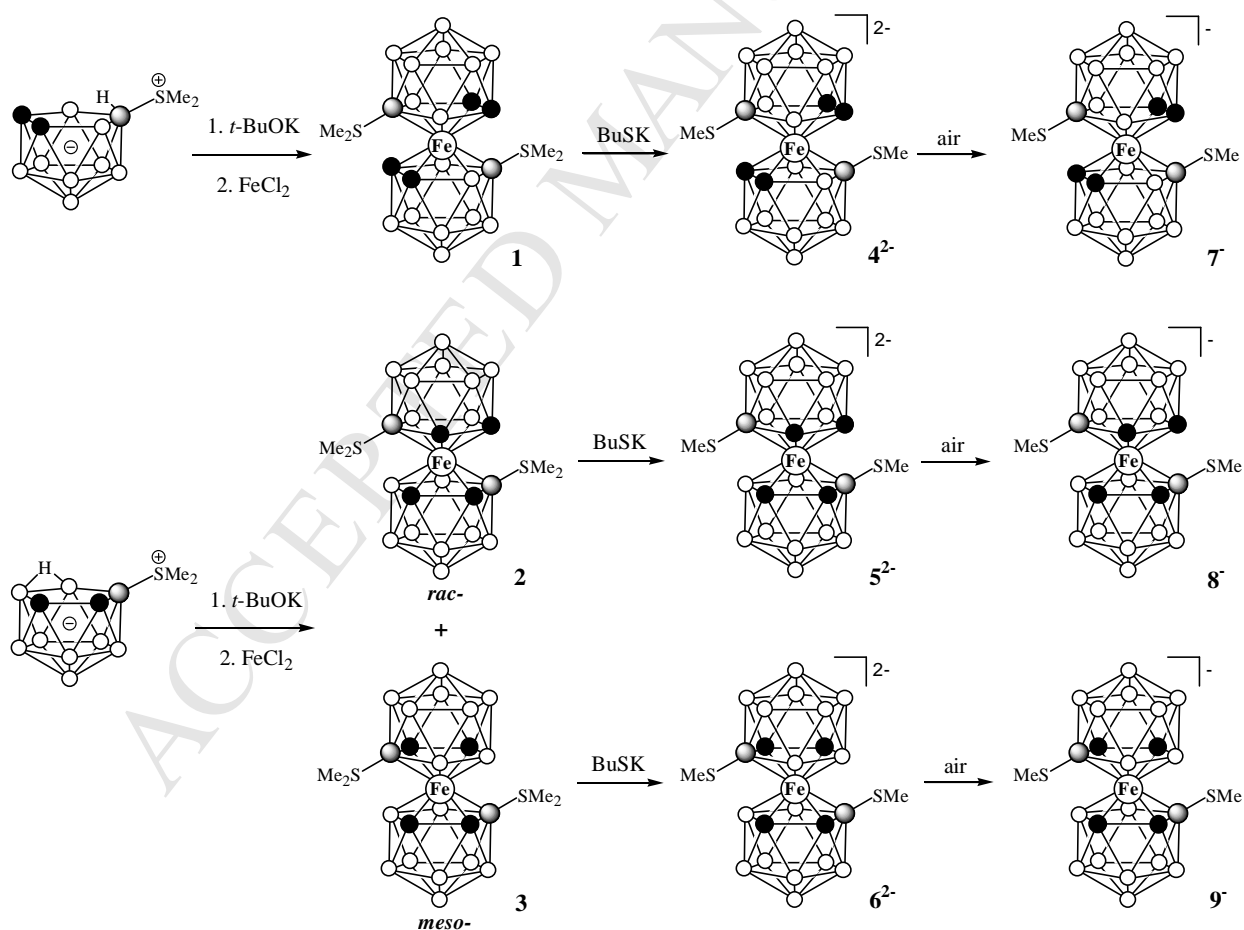

Figure 1. Scheme of synthesis of bis(methylsulfanyl) derivatives of iron bis(dicarbollide) (for mutial orientation of the dicarbollide ligands see Figs. 2, 4 and 5).

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The symmetrically substituted 8,8'-dimethylsulfonium derivative of iron(II) bis-(dicarbollide) [8,8'-(Me$_2$S)$_2$-3,3'-Fe(1,2-C$_2$B$_9$H$_{10}$)$_2$] (**1**) was prepared in 62 % yield by non-aqueous method using anhydrous FeCl$_2$ and *t*-BuOK as a base. This approach has advantages of simplicity and higher yield of the goal product in comparison with the described in the literature aqueous method [23].

The same approach was used for synthesis of asymmetrically substituted 4,8'-dimethylsulfonium derivative of iron(II) bis(dicarbollide) [*rac*-4,4'-(Me$_2$S)$_2$-3,3'-Fe(1,2-C$_2$B$_9$H$_{10}$)$_2$] (**2**) and [*meso*-4,7'-(Me$_2$S)$_2$-3,3'-Fe(1,2-C$_2$B$_9$H$_{10}$)$_2$] (**3**). The diastereomers were separated due to their different solubility in dichloromethane and purified by column chromatography on silica. This approach is superior the earlier described method using pre-synthesized [FeCl$_2$(THF)$_2$] complex [24] due to more convenient purification procedure and higher yields.

The partial demethylation of the dimethylsulfonium groups in compounds **1**-**3** was performed using *n*-BuSK in THF (Figure 1). The similar approach was used earlier for partial demethylation of dimethylsulfonium derivatives of *closo*-decaborate [25] and *closo*-dodecaborate [26] anions as well as some metallacarboranes [27,28]. The obtained bis(methylsulfanyl) derivatives of iron(II) bis(dicarbollide) **4**-**6** were isolated as the tetrabutylammonium salts. Despite the fact that iron(II) bis(dicarbollide) is diamagnetic the ^{11}B NMR spectra of compounds **4**-**6** contain very broadened signals and are not informative. The solid state structure of (Bu$_4$N)$_2$[8,8'-(MeS)$_2$-3,3'-Fe(1,2-C$_2$B$_9$H$_{10}$)$_2$] ((Bu$_4$N)$_2$[**4**]) was determined by single crystal X-ray diffraction. Similarly to the corresponding derivative of cobalt(III) bis(dicarbollide), the dicarbollide ligands in **4**$^{2-}$ adopt *transoid* configuration stabilized by four (two pairs) intramolecular CH···S contacts between the dicarbollide ligands (Figure 2). The structure of **4**$^{2-}$ is significantly different from the structure of the corresponding dimethylsulfonium derivative **1**, where the dicarbollide ligands adopt *gauche* conformation due

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to two longer CH···S contacts (2.91 Å) between the ligands [23]. This difference can be explained by availability of two lone electron pairs for intramolecular bonding in the MeS substituent, whereas the Me_2S substituent has only one free electron pair and is unable to form hydrogen bonds with both CH groups of the opposite dicarbollide ligand.

To confirm existence of the observed intramolecular CH···S interactions, we have carried out quantum chemical calculations at PBE0/6-311G(df,pd) level of theory followed by topological analysis of calculated electron density and energy estimation [29-32]. It was shown that such procedure provides reliable results for variety of nonbonded inter-, and intramolecular interactions [33,34]. The GAUSSIAN program was used for calculation [35]. The optimization leads to slightly more symmetrical structure: all S···H contacts are equal (2.74 Å). Experimental values of S···H distances are slightly different (see capture to Fig. 2) that can be attributed to the crystal packing effect. As expected, four bond critical points (BCP) indicating the presence of attractive interactions (CH···S) are observed. Energy of each interaction is 1.8 kcal/mol.
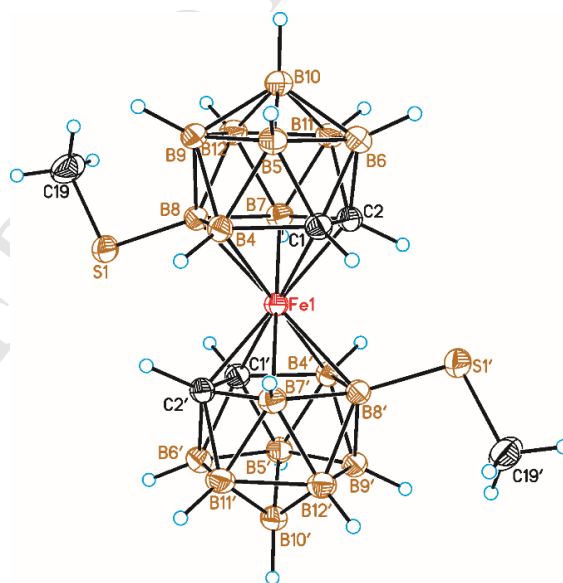

Figure 2. General view of the structure **4²⁻** with the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Shortest C-H···S contacts are C1-H1···S1' (2.82 Å), C2-H2···S1' (2.69 Å), and two symmetrically equivalent C1'-H1'···S1 and C2'-H2'···S1.

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The iron(II) bis(dicarbolides) **4**-**6** are easily oxidized by air in aqueous solution to the corresponding iron(III) complexes **7**-**9** (Figure 1), which isolated as the tetramethylammonium salts. In spite of paramagnetic character of iron(III) bis(dicarbollide), compounds **7**-**9** were reliably characterized by NMR spectroscopy. The ^{11}B NMR chemical shift range from 120 to –530 ppm is rather typical for derivatives of iron(III) bis(dicarbollide). The spectral pattern of symmetrically substituted compound **7**⁻ is typical for the parent iron(III) bis(dicarbollide) [38] and its 8,8'-disubstituted derivatives [19,20,37,38], whereas the spectra of asymmetrically substituted compounds **8**⁻ and **9**⁻ are remarkably different from each other (Figure 3).
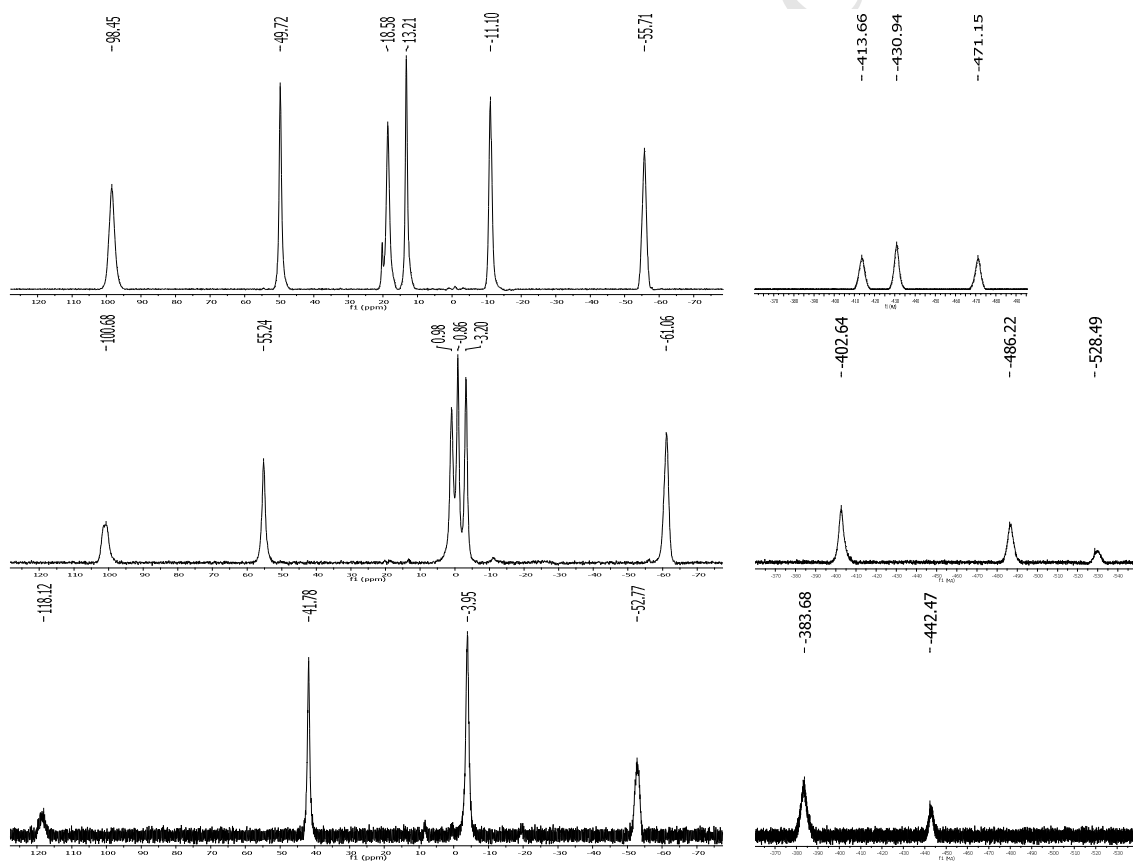
Figure 3. ^{11}B NMR spectra of [8,8'-(MeS)$_2$-3,3'-Fe[III](1,2-C$_2$B$_9$H$_{10}$)$_2$]⁻ (**7**⁻), [4,4'-(MeS)$_2$-3,3'-Fe[III](1,2-C$_2$B$_9$H$_{10}$)$_2$]⁻ (**8**⁻) and [4,7'-(MeS)$_2$-3,3'-Fe[III](1,2-C$_2$B$_9$H$_{10}$)$_2$]⁻ (**9**⁻) (from bottom to top) in acetone-d_6.

The ^{1}H NMR spectra of compounds **7**-**9** demonstrate full set of the carborane ligand hydrogens in the range from 130 to –25 ppm and the MeS group signals in the field 1.2 - –4.4

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ppm. The ^{13}C NMR spectra of compounds **8** and **9** contain broad signals of the cluster carbons at ~ –405 ppm and signals of the MeS group at ~ –50 ppm.

The solid state structure of $(Bu_4N)[4,4'-(MeS)_2-3,3'-Fe(1,2-C_2B_9H_{10})_2]$ $((Bu_4N)[$**8**$])$ was determined by single crystal X-ray diffraction. Similarly to the structure of the cobalt(III) analogue $[4,4'-(MeS)_2-3,3'-Co(1,2-C_2B_9H_{10})_2]^-$ [21], the dicarbollide ligands in **8** adopt *gauche* conformation stabilized by four (two pairs) intramolecular CH···S contacts between the dicarbollide ligands with somewhat different CH···S distances (Figure 4). This structure is significantly different from the structures of the corresponding dimethylsulfonium derivatives **2** and **2**$^+$, where the dicarbollide ligands adopt *cisoid* conformation [24]. In the theoretically optimized structure, both sulfur atoms interact with both C-H hydrogens (four interactions in total). In agreement with experiment, the S1···H1A and S1···H2A distances are not equal (see capture to Fig. 4 where calculated values are given in italic). Four S···H BCPs are observed with energies equal to 1.8 and 2.3 kcal/mol for each of two shorter and longer contacts, respectively.

Figure 4. General view of the structure **8** with the atom numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Shortest C-H···S contacts are C1-H1···S1' (2.78 *(2.77)* Å), C2-H2···S1' (2.71 *(2.61)* Å), and two symmetrically equivalent C1'-H1'···S1 and C2'-H2'···S1.

The solid state structure of $(Me_4N)[4,7'-(MeS)_2-3,3'-Fe(1,2-C_2B_9H_{10})_2]$ $((Me_4N)[$**9**$])$ was determined by single crystal X-ray diffraction. Similarly to the structure of the cobalt(III) analogue $[4,7'-(MeS)_2-3,3'-Co(1,2-C_2B_9H_{10})_2]^-$ [21], the dicarbollide ligands in **9** adopt *gauche*

conformation stabilized by one pair of intramolecular CH⋯S hydrogen bonds with one MeS group and one short BH…S contact with another one (Figure 5). The structure of **9⁻** is significantly different from the structure of the corresponding dimethylsulfonium derivative **3**, where the dicarbollide ligands are in *transoid* conformation stabilized by two CH⋯S hydrogen bonds with different MeS groups [39]. The quantum chemical calculations lead to some unequivalence of S…H contacts similar to those observed experimentally (see capture to Fig. 5 where calculated values are given in italic). Only three BCPs (two with the C-H hydrogen atoms, and one with the B-H one) are observed. Energies of interactions between S and C-H group are equal to 2.5 and 1.7 kcal/mol, and B-H⋯S interaction is of 1.8 kcal/mol. The solid state structure of $(Bu_4N)[4,7'-(MeS)_2-3,3'-Fe(1,2-C_2B_9H_{10})_2]$ $((Bu_4N)[9])$ was determined as well (See Experimental)ingle crystal X-ray diffraction.
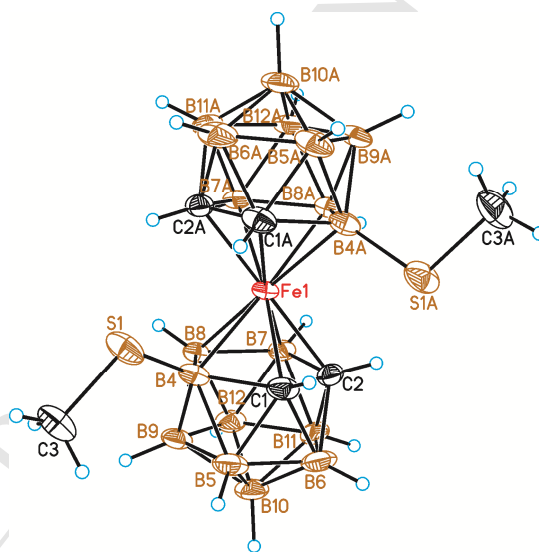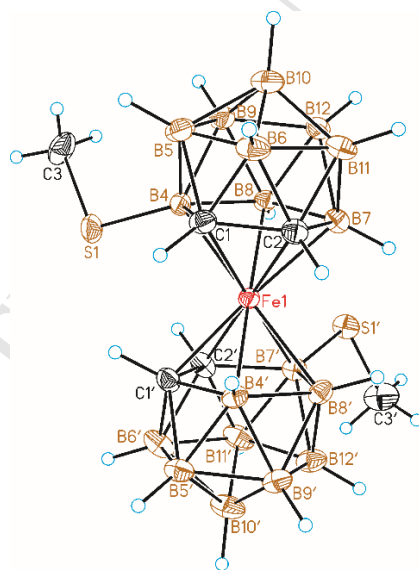

Figure 5. General view of the structure **9⁻** with the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Shortest C-H⋯S contacts are C1'-H1'⋯S1 (2.65 (*2.56*) Å) C2'-H2'⋯S1(2.76 (*2.82*) Å), shortest B-H⋯S contact is B8-H8⋯S1' (2.73 Å).

Electrochemical properties of this family of ferracarboranes were studied by cyclic voltammetry. The redox potential values of $(Me_4N)[7]$, $(Me_4N)[8]$ and $(Me_4N)[9]$ are collected in Table 1, together with that of $[3,3'-Fe(1,2-C_2B_9H_{11})_2]^-$ [40], reported by comparison. As it is shown in Figure 6 for the case of $(Me_4N)[7]$, the cyclic voltammetry of these methyl sulfide

derivatives shows in all cases a one-electron cathodic process, corresponding to the redox change Fe(III)/Fe(II), and one anodic process, ascribed to the oxidation of the two sulfides. As in the case of the cobalt analogues [21], this attribution of the redox properties is quite straightforward, being supported by the two-electron nature of the oxidation and by the redox potential values of these anodic processes, which are very similar for the ferracarborane and cobaltacarborane families. Thus, since it would involve the removal of one electron from a species with an high positive charge, the Fe(III)Fe/(IV) oxidation is not observed. Again, the metal-centered redox change is a well-shaped, chemically reversible, process, anodically shifted by ~130 mV with respect to $[3,3'-Fe(1,2-C_2B_9H_{11})_2]^-$, as a result of the electron-withdrawing effect of the sulfides. While the Fe(III)/Fe(II) change is almost unaffected by the nature of the electrode material, the kinetic of the oxidation of the B-methylsulfide moieties strongly depends on the electrode material. As a common feature, two very closely-spaced peaks are observed, which, in cases, entirely merge, so that a single shouldered process is usually observed at scan rates higher than 0.1 V s^{-1}. As anticipated, the redox potential values of this process follows the trend expected in view of the weaker electron-donating effect of ferracarborane upon substitution at position 4 than 8. On the other side, some features change by changing the working electrode material. In fact, the adsorption of the sulfide pendant arms on the gold surface is clearly revealed by the discharge process of the adsorbed material at E > +1.5 V, shown in Figure 6 for 7$^-$. Also, and at variance with 8$^-$ and 9$^-$, the persistent contact of the gold electrode with a solution of 7$^-$ makes a new oxidation process to emerge at a potential slightly less positive than the pristine one (Figure 7). It appears reasonable that this process may be due the sulfides oxidation of the surface-adsorbed molecules. In our previous paper [21] we suggested that an inter- or intra-molecular coupling with the formation of a disulfide bridge could accompany the sulfides oxidation: current data support this hypothesis, strengthening the fact that the sulfides oxidation is accompanied by chemical reactions which mechanism varies depending on both the molecule geometry and the electrode material. It is clear at this stage that a dedicated study is essential to further clarify this mechanism and this will be the subject of our future work.

Table 1. Formal Electrode Potentials (in V, *vs* AgCl/Ag) and Peak-to-Peak Separations (ΔE_p in mV) for the Redox Changes Exhibited by the Compounds 7$^-$, 8$^-$ and 9$^-$ in CH$_3$CN Solution.

Compound	E_{ox}	ΔE_p	E_{red1}	ΔE_p	Electrode
7$^-$	+0.72	*40*	-0.20	*62*	Au
	+0.71	*20*	-0.20	*60*	Pt

8⁻	+0.76	*60*	-0.21	*60*	Au
	+0.76	*60*	-0.20	*60*	Pt
9⁻	+0.85	*160*	-0.19	*65*	Au
	+0.89	*230*	-0.19	*60*	Pt
$[3,3'\text{-}Fe(1,2\text{-}C_2B_9H_{11})_2]^-$ [40]	+1.21		-0.33		GC
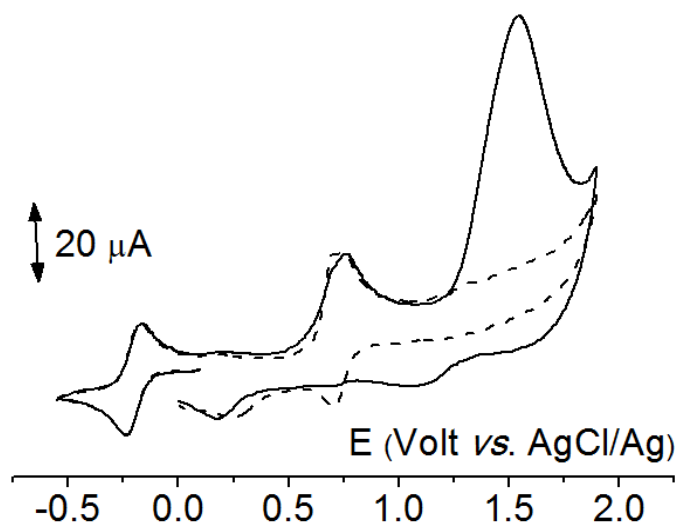
Figure 6. Cyclic voltammetric responses recorded at Pt (dash line) or Au (full line) in CH_3CN solutions of (Me_4N)[**7**] $(0.8 \times 10^{-3}$ M); $[Bu_4N][PF_6]$ (0.2 M) supporting electrolyte. Scan rate 0.2 V s^{-1}.

Figure 7. Cyclic voltammetric responses in the anodic region recorded at Pt (dash line), freshly-cleaned Au (full line), or in Au after prolonged dipping (dot-dash grey line) in CH_3CN solutions of (Me_4N)[**7**] $(0.8 \times 10^{-3}$ M); $[Bu_4N][PF_6]$ (0.2 M) supporting electrolyte. Scan rate 0.2 V s^{-1}.

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3. Conclusions

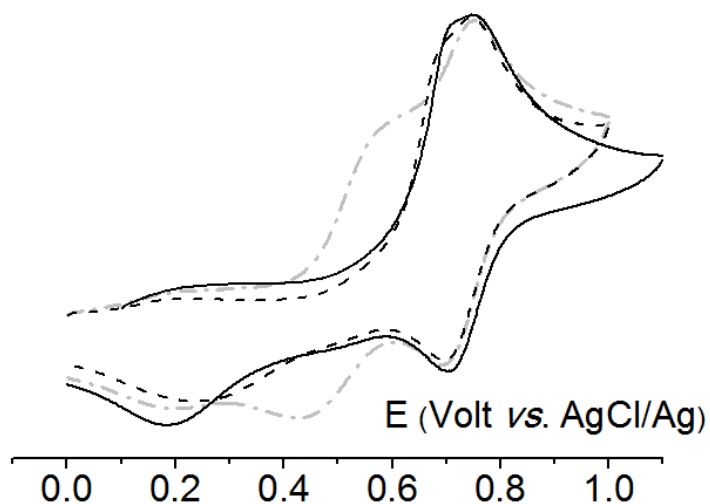A series of isomeric derivatives of iron bis(dicarbollide) containing methylsulfanyl substituents at the boron atoms in the pentagonal face of the dicarbollide ligands, $[8,8'-(MeS)_2-3,3'-Fe(1,2-C_2B_9H_{10})_2]^{2-/1-}$, $[4,4'-(MeS)_2-3,3'-Fe(1,2-C_2B_9H_{10})_2]^{2-/1-}$, and $[4,7'-(MeS)_2-3,3'-Fe(1,2-C_2B_9H_{10})_2]^{2-/1-}$, were synthesized. In the solid state, the rotation of the two dicarbollide ligands with respect to each other is hampered by the formation of intramolecular $CH_{carb}\cdots S(Me)$ hydrogen bonds between the ligands resulting in stabilization of *transoid*-conformation for the 8,8'-isomer and *gauche*-conformation for the 4,4'- and 4,7'-isomers similarly to analogous derivatives of cobalt bis(dicarbollide).

4. Experimental

4.1. Materials and methods

Dimethylsulfonium derivatives of *nido*-carborane $9-Me_2S-7,8-C_2B_9H_{11}$ [24] and $10-Me_2S-7,8-C_2B_9H_{11}$ [41] were synthesized as described in the literature. Anhydrous $FeCl_2$ (98 %) was purchased from Aldrich. THF was distilled under sodium. All other chemicals were reagent grade and received from commercial vendors. The ^1H, ^{11}B, $^{11}B\{^1H\}$ and ^{13}C NMR spectra were recorded on Bruker Avance-400 spectrometer. ^1H chemical shifts were referenced to residual protons in the lock solvents. ^{11}B chemical shifts were referenced externally to $BF_3 \cdot OEt_2$. The reaction progress was monitored by TLC (Merck F254 silica gel on aluminum plates) and visualized using 0.5% $PdCl_2$ in 1% HCl in aq. MeOH (1:10). Acros Organics silica gel (0.060-0.200 mm) was used for column chromatography. The high-resolution mass spectra were obtained with a Bruker Daltonics microOTOF II instrument.

4.2. Synthesis of 8,8'-(Me₂S)₂-3,3'-Fe(1,2-C₉B₉H₁₀)₂ (**1**)

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Solution of $10\text{-}Me_2S\text{-}7,8\text{-}C_2B_9H_{11}$ (0.58 g, 2.97 mmol) and t-BuOK (1.68 g, 15.00 mmol) in THF (40 ml) was heated under reflux for 0.5 h under argon. Then solid $FeCl_2$ (0.95 g, 7.50 mmol) was added to the reaction mixture and heated under reflux for 20 h under argon. The reaction mixture was allowed to cool to room temperature and concentrated to dryness *in vacuo*. The crude product was washed by 5% aq. HCl until the washings became colorless and dried over P_2O_5 to give 0.40 g (61%) of red powder $[8,8'\text{-}(Me_2S)_2\text{-}3,3'\text{-}Fe(1,2\text{-}C_2B_9H_{10})_2]$ (**1**). ^{1}H NMR (acetone-d_6, ppm): 3.62 (4H, br s, CH_{carb}), 2.58 (12H, s, SCH_3). ^{13}C NMR (acetone-d_6, ppm): 43.3 (C_{carb}), 25.5 (SCH$_3$). ^{11}B NMR (acetone-d_6, ppm): 0.8 (2B, s), –9.6 (2B, d, J = 144 Hz), –12.0 (4B, d, J = 134 Hz), –14.9 (4B, d, J = 134 Hz), –23.1 (4B, d, J = 151 Hz), –26.2 (2B, d, J = 158 Hz).

4.3. Synthesis of $4,4'\text{-}(Me_2S)_2\text{-}3,3'\text{-}Fe(1,2\text{-}C_2B_9H_{10})_2$ (2) and $4,7'\text{-}(Me_2S)_2\text{-}3,3'\text{-}Fe(1,2\text{-}C_2B_9H_{10})_2$ (3)

Solution of $9\text{-}Me_2S\text{-}7,8\text{-}C_2B_9H_{11}$ (0.58 g, 2.97 mmol) and t-BuOK (1.68 g, 15.00 mmol) in THF (40 ml) was heated under reflux for 0.5 h under argon. Then solid $FeCl_2$ (0.95 g, 7.50 mmol) was added to the reaction mixture and heated under reflux for 20 h under argon. The reaction mixture was allowed to cool to room temperature and concentrated to dryness *in vacuo*. The residue was washed by 5% aq. HCl until the washings became colorless, filtered and dried over P_2O_5. Then the dark red powder was washed by CH_2Cl_2 and dried to give 0.18 g (27%) of pink powder $[4,7'\text{-}(Me_2S)_2\text{-}3,3'\text{-}Fe(1,2\text{-}C_2B_9H_{10})_2]$ (**3**). The red organic filtrate was evaporated *in vacuo*. The crude product was purified by column chromatography on silica using CH_2Cl_2 as eluent to give 0.28 g (43%) of red powder $[4,4'\text{-}(Me_2S)_2\text{-}3,3'\text{-}Fe(1,2\text{-}C_2B_9H_{10})_2]$ (**2**). Compound **2**. ^{1}H NMR (acetone-d_6, ppm): 4.11 (2H, br s, CH_{carb}), 3.19 (2H, br s, CH_{carb}), 2.85 (6H, s, SCH_3), 2.61 (6H, s, SCH_3). ^{13}C NMR (acetone-d_6, ppm): 44.0 (C_{carb}), 42.1 (C_{carb}), 27.3 (SCH$_3$), 26.3 (SCH$_3$). ^{11}B NMR (acetone-d_6, ppm): –3.8 (2B, s), –5.3 (2B, d, J = 146 Hz), –8.9 (4B, d, J

= 139 Hz), –11.0 (2B, d, J = 149 Hz), –14.5 (2B, d, J = 137 Hz), –23.6 (2B, d, J = 144 Hz), –24.3 (2B, d, J = 146 Hz), –26.7 (2B, d, J = 167 Hz). Compound **3**. ^{1}H NMR (acetone-d_6, ppm): 4.15 (2H, br s, CH_{carb}), 3.95 (2H, br s, CH_{carb}), 2.76 (6H, s, SCH_3), 2.69 (6H, s, SCH_3). ^{11}B NMR (acetone-d_6, ppm):–3.8 (2B, d, J = 125 Hz), –5.5 (2B, s), –8.9 (2B, d, J = 120 Hz), –9.6 (2B, d, J = 125 Hz),–11.8 (2B, d, J = 144 Hz), –15.5 (2B, d, J = 139 Hz), –22.9 (2B, d, J = 139 Hz), –24.9 (2B, d, J = 174 Hz), –26.4 (2B, d, J = 191 Hz).

4.4. Synthesis of $(Bu_4N)_2[8,8'-(MeS)_2-3,3'-Fe(1,2-C_2B_9H_{10})_2]$ $((Bu_4N)_2[4])$ and $(Me_4N)[8,8'-(MeS)_2-3,3'-Fe(1,2-C_2B_9H_{10})_2]$ $((Me_4N)[7])$

t-BuOK (0.85 g, 7.59 mmol) was added to solution of BuSH (406 µl, 0.34 g, 3.79 mmol) in THF (20 ml) was stirred under argon at room temperature for 0.5 h, then solution of **1** (0.56 g, 1.26 mmol) in THF (20 ml) was added over 15 min and the reaction mixture was heated under reflux for 2 h. The reaction mixture was allowed to cool to room temperature and concentrated to dryness *in vacuo*. The residue was dissolved in water (50 ml) and divided in halves. The first part was treated with Bu_4NBr (0.61 g, 1.89 mmol) in water (10 ml). The precipitate was filtered off and dried over P_2O_5 to give 0.49 g (86%) of pink powder $(Bu_4N)_2[8,8'-(MeS)_2-3,3'-Fe(1,2-C_2B_9H_{10})_2]$ $((Bu_4N)_2[4])$. ^{11}B{^{1}H} NMR (acetone-d_6, ppm): 1.5, –13.1, –13.7, –24.6. The second part was stirred in air at room temperature for 72 h, filtered and treated with Me_4NBr (0.15 g, 0.95 mmol) in water (10 ml). The precipitate was filtered and dried over P_2O_5 to give 0.15 g (49%) of dark red powder $(Me_4N)[8,8'-(Me_2S)_2-3,3'-Fe(1,2-C_2B_9H_{10})_2]$ $((Me_4N)[7])$. ^{1}H NMR (acetone-d_6, ppm): 107.4 (4H, br s, CH_{carb}/BH), 54.9 (4H, br s, CH_{carb}/BH), 41.5 (2H, br q, BH), 3.3 (12H, s, Me$_4$N$^+$), –3.8 (4H, br m, BH), –4.4 (6H, s, SCH_3), –6.9 (4H, br q, BH), –22.6 (2H, br q, BH). ^{11}B NMR (acetone-d_6, ppm): 118.8 (2B, d), 41.8 (4B, d), –4.0 (4B, d), –52.8 (2B, d), –383.7 (4B, br s), –442.5 (2B, br s). HRMS (ESI): m/z for $C_6H_{26}B_{18}FeS_2$: calcd. 413.2621, obsd. 413.2609 [M]$^-$.

*4.5.   Synthesis   of   (Bu₄N)₂[4,4'-(MeS)₂-3,3'-Fe(1,2-C₂B₉H₁₀)₂]   ((Bu₄N)₂[**5**])   and (Me₄N)[4,4'-(MeS)₂-3,3'-Fe(1,2-C₂B₉H₁₀)₂] (Me₄N[**8**])*

t-BuOK (0.70 g, 6.27 mmol) was added to solution of BuSH (336 μl, 0.28 g, 3.14 mmol) in THF (20 ml) was stirred under argon at room temperature for 0.5 h, then solution of **2** (0.46 g, 1.05 mmol) in THF (20 ml) was added over 15 min and the reaction mixture was heated under reflux for 2 h. The reaction mixture was allowed to cool to room temperature and concentrated to dryness *in vacuo*. The residue was dissolved in water (50 ml) and divided in halves. The first part was treated with Bu₄NBr (0.51 g, 1.58 mmol) in water (10 ml). The precipitate was filtered off and dried over P_2O_5 to give 0.47 g (99%) of pink powder (Bu₄N)₂[4,4'-(MeS)₂-3,3'-Fe(1,2-C₂B₉H₁₀)₂] ((Bu₄N)₂[**5**]). ^{11}B NMR (acetone-d_6, ppm): –10.7, –12.5, –15.0, –23.2. The second part was stirred in air at room temperature for 48 h, filtered and treated with Me₄NBr (0.12 g, 0.78 mmol) in water (10 ml). The precipitate was filtered and dried over P_2O_5 to give 0.12 g (47%) of dark red powder (Me₄N)[4,4'-(Me₂S)₂-3,3'-Fe(1,2-C₂B₉H₁₀)₂] ((Me₄N)[**8**]). ^{1}H NMR (acetone-d_6, ppm): 129.0 (2H, br s, C*H*carb/B*H*), 125.1 (2H, br s, C*H*carb/B*H*), 62.3 (2H, br s, C*H*carb/B*H*), 37.0 (2H, br q, B*H*), 3.7 (2H, br q, B*H*), 3.2 (12H, s, Me₄N⁺), –2.4 (6H, s, SC*H₃*), –3.6 (2H, br s, C*H*carb/B*H*), –5.7 (4H, br m, B*H*), –13.7 (2H, br q, B*H*), –22.6 (2H, br q, B*H*). ^{13}C NMR (acetone-d_6, ppm): 55.9 (Me₄N⁺), –54.4 (S*C*H₃), –405.7 (*C*carb). ^{11}B NMR (acetone-d_6, ppm): 100.7 (2B, d), 55.2 (2B, d), 1.0 (2B, d), –0.9 (2B, d), –3.2 (2B, d), –61.1 (2B, d), –402.6 (2B, br s), –486.2 (2B, br s), –528.9 (2B, br s). HRMS (ESI): m/z for $C_6H_{26}B_{18}FeS_2$: calcd. 413.2621, obsd. 413.2628 [M]⁻.

*4.6. Synthesis of (Bu₄N)[4,4'-(MeS)₂-3,3'-Fe(1,2-C₂B₉H₁₀)₂] ((Bu₄N)[**8**])*

Solution of FeCl₃ (0.02 g, 0.11 mmol) in MeCN (15 ml) was added to solution of (Bu₄N)₂[**5**] (0.05 g, 0.06 mmol) in MeCN (15 ml) and the reaction mixture was stirred at room temperature overnight. The reaction mixture was concentrated to dryness *in vacuo*, the residue

was washed by water until the washings became colorless and dried in air to give 0.03 g (86%) of dark red powder $(Bu_4N)[4,4'-(MeS)_2-3,3'-Fe(1,2-C_2B_9H_{10})_2]$ $((Bu_4N)[\mathbf{8}])$. ^{11}B NMR (acetone-d_6, ppm): 101.5 (2B, d), 55.7 (2B, d), 1.0 (2B, d), –0.9 (2B, d), –3.3 (2B, d), –61.7 (2B, d), –406.1 (2B, br s), –490.6 (2B, br s), –534.1 (2B, br s).

4.7.   Synthesis   of $(Bu_4N)_2[4,7'-(MeS)_2-3,3'-Fe(1,2-C_2B_9H_{10})_2]$ $((Bu_4N)_2[\mathbf{6}])$ and $(Me_4N)[4,7'-(MeS)_2-3,3'-Fe(1,2-C_2B_9H_{10})_2]$ $((Me_4N)[\mathbf{9}])$

t-BuOK (0.59 g, 5.28 mmol) was added to solution of BuSH (283 μl, 0.24 g, 2.64 mmol) in THF (20 ml) was stirred under argon at room temperature for 0.5 h, then solution of **3** (0.39 g, 0.88 mmol) in THF (20 ml) was added over 15 min and the reaction mixture was heated under reflux for 2 h. The reaction mixture was allowed to cool to room temperature and concentrated to dryness *in vacuo*. The residue was dissolved in water (50 ml) and divided in halves. The first part was treated with Bu_4NBr (0.43 g, 1.32 mmol) in water (10 ml). The precipitate was filtered off and dried over P_2O_5 to give 0.35 g (88%) of pink powder $(Bu_4N)_2[4,7'-(MeS)_2-3,3'-Fe(1,2-C_2B_9H_{10})_2]$ $((Bu_4N)_2[\mathbf{6}])$. ^{11}B NMR (acetone-d_6, ppm): –11.7, –13.0, –13.6, –23.0, –24.3. The second part was stirred in air at room temperature for 48 h, filtered and treated with Me_4NBr (0.10 g, 0.66 mmol) in water (10 ml). The precipitate was filtered and dried over P_2O_5 to give 0.09 g (42%) of dark red powder $(Me_4N)[4,7'-(Me_2S)_2-3,3'-Fe(1,2-C_2B_9H_{10})_2]$ $((Me_4N)[\mathbf{9}])$. ^{1}H NMR (acetone-d_6, ppm): 117.2 (2H, br s, C*H*carb/B*H*), 86.0 (2H, br s, C*H*carb/B*H*), 60.0 (2H, br s, C*H*carb/B*H*), 39.9 (2H, br q, B*H*), 32.6 (2H, br s, C*H*carb/B*H*), 3.2 (12H, s, Me_4N^+), 1.2 (6H, s, SC*H*$_3$), 0.9 (2H, br m, B*H*), –1.5 (2H, br q, B*H*), –4.2 (2H, br q, B*H*), –13.2 (2H, br q, B*H*), –22.0 (2H, br q, B*H*). ^{13}C NMR (acetone-d_6, ppm): 55.2 (Me_4N^+), –49.6 (S*C*H$_3$), –402.8 (*C*carb). ^{11}B NMR (acetone-d_6, ppm): 98.8 (2B, d), 50.3 (2B, d), 18.8 (2B, d), 13.4 (2B, d), –11.2 (2B, d), –56.0 (2B, d), –417.3 (2B, br s), –434.5 (2B, br s), –475.7 (2B, br s). HRMS (ESI): m/z for $C_6H_{26}B_{18}FeS_2$: calcd. 413.2621, obsd. 413.2631 [M]$^-$.

4.8. X-ray diffraction study

Single crystal X-ray study of compounds (Bu$_4$N)$_2$**[4]** and (Me$_4$N)**[9]** were carried out with SMART APEX II CCD difractometer (λ(Mo-Kα)=0.71073 A, graphite monochromator, ω-scans) at 120 K.

Compound (Bu$_4$N)$_2$**[4]**: crystals (C$_6$H$_{26}$B$_{18}$S$_2$Fe^{2-}·2(NC$_{16}$H$_{36}$$^+$) are monoclinic, space group *C2/c*: *a* = 21.7800(15) Å, *b* = 10.7466(7) Å, *c* = 24.395(2) Å, β = 110.2550(10), *V* = 5356.9(7) Å^3, *Z* = 8, *d*$_{calc}$ = 1.113 g·cm^{-3}, μ = 0.389 mm^{-1}, *wR2* = 0.1125 calculated on *F*^{2}$_{hkl}$ for all 5939 independent reflections with 2θ < 54.3°, (*GOF* = 1.029, *R* = 0.0417 calculated on *F*$_{hkl}$ for 4983 reflections with *I* > 2σ(*I*)). Crystallographic data (excluding structure factors) for the structure have been deposited at the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication No. CCDC 1821108.

Compound (Bu$_4$N)**[8]**: crystals (C$_6$H$_{26}$B$_{18}$S$_2$Fe$^-$·NC$_{16}$H$_{36}$$^+$) are monoclinic, space group *P2/n*: *a* = 12.4104(11) Å, *b* = 10.9836(10) Å, *c* = 14.0617(12) Å, β = 102.367(2), *V* = 1872.3(3) Å^3, *Z* =2, *d*$_{calc}$ = 1.162 g·cm^{-3}, μ = 0.532 mm^{-1}, *wR2* = 0.1679 calculated on *F*^{2}$_{hkl}$ for all 5491 independent reflections with 2θ < 60.11°, (*GOF* = 0.990, *R* = 0.0611 calculated on *F*$_{hkl}$ for 2776 reflections with *I* > 2σ(*I*)). Crystallographic data (excluding structure factors) for the structure have been deposited at the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication No. CCDC 1832930.

Compound (Me$_4$N)**[9]**: crystals (C$_6$H$_{26}$B$_{18}$S$_2$Fe$^-$·NC$_4$H$_{12}$$^+$·0.375CHCl$_3$) are orthorhombic, space group *Pbca*: *a* = 14.4681(4) Å, *b* = 13.3460(4) Å, *c* = 28.8831(9) Å, *V* = 5577.1(3) Å^3, *Z* = 8, *d*$_{calc}$ = 1.267 g·cm^{-3}, μ = 0.803 mm^{-1}, *wR2* = 0.1117 calculated on *F*^{2}$_{hkl}$ for all 8815 independent reflections with 2θ < 61.8°, (*GOF* = 1.077, *R* = 0.0405 calculated on *F*$_{hkl}$ for 7124 reflections with *I* > 2σ(*I*)). Crystallographic data (excluding structure factors) for the structure

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have been deposited at the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication No. CCDC 1821109.

Compound (Bu$_4$N)[9]: crystals (C$_6$H$_{26}$B$_{18}$S$_2$Fe$^-$·NC$_{16}$H$_{36}^+$) are monoclinic, space group $P2_1/c$: a = 14.9796(2) Å, b = 17.5585(3) Å, c = 14.8648(2) Å, β = 111.2800(10), V = 3643.15(10) Å^3, Z =4, d_{calc} = 1.195 g·cm^{-3}, μ = 0.547 mm^{-1}, $wR2$ = 0.1016 calculated on F^2_{hkl} for all 10741 independent reflections with $2\theta < 60.36°$, (GOF = 1.038, R = 0.0365 calculated on F_{hkl} for 8621 reflections with $I > 2\sigma(I)$). Crystallographic data (excluding structure factors) for the structure have been deposited at the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication No. CCDC 1832931.

4.9. Electrochemical Measurements

In all the experiments N$_2$-saturated solutions of the compound under study were used with [Bu$_4$N][PF$_6$] (0.2 M) as supporting electrolyte (Fluka, electrochemical grade) and freshly distilled CH$_3$CN. Cyclic voltammetry was performed in a three-electrode cell containing a platinum or gold working electrode, a platinum counter electrode, and an AgCl/Ag (KCl sat) reference electrode. A BAS 100W electrochemical analyzer was used as polarizing unit. All the potential values are referred to the AgCl/Ag (KCl sat).

Acknowledgments

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A series of methylsulfanyl derivatives of iron bis(dicarbollide) were synthesized.

Structures of 8,8'-, 4,4'- and 4,7'-isomers were determined by X-ray diffraction.

The ligand rotation is hampered by intramolecular $CH_{carb}\cdots S(Me)$ hydrogen bonds.