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Review

Chemistry of nickel and iron bis(dicarbollides). A review

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Dedicated to Professor Sheldon G. Shore on the occasion of his 70th birthday in recognition of his notable contributions to organometallic and boron chemistry

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Abstract

Synthesis and chemical properties of nickel and iron bis(dicarbollides) and their derivatives are reviewed. A review with 81 references. © 2000 Published by Elsevier Science B.V. All rights reserved.

Keywords: Metallacarboranes; Nickelacarboranes; Ferracarboranes; Sandwich complexes

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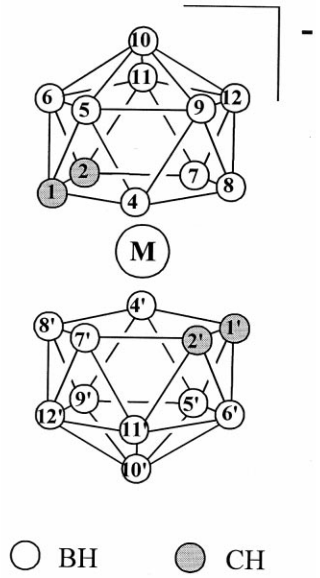
1. Introduction

Since the synthesis of the first metallacarboranes $[3,3'\text{-Fe}(1,2\text{-}C_2B_9H_{11})_2]^{n-}$ ($n = 1, 2$) in 1965 [1], metallacarboranes from all areas of the periodic table have been prepared. Metallacarborane chemistry is characterized by great diversity of structural types and bonding modes. Before the first metallacarboranes were prepared, the higher boranes had tended to be regarded as chemical curiosities, compounds whose peculiar structures, apparently without parallel elsewhere in chemistry, required their own bonding rules. However, with the discovery of metallacarboranes, it became evident that carbon and metal atoms could participate in the same type of bonding, as the boron atoms in boranes. Ideas developed for polyhedral boron hydrides and their metal derivatives are used now to describe bonding in organometallic clusters, metal π-complexes, and aromatic ring systems. It is not surprising therefore that synthesis of compounds of novel structural types and study of their interconversions are the main directions in development of metallaborane and metallacarborane chemistry. At the same time much less attention is paid to synthesis of substituted derivatives of metallaboranes and metallacarboranes. No wonder, however, that the systems known for long time, namely *commo*-bis(dicarbollide) $[M(C_2B_9H_{11})_2]^{n-}$ and cyclopentadienyl-dicarbollide $[CpM(C_2B_9H_{11})]^{m-}$ complexes, are the most studied in this sense. The present state of aluminum [2] and cobalt [3] bis(dicarbollide) chemistry has been surveyed recently. The more recent publications in these fields include Refs. [4–9]. Herein we present a review of the present state of the nickel and iron bis(dicarbollide) chemistry with special emphasis on synthesis and properties of their substituted derivatives.



Scheme 1. Structure and numbering of atoms in the $[3,3'\text{-M}(1,2\text{-}C_2B_9H_{11})_{12}]^-$ bis(dicarbollides).

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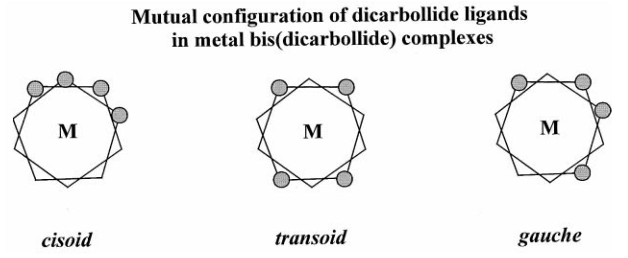


Scheme 2. Mutual configuration of dicarbollide ligands in metal bis(dicarbollide) complexes.

2. Nickel bis(dicarbollides)

2.1. Nickel bis(1,2-dicarbollides). Synthesis and properties

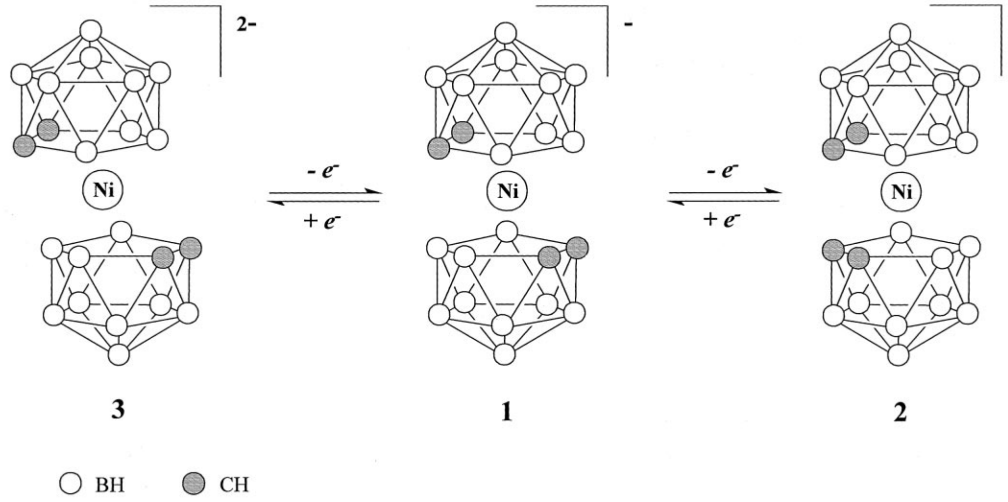
The traditional approach to the synthesis of the [3,3′-Ni(1,2-$C_2B_9H_{11})_2]^-$ anion consists in the partial degradation of *ortho*-carborane with base into *nido*-[7,8-$C_2B_9H_{12}]^-$ followed by its deprotonation to the [7,8-$C_2B_9H_{11}]^{2-}$ dianion and reaction with nickel(II) salts. Usually the dicarbollide dianion is generated *in situ* by the treatment of *nido*-[7,8-$C_2B_9H_{12}]^-$ with sodium hydride in tetrahydrofuran or with sodium hydroxide in aqueous solution. The yellow–brown paramagnetic [3,3′-Ni(1,2-$C_2B_9H_{11})_2]^-$ ion (**1**) ($\mu_{\text{eff}} =$ 1.76 μB) was isolated after air oxidation in 76–84% yield as the tetramethylammonium salt [10,11]. The electrolysis of a solution of K[7,8-$C_2B_9H_{12}$] in dimethyl sulfoxide on the nickel anode was shown to give mixture of [3,3′-Ni(1,2-$C_2B_9H_{11})_2]^-$ and [3,3′-Ni(1,2-$C_2B_9H_{11})_2$] in more than 70% total yield [12] (Scheme 1).

The crystal and molecular structure of (Me_4N)[3,3′-Ni(1,2-$C_2B_9H_{11})_2$] has been determined by the single-crystal X-ray diffraction method [13]. The structure of the [3,3′-Ni(1,2-$C_2B_9H_{11})_2]^-$ anion is of a symmetrical π-sandwich type with the two dicarbollyl icosahedra joined at the Ni(III) apex. The carbon atoms of the η^5-dicarbollide ligands occupy *transoid* rotational geometry about the nickel center. The average Ni–C and Ni–B distances are 2.146(26) and 2.134(26) Å, respectively. The [3,3′-Ni(1,2-$C_2B_9H_{11})_2]^-$ anion was characterized by the methods of UV [10,11,14], IR [11,15], Raman [15], NMR [16], X-ray [17], and X-ray photoelectron [18] spectroscopy.

Oxidation of **1** with one equivalent of ferric ion in aqueous solution gives in 90% yield orange air-stable diamagnetic nickela(IV)carborane [3,3′-Ni(1,2-$C_2B_9H_{11})_2$] (**2**), which can be reverted back to **1** by the borohydride reduction [10,14].

The crystal structure of **2** has been determined by the single-crystal X-ray diffraction method [19]. The molecule has the sandwich type structure. The positions of the carbon atoms in opposite dicarbollide ligands are as close to each other as is possible forming the staggered *cisoid* conformation. The average Ni–C and Ni–B distances are 2.071(6) and 2.103(18) Å, respectively. Nickel(IV) bis(1,2-dicarbollide) was also characterized by the methods of UV [10,11,14,20,21], IR [10,15,22–24], Raman [15,23,24], NMR [25,26], X-ray [17,22], and X-ray photoelectron [18] spectroscopy, as well as magnetic susceptibility measurements [27] (Scheme 2).

Reduction of **1** gives the air-sensitive pale-brown paramagnetic [3,3′-Ni(1,2-$C_2B_9H_{11})_2]^{2-}$ ion (**3**) ($\mu_{\text{eff}} =$ 2.90 μB) [10]. The structure of [3,3′-Ni(1,2-$C_2B_9H_{11})_2]^{2-}$ anion has not been determined, however it was supposed that **3** has ‘slipped’ *transoid* sandwich structure with the η^3-dicarbollide ligands coordinated to the metal atom via boran atoms of the open pentagonal face. Such a type of dicarbollide coordination was found in other metallacarboranes on the base of d^8 metal ions [28]. The [3,3′-Ni(1,2-$C_2B_9H_{11})_2]^{2-}$ anion was characterized by UV [14,20], IR [11], and X-ray photoelectron [18] spectroscopy.



Scheme 3. Interconversions of the [3,3-Ni^{II}(1,2-$C_2B_9H_{11})_2]^{2-}$, [3,3-Ni^{III}(1,2-$C_2B_9H_{11})_2]^-$ and [3,3-Ni^{IV}(1,2-$C_2B_9H_{11})_2$] bis(dicarbollides).

Both the electrochemical and the chemical redox reactions were shown to be reversible [11,29,30] (Scheme 3).

Thermal behavior of **2** in the solid [21,31,32] and gaseous [25] state was studied. It was shown that in the gas phase at 360–400°C **2** undergoes the consecutive rearrangement into [3,4′(5′)-Ni(1,2-$C_2B_9H_{11})_2$] (**4**) and [4(5),4′(5′)-Ni(1,2-$C_2B_9H_{11})_2$] (**5**). The solid-state pyrolysis of **2** at 210–220°C gives the isomerization products as well as nickel borides and small carboranes. The cage isomerization was found to proceed also under UV irradiation of **2** in a benzene or hexane solution [22,26]. This type of rearrangement is more characteristic for the *C*-alkyl derivatives [1,1′,2,2′-R_4-3,3′-Ni(1,2-$C_2B_9H_9)_2$] (see below).

Treatment of **2** with hard Lewis bases, such as hydroxide ion, amines, etc., results in its reduction to the **1** anion accompanying by some degradation [25]. The C–H protons in [3,3′-Ni(1,2-$C_2B_9H_{11})_2$] are acidic and the base-degradation reaction carried out in D_2O gives the completely *C*-deuterated [1,1′,2,2′-D_4-3,3′-Ni(1,2-$C_2B_9H_9)_2]^-$ anion (**1a**), which can be oxidized to the corresponding *C*-deuterated nickel(IV) carborane [1,1′,2,2′-D_4-3,3′-Ni(1,2-$C_2B_9H_9)_2$] (**2a**). Under strongly acid conditions (10% D_2SO_4 in AcOD), very slow deuterium exchange in **2** was found to occur exclusively at B–H positions [25].

2.2. Complex compounds

Nickel(IV) bis(dicarbollide) is a rather strong and versatile Lewis acid, capable of forming addition compounds with a variety of soft Lewis bases. The addition of chloride, bromide, or thiocyanate ions to solutions of [3,3′-Ni(1,2-$C_2B_9H_{11})_2$] in aprotic solvents results in formation of the corresponding 1:1 complexes [25]. The charge transfer adduct formation was observed also for a variety of neutral donors including aromatic hydrocarbons (naphthalene, phenanthrene, and pyrene), nitrogen donors (*N*,*N*-dimethylaniline, 2,2′-bipyridine, and 1,10-phenathroline), as well as sulfur and selenium donors (diethyl sulfide, dicyclohexyl thiourea, tetrathiafulvalene, tetrathio- and tetraselenotetracene) [25,33–36]. By contrast with organometallic and coordination compounds which act, as a rule, as donors in charge-transfer complexes, the adducts of [3,3′-Ni(1,2-$C_2B_9H_{11})_2$] represent rare examples of charge-transfer complexes in which the metal-centered species acts as an acceptor. The crystal structures of [3,3′-Ni(1,2-$C_2B_9H_{11})_2$]∗$PhNMe_2$ [37], [3,3′-Ni(1,2-$C_2B_9H_{11})_2$]∗-naphthalene [37], [3,3′-Ni(1,2-$C_2B_9H_{11})_2$]∗pyrene [37], [3,3′-Ni(1,2-$C_2B_9H_{11})_2$]∗tetrathiafulvalene [33], [3,3′-Ni(1,2-$C_2B_9H_{11})_2$]∗2-tetrathiotetracene∗1,2,4-trichlorobenzene [34], and [3,3′-Ni(1,2-$C_2B_9H_{11})_2$]∗tetraselenotetracene [34] complexes have been determined by the single-crystal X-ray diffraction method. It was shown that the structure of the complexed **2** does not deviate significantly from that of uncomplexed **2**. The dicarbollide ligands in all the complexes have staggered *cisoid* coformation except the tetrathiotetracene complex where the dicarbollide ligands adopt *transoid* conformation. The reason for this exception is not definitely clear. The complexes with tetrathiafulvalene, tetrathio and tetraselenotetracene were supposed to have ionic character.

Reactions of [3,3′-Ni(1,2-$C_2B_9H_{11})_2$] with ferro- and nickelocene, as well as with decamethylferrocene were found to produce the corresponding 1:1 complexes of ionic character [38,39]. The structure of $[Fe^{III}Cp^*_2]^+$ [3,3′-Ni^{III}(1,2-$C_2B_9H_{11})_2]^-$ has been determined by single-crystal X-ray diffraction study. Two dicarbollide ligands are twisted with respect to each other by ca. 108°, adopting *gauche* conformation [40]. Synthesis of the complex of **1** with substituted ferrocene cation, $[(\eta^5\text{-}C_5H_5)Fe^{II}(E\text{-}\eta^5\text{-}C_5H_4\text{–}CH{=}CH\text{-}p\text{-}C_5H_4NMe]^+$ [3,3′-Ni^{III}(1,2-$C_2B_9H_{11})_2]^-$, was also described [40]. It should be noted that these results are contrary to observation on oxidation of **1** to **2** by the $[FeCp_2]^+$ cation [41].

Another interesting compound with cluster cation $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S)_3(Et_2NCS_2)_3]^+$[3,3′-$Ni^{III}$(1,2-$C_2B_9H_{11})_2]^-$ was reported recently [7].

A series of the [3,3′-Ni(1,2-$C_2B_9H_{11})_2]^-$ complexes with various nitrogen donors (such as pyridine, 2,2′-bipyridine, and 1,10-phenanthroline), Na[3,3′-Ni(1,2-$C_2B_9H_{11})_2$]∗2Bipy, Na[3,3′-Ni(1,2-$C_2B_9H_{11})_2$]∗2Phen, Ni[3,3′-Ni(1,2-$C_2B_9H_{11})_2]_2$∗4Py, M[3,3′-Ni(1,2-$C_2B_9H_{11})_2]_2$∗4Bipy (M = Ni, Co, Mn, Cu), Ni[3,3′-Ni(1,2-$C_2B_9H_{11})_2]_2$∗4Phen, Fe[3,3′-Ni(1,2-$C_2B_9H_{11})_2]_2$∗6Phen were prepared [6,35,42]. Pyrolysis of the M[3,3′-Ni(1,2-$C_2B_9H_{11})_2]_2$∗4Bipy (M = Ni, Co, Mn, Cu) complexes in refluxed ethanol was shown to result in their decomposition to [3-Bipy-3,1,2-$NiC_2B_9H_{11}$], whereas the pyrolysis in *n*-dodecane at 216°C results in [2-Bipy-2,1,7-$NiC_2B_9H_{11}$] [42–45]. Similarly, the decomposition of Ni[3,3′-Ni(1,2-$C_2B_9H_{11})_2]_2$∗4Phen in ethanol or refluxed dodecane gives [3-Phen-3,1,2-$NiC_2B_9H_{11}$] and [2-Phen-2,1,7-$NiC_2B_9H_{11}$], respectively [35].

2.3. Nickel bis(1,7-dicarbollides)

The olive-green paramagnetic [2,2′-Ni(1,7-$C_2B_9H_{11})_2]^-$ anion (**6**) ($\mu_{eff} = 1.74$ μB) was prepared by the reaction of the $[7,9\text{-}C_2B_9H_{11}]^{2-}$ dianion, which was generated in situ by the treatment of *nido*-[7,9-$C_2B_9H_{12}]^-$ with sodium hydride in tetrahydrofuran, with nickel(II) salts and isolated after air-oxidation in 78% yield as the tetramethylammonium salt [11]. The [2,2′-Ni(1,7-$C_2B_9H_{11})_2]^-$ anion was characterized by the methods of UV [11], IR [11], X-ray [17], and X-ray photoelectron [18] spectroscopy.

Oxidation of **6** with ferric ion in aqueous solution gives orange diamagnetic nickel (IV) carborane [2,2′-

$Ni(1,7-C_2B_9H_{11})_2]$ (**7**) in 85% yield [11]. This compound was characterized by the methods of UV [11], IR [11,15,22,23], Raman [15,23,24], NMR [26], and X-ray [17] spectroscopy. Reduction of **7** with cadmium in acetone gives the nickel(III) metallacarborane **6** [11].

The one-electron reduction of **6** gives the red nickel(II) metallacarborane $[2,2'-Ni(1,7-C_2B_9H_{11})_2]^{2-}$ (**8**) [11], which was characterized by the single-crystal X-ray diffraction as the *N*,*N*′-dimethyltriethylenediammonium salt [46].

2.4. *C*-substituted derivatives

A number of carbon-substituted derivatives of the $[3,3'-Ni(1,2-C_2B_9H_{11})_2]^-$ anion were prepared by the tradition approach starting from the corresponding substituted *ortho*-carboranes via the *nido*-derivatives: $[1,1'-Me_2-3,3'-Ni(1,2-C_2B_9H_{10})_2]^-$ (**9**) [25], $[1,1'-Ph_2-3,3'-Ni(1,2-C_2B_9H_{10})_2]^-$ (**10**) [25], $[1,1',2,2'-Me_4-3,3'-Ni(1,2-C_2B_9H_9)_2]^-$ (**11**) [25], $[1,2:1',2'-di-\mu-(CH_2CH_2CH_2)_2 3,3'-Ni(1,2-C_2B_9H_9)_2]^-$ (**12**) [47], and $[1,2:1',2'-di-\mu-(CH{=}CH-CH{=}CH)_2-3,3'-Ni(1,2-C_2B_9H_9)_2]^-$ (**13**) [48] were prepared in this way. A mixture of two geometric isomers (racemic mixture and *meso* form) arises from initial carboranes bearing non-identical substituents.

The *C*-substituted derivatives of the $[3,3'-Ni(1,2-C_2B_9H_{11})_2]^-$ anion can be easily converted into the corresponding nickel(IV) metallacarboranes with ferric ion: $[1,1'-Me_2-3,3'-Ni(1,2-C_2B_9H_{10})_2]$ (**14**) [25], $[1,1'-Ph_2-3,3'-Ni(1,2-C_2B_9H_{10})_2]$ (**15**) [25], $[1,1'-(3-FC_6H_4)_2-3,3'-Ni(1,2-C_2B_9H_{10})_2]$ (**16**) [49], and $[1,1'-(4-FC_6H_4)_2-3,3'-Ni(1,2-C_2B_9H_{10})_2]$ (**17**) [49] were obtained in this way.

The same approach was used to synthesize the nickelacarborane with tetramethylene-bridged carbon-linked ligands $[1,1'-\mu-(CH_2)_4-3,3'-Ni(1,2-C_2B_9H_{10})_2]$ (**18**) (Fig. 1). The crystal structure of **18** has been determined by the single-crystal X-ray diffraction method. The C_2B_9 faces of the dicarbollide ligands were found to be noticeably non-parallel (the angle between normals to these two bonding planes is 13.6°) [50].

However, oxidation of *C*-tetrasubstituted nickel(III) metallacarboranes **11** and **12** with ferric ion in aqueous solution or with iodine in dichloromethane is accompanied by rearrangement to $[1,1',2,2'-Me_4-3,4'(5')-Ni(1,2-C_2B_9H_9)_2]$ (**19**) [25] (Scheme 4) and $[1,2-1',2'-di-\mu-(CH_2CH_2CH_2)_2-3,4'(5')-Ni(1,2-C_2B_9H_9)_2]$ (**20**) [47], respectively.

It was supposed that the oxidation causes the rotation of the ligand from the *transoid* to *cisoid* configuration. This provokes significant steric interactions between the

X	M	*n*	
$(CH_2)_4$	Ni	0	18
$(CH_2)_4$	Fe	1	39
$TsN(CH_2CH_2)_2$	Fe	1	40

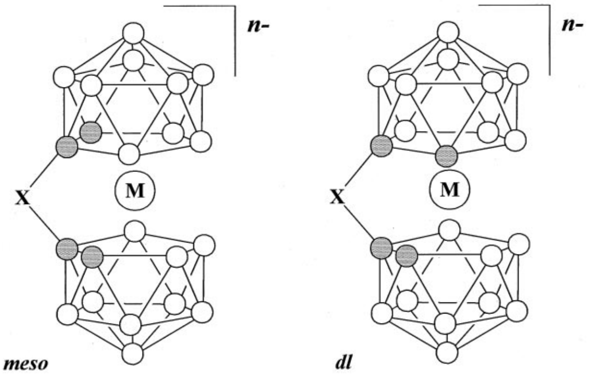
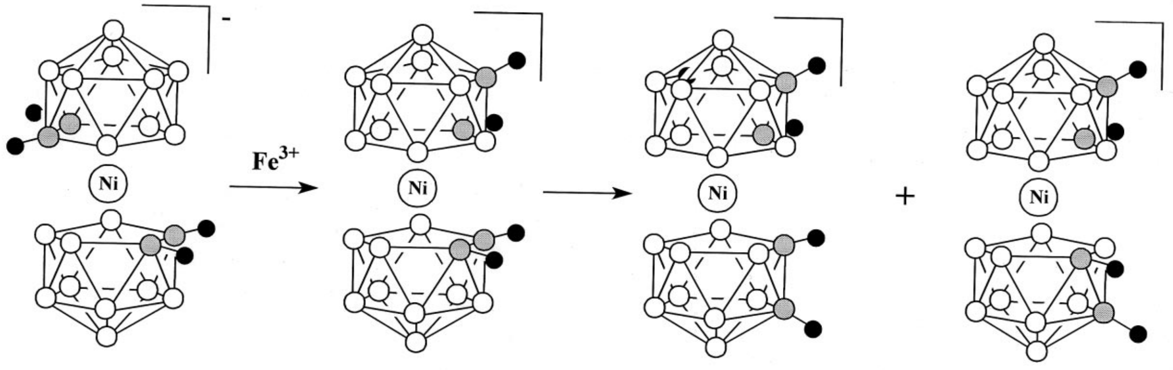
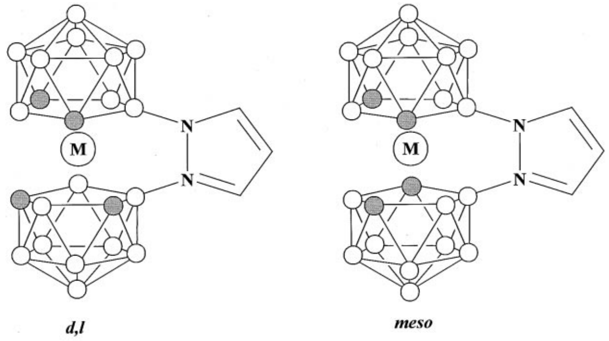


Fig. 1. C-bridged nickel and iron bis(1,2-dicarbollides).



11 **19** *meso* **21** *d,l*

Scheme 4. Oxidative rearrangement of $\{1,1',2,2'-Me_4-3,3-Ni(1,2-C_2B_9H_9)_2]$.



28 M = Ni **29**
58 M = Fe

Fig. 2. C-bridged nickel and iron bis(1,7-dicarbollides).

substituents at the carbon atoms and, as a consequence, results in the ligand rearrangement [25]. However, more recently a similar type of the dicarbollide rearrangement was found in the [1,2-Ph_2-3,3-$(PR_3)_2$-3,1,2-$NiC_2B_9H_9$] ($PR_3 = PEt_3$, PMe_2Ph; $(PR_3)_2$ = dppe) [51] and [(3-CO-1,2-Me_2-3,1,2-$NiC_2B_9H_9)_2$] complexes [52]. In the last complex, steric interactions between the methyl substituents at the carbon atoms of two the dicarbollide ligands are practically nullified. At the same time, no rearrangement was found in the [1,1′,2,2′-Et_4-3,3′-Co(1,2-$C_2B_9H_9)_2$]$^-$ complex [53], which is isoelectronic with [1,1′,2,2′-Me_4-3,3′-Ni(1,2-$C_2B_9H_9)_2$]. More probably, this type of rearrangement is characteristic for nickelacarboranes containing the [1,2-R_2-3,1,2-$NiC_2B_9H_9$] fragment.

The crystal structure of **19** has been determined by the single-crystal X-ray diffraction method. In each dicarbollide ligand the two carbon atoms of the icosahedral framework remain adjacent to each other. However, the ligands have different configurations. One of them has its two icosahedral carbon atoms in the bonding pentagonal face. The other one has only one carbon atom in the basal pentagonal face; the second icosahedral carbon of this ligand does not bond directly to the nickel atom. Two of the dicarbollide ligands are distinctly non-parallel: there is a dihedral angle of 14.8° between the pentagonal planes of the dicarbollide ligands [54].

Short heating a toluene or cyclooctane solution of **19** and **20** to boiling results in further rearrangement into [1,1′,2,2′-Me_4-4(5),4′(5′)-Ni(1,2-$C_2B_9H_9)_2$] (**21**) [25] and [1,2-1′,2′-di-μ-$(CH_2CH_2CH_2)_2$-4(5),4′(5′)-Ni(1,2-$C_2B_9H_9)_2$] (**22**) [47], respectively (Scheme 2). Compounds **19** and **20** exist as a DL enantiomeric mixture whereas **21** and **22** may exhibit both DL and *meso* forms. Activation parameters for the polyhedral rearrangements [1,1′,2,2′-Me_4-3,3′-Ni(1,2-$C_2B_9H_9)_2$] → **19** → **21** and [1′,2′-di-μ-$(CH_2CH_2CH_2)_2$-3,3′-Ni(1,2-$C_2B_9H_9)_2$] → **20** → **22** have been calculated [47].

The nickel(III) metallacarboranes [1,1′,2,2′-Me_4-3,4′(5′)-Ni(1,2-$C_2B_9H_9)_2$]$^-$ (**23**) and [1,1′,2,2′-Me_4-4(5),4′(5′)-Ni(1,2-$C_2B_9H_9)_2$]$^-$ (**24**) can be obtained by the borohydride reduction of the corresponding nickel(IV) complexes [25].

The [1,1′,2,2′-Me_4-3,4′-Ni(1,2-$C_2B_9H_9)_2$]$^-$ and [1,1′,2,2′-Me_4-3,5′-Ni(1,2-$C_2B_9H_9)_2$]$^-$ enantiomers were separated by fraction crystallization as the *d-N,N,N*-trimethyl-α-phenylethylammonium salts. Their oxidation with iodine gives the corresponding nickel(IV) enantiomers with the change of the rotation direction to opposite one. Further thermal isomerization of the nickel(IV) enantiomers results in the corresponding enantiomeric and *meso* forms of **21**, which can be separated chromatographically [25].

The **14**∗Bipy and **15**∗Bipy complexes were prepared by the direct electrochemical synthesis from the corresponding *o*-carboranes on nickel anode in the presence of 2,2′-bipyridyl [36].

2.5. *B-substituted derivatives*

Chemistry of boron-substituted derivatives of nickel bis(dicarbollides) has seen very little development. The reaction of **1** with formaldehyde in strongly acidic medium gives [8-CH_3O-3,3′-Ni(1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)] (**25**) and [8,8′-$(CH_3O)_2$-3,3′-Ni(1,2-$C_2B_9H_{10})_2$] (**26**) isolated in **15** and 18% yield, respectively [55]. The crystal molecular structure of **26** has been determined by the single-crystal X-ray diffraction method. The substituted dicarbollide ligands are rotated by ca. 112° about their centroid–centroid axis from the position in which the methoxy groups are eclipsed, adopting *gauche* conformation [56].

The reaction of **2** with two equivalents of HgO in refluxed trifluoroacetic acid followed by the treatment with sodium chloride gives [$(ClHg)_2$-3,3′-Ni(1,2-$C_2B_9H_{10})_2$] (**27**) [57].

An original approach to the synthesis of bridged boron-substituted derivatives of nickel bis(1,7-dicarbollide) was proposed by Hawthorne et al. The reaction of 2 equivalents of *closo*-1,8-$C_2B_9H_{11}$ with sodium salt of pyrazole in benzene gives the mixture of [10,10′-μ-1,2-(1,2-$N_2C_3H_3$)-(*nido*-7,9-$C_2B_9H_{10})_2$]$^-$ and [10,11′-μ-1,2-(1,2-$N_2C_3H_3$)-(*nido*-7,9-$C_2B_9H_{10})_2$]$^-$ (DL- and *meso*-isomers, respectively). The reaction of this mixture with $NiCl_2$ in alkaline aqueous solution gives the corresponding mixture of [6,6′-μ-1,2-(1,2-$N_2C_3H_3$)-2,2′-Ni(1,7-$C_2B_9H_{10})_2$] (**28**) (DL-isomer) and [6,11′-μ-1,2-(1,2-$N_2C_3H_3$)-2,2′-Ni(1,7-$C_2B_9H_{10})_2$] (**29**) (*meso*-isomer) (Fig. 2) that can be separated by preparative TLC techniques or by column chromatography [58]. The molecular structures of **28** and **29** were determined from the single-crystal X-ray diffraction experiments. Due to the tight bridging of the planar pyrazole moiety, the bonding faces of the dicarbollide ligands are eclipsed. The angles between normals to the two bonding planes are 10.4° [58].

3. Iron bis(dicarbollides)

3.1. Iron bis(1,2-dicarbollides). Synthesis and properties

The classical approach to the synthesis of the red paramagnetic [3,3′-Fe(1,2-$C_2B_9H_{11}$)$_2$]$^-$ anion (**30**) ($\mu_{eff} = 2.10$ μB) consists in the partial degradation of *ortho*-carborane with base into *nido*-[7,8-$C_2B_9H_{12}$]$^-$ followed by its deprotonation to the [7,8-$C_2B_9H_{11}$]$^{2-}$ dianion and reaction with ferrous chloride. Usually the dicarbollide dianion is generated in situ by the treatment of *nido*-[7,8-$C_2B_9H_{12}$]$^-$ with sodium hydride in tetrahydrofuran [1,11] (61% yield as the tetramethylammonium salt), or with sodium in dimethyl sulfoxide [59] (19% as the cesium salt), or with sodium hydroxide in aqueous solution [11] (56% yield as the cesium salt). Compound **30** was also prepared in 62% yield as the tetramethylammonium salt by the solid-state mechanochemical reaction of Tl_2[7,8-$C_2B_9H_{11}$] with $FeCl_3$ [60,61]. The best method giving up to 98% yield of **30** as the tetramethylammonium salt is the electrolysis of a solution of K[7,8-$C_2B_9H_{12}$] in dimethyl sulfoxide on the iron anode [59,62].

The crystal molecular structure of the *N*-methyl-4-methylpyridinium salt ((4-MeC_5H_4NMe)[3,3′-Fe(1,2-$C_2B_9H_{11}$)$_2$] has been determined by the single-crystal X-ray diffraction method [40]. The [3,3′-Fe(1,2-$C_2B_9H_{11}$)$_2$]$^-$ anion has the sandwich structure with the dicarbollide ligands in the *transoid* arrangement. The [3,3′-Fe(1,2-$C_2B_9H_{11}$)$_2$]$^-$ anion was also characterized by the methods of UV [1,11], IR [11], Raman [23], NMR [16], ESR [16,63], Mössbauer [64,65], and X-ray [17] spectroscopy, and magnetic susceptibility measurements [66].

At present, a number of salts of the [3,3′-Fe(1,2-$C_2B_9H_{11}$)$_2$]$^-$ anion with various metal (Na^+, K^+, Cs^+, Rb^+, Ca^{2+}, Cu^+, Ag^+) and ammonium (NH_4^+, $Me_2NH_2^+$, Me_3NH^+, Me_4N^+, Et_3NH^+ [67], Et_4N^+, *n*-$BuNH_3^+$, *t*-$BuNH_3^+$, Bu_4N^+, $PhNH_3^+$, piperidinium, pyridinium, *N*-methylpyridinium [40], *N*-methyl-4-methylpyridinum [40], *N*-methyl-4-phenylpyridinium [40], *N*-methylquinolinium [40], mono-, di-, and triethanolammonium) cations, as well as with protonated amino acids, such as L-ornitine, were prepared [68]. In addition, the synthesis of various complexes of **30**, such as Na[3,3′-Fe(1,2-$C_2B_9H_{11}$)$_2$]*2Phen [69], Fe[3,3′-Fe(1,2-$C_2B_9H_{11}$)$_2$]$_2$*4Phen [69], M[3,3′-Fe(1,2-$C_2B_9H_{11}$)$_2$]$_2$*4Bipy (M = Ni, Co, Mn, Cu) [6], [$Fe^{III}Cp_2$][3,3′-Fe^{III}(1,2-$C_2B_9H_{11}$)$_2$] [40], [$Fe^{III}Cp^*_2$][3,3′-Fe^{III}(1,2-$C_2B_9H_{11}$)$_2$] [39], [Fe^{III}(hydrotris(pyrazolyl)borate)$_2$][3,3′-Fe^{III}(1,2-$C_2B_9H_{11}$)$_2$] [40], [Fe^{III}{(*p*-OC_6H_4C(Me)=N(CH_2)$_2$NH(CH_2)$_2$)$_2$}][3,3′-Fe^{III}(1,2-$C_2B_9H_{11}$)$_2$] [40], [Mo_3(μ_3-S)(μ_2-S)$_3$(Et_2NCS_2)$_3$][3,3′-Fe^{III}(1,2-$C_2B_9H_{11}$)$_2$] [7] were been described.

The crystal structure of [$Fe^{III}Cp^*_2$][3,3′-Fe^{III}(1,2-$C_2B_9H_{11}$)$_2$] has been determined by the single-crystal X-ray diffraction method. As in the case of [$Fe^{III}Cp^*_2$][3,3′-Ni^{III}(1,2-$C_2B_9H_{11}$)$_2$], two dicarbollide ligands are twisted with respect to each other by approximately 109°, adopting *gauche* conformation [39].

The tetrathiafulvalenium complex [ttf][3,3′-Fe(1,2-$C_2B_9H_{11}$)$_2$] was prepared and characterized by the X-ray diffraction method. As in the case of the [ttf][3,3′-Ni(1,2-$C_2B_9H_{11}$)$_2$] complex, the dicarbollide ligands adopt *cisoid* conformation [33].

Reduction of **30** with sodium amalgam in aqueous acetone in inert atmosphere results in the pink diamagnetic iron(III) metallacarborane [3,3′-Fe(1,2-$C_2B_9H_{11}$)$_2$]$^{2-}$ anion (**31**), which is oxidized by air slowly in the solid state and moderately fast in a solution to the parent [3,3′-Fe(1,2-$C_2B_9H_{11}$)$_2$]$^-$ anion [11]. The oxidation is greatly accelerated by the addition of a small amount of ferric ion. Compund **31** can be converted to **30** also by the addition of $CuCl_2$ [68].

The crystal molecular structure of (Me_4N)$_2$[3,3′-Fe(1,2-$C_2B_9H_{11}$)$_2$] has been determined by the method of single-crystal X-ray diffraction [70]. The [3,3′-Fe(1,2-$C_2B_9H_{11}$)$_2$]$^{2-}$ anion consists of two 1,2-dicarbollide units sandwiched around a formal Fe^{2+} ion. The bonding faces of the dicarbollide ligands are staggered approaching *transoid* configuration. The similar structure of the ferracarborane cage was found in [Cp^*_2ThMe]$_2$[3,3′-Fe(1,2-$C_2B_9H_{11}$)$_2$] [67]. In this complex each thorium center is coordinated to the B(8)–B(9)–B(12) triangles of the dicarbollide ligands, with Th···H–B distances ranging from 2.42(3) to 2.67(4) Å. The [3,3′-Fe(1,2-$C_2B_9H_{11}$)$_2$]$^{2-}$ anion was also characterized by the methods of UV [11,21], NMR [11], and Mössbauer [65] spectroscopy.

The addition of concentrated hydrochloric or perchloric acids to a solution of Cs_2[3,3′-Fe(1,2-$C_2B_9H_{11}$)$_2$] in anhydrous methanol results in formation of the orange protonated form [H-3,3′-Fe(1,2-$C_2B_9H_{11}$)$_2$]$^-$ (**32**), which was isolated as the triphenylmethylphosphonium salt [71].

3.2. Iron bis(1,7-dicarbollide)

The chemistry of iron bis(1,7-dicarbollide) has been studied to a lesser extent. The [2,2′-Fe(1,7-$C_2B_9H_{11}$)$_2$]$^-$ anion (**33**) was prepared in 21% yield by the electrolysis of a solution of K[7,9-$C_2B_9H_{12}$] in dimethyl sulfoxide on the iron anode and characterized by the IR spectroscopy method [59].

3.3. C-substituted derivatives

A number of carbon-substituted derivatives of the [3,3′-Fe(1,2-$C_2B_9H_{11}$)$_2$]$^-$ anion were synthesized from the corresponding *C*-substituted *ortho*-carboranes via their degradation into the *nido*-7,8-dicarbaundecaborates followed by the deprotonation with sodium hydride in tetrahydrofuran and the reaction with anhydrous ferrous chloride. $[1,1',2,2'\text{-Me}_4\text{-}3,3'\text{-Fe}(1,2\text{-C}_2B_9H_9)_2]^-$ (**34**) [11], $[1,1'\text{-Ph}_2\text{-}3,3'\text{-Fe}(1,2\text{-C}_2B_9H_{10})_2]^-$ (**35**) [11], $[1,1'\text{-}(3\text{-FC}_6H_4)_2\text{-}3,3'\text{-Fe}(1,2\text{-C}_2B_9H_{10})_2]^-$ (**36**) [49], $[1,1'\text{-}(4\text{-FC}_6H_4)_2\text{-}3,3'\text{-Fe}(1,2\text{-C}_2B_9H_{10})_2]^-$ (**37**) [49], and $[1,1'\text{-}(2\text{-C}_4H_3S)_2\text{-}3,3'\text{-Fe}(1,2\text{-C}_2B_9H_{10})_2]^-$ (**38**) [72] were prepared by this way. The attempted preparation of the carbon-substituted derivatives using sodium hydroxide in aqueous solution was unsuccessful.

The same approach was used to synthesize ferracarboranes containing *C*-bridged dicarbollide ligands $[1,1'\text{-}\mu\text{-}(CH_2)_4\text{-}3,3'\text{-Fe}(1,2\text{-C}_2B_9H_{10})_2]^-$ (**39**) and $[1,1'\text{-}\mu\text{-}\{TsN(CH_2CH_2)_2\}\text{-}3,3'\text{-Fe}(1,2\text{-C}_2B_9H_{10})_2]^-$ (**40**) (Fig. 1) [50]. The crystal structure of $(Ph_3PMe)[1,1'\text{-}\mu\text{-}(CH_2)_4\text{-}3,3'\text{-Fe}(1,2\text{-C}_2B_9H_{10})_2]$ has been determined by the single-crystal X-ray diffraction method. The C_2B_3 faces of the dicarbollide ligands in **39** were found to be not parallel, being inclined by 8.7(3)° to each other (in comparison with ca. 3° in **30**) [50].

A series of the **38** complexes with organosulfur cation-radicals, such as tetrathiafulvalenium ($ttf^{\bullet+}$) and bis(ethylenedithio)tetrathiafulvalenium ($et^{\bullet+}$), $[ttf][1,1'\text{-}(2\text{-C}_4H_3S)_2\text{-}3,3'\text{-Fe}(1,2\text{-C}_2B_9H_{10})_2]$ [72,73], $[ttf]_5[1,1'\text{-}(2\text{-C}_4H_3S)_2\text{-}3,3'\text{-Fe}(1,2\text{-C}_2B_9H_{10})_2]$ [72,73], and $[et]_2[1,1'\text{-}(2\text{-C}_4H_3S)_2\text{-}3,3'\text{-Fe}(1,2\text{-C}_2B_9H_{10})_2]$ [74] were synthesized. The crystal structures of $[ttf][1,1'\text{-}(2\text{-C}_4H_3S)_2\text{-}3,3'\text{-Fe}(1,2\text{-C}_2B_9H_{10})_2]*C_6H_5Me$, $[ttf]_5[1,1'\text{-}(2\text{-C}_4H_3S)_2\text{-}3,3'\text{-Fe}(1,2\text{-C}_2B_9H_{10})_2]$, and $[et]_2[1,1'\text{-}(2\text{-C}_4H_3S)_2\text{-}3,3'\text{-Fe}(1,2\text{-C}_2B_9H_{10})_2]$ have been determined. In the all structures, **38** was found to be the DL form. The dicarbollide ligands in **38** are partially eclipsed in a *cisoid* configuration with the bonding C_2B_3 faces rotated by ca. 89° from the position in which the thiophen-2-yl groups are eclipsed.

The carbon-substituted derivatives of **30** can be easily converted into the corresponding iron(II) metallacarboranes by the reduction with sodium amalgam: $[1,1',2,2'\text{-Me}_4\text{-}3,3'\text{-Fe}(1,2\text{-C}_2B_9H_9)_2]^{2-}$ (**41**) [11], $[1,1'\text{-Ph}_2\text{-}3,3'\text{-Fe}(1,2\text{-C}_2B_9H_{10})_2]^{2-}$ (**42**) [11], $[1,1'\text{-}(3\text{-FC}_6H_4)_2\text{-}3,3'\text{-Fe}(1,2\text{-C}_2B_9H_{10})_2]^{2-}$ (**43**) [49], and $[1,1'\text{-}(4\text{-FC}_6H_4)_2\text{-}3,3'\text{-Fe}(1,2\text{-C}_2B_9H_{10})_2]^{2-}$ (**44**) [49] were prepared in this way.

In contrast with unsubstituted **30**, which is stable toward strong mineral acids and bases, the carbon-substituted derivatives are degraded in aqueous potassium hydroxide at the reflux temperature [11].

3.4. B-substituted derivatives

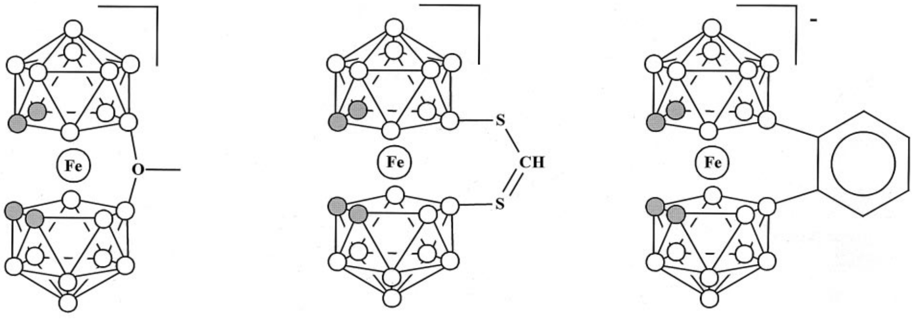
The chemistry of boron-substituted derivatives of iron bis(dicarbollides) has received more development than the chemistry of boron-substituted nickel bis(dicarbollides), but is much less studied than the chemistry of boron-substituted cobalt bis(dicarbollides) [3]. There are two general approaches to synthesis of B-substituted iron bis(dicarbollides). The first one consists of the introduction of a substituent in the metallacarborane cage under electrophilic conditions (substitution at the position 8 of the dicarbollide ligand). The second approach includes preparation of substituted *nido*-carboranes followed by their deprotonation and reaction with ferrous chloride.

Chlorination of **30** gives $[8,8'\text{-Cl}_2\text{-}3,3'\text{-Fe}(1,2\text{-C}_2B_9H_{10})_2]^-$ (**45**). The crystal molecular structure of $K[8,8'\text{-Cl}_2\text{-}3,3'\text{-Fe}(1,2\text{-C}_2B_9H_{10})_2]$ has been determined by the single-crystal X-ray diffraction method. The dicarbollide ligands in **45** have *transoid* conformation [75].

Reaction of **30** with formaldehyde in the presence of hydrochloric acid gives the methoxy-bridged neutral derivative $[8,8'\text{-}\mu\text{-MeO-}3,3'\text{-Fe}(1,2\text{-C}_2B_9H_{10})_2]$ (**46**). The structure of **46** has been determined by single-crystal X-ray diffraction. The dicarbollide ligands in **46** are linked via the oxygen atom of the methoxy group. The pentagonal planes of the ligands are inclined at an angle of 31.2(5)° due to the short oxygen bridge between the ligands [76].

The treatment of a suspension of $(Ph_3PMe)[3,3'\text{-Fe}(1,2\text{-C}_2B_9H_{11})_2]$ in diethyl sulfide with anhydrous hydrogen chloride gives a mixture of the neutral iron(II) $[8,8'\text{-}(Et_2S)_2\text{-}3,3'\text{-Fe}(1,2\text{-C}_2B_9H_{10})_2]$ (**47**) and iron(III) $[8\text{-Et}_2S\text{-}3,3'\text{-Fe}(1,2\text{-C}_2B_9H_{10})(1',2'\text{-C}_2B_9H_{11})]$ (**48**)complexes [71]. Compound **48** was also obtained by the oxidation of the corresponding iron(II) complex $[8\text{-Et}_2S\text{-}3,3'\text{-Fe}(1,2\text{-C}_2B_9H_{10})(1',2'\text{-C}_2B_9H_{11})]^-$ (**49**) (prepared by the reaction of **33** and diethylsulfide) with anhydrous ferric chloride in dichloromethane [71]. The $[8\text{-Me}_2S\text{-}3,3'\text{-Fe}(1,2\text{-C}_2B_9H_{10})(1',2'\text{-C}_2B_9H_{11})]^-$ complex **50** was prepared by the reaction of **33** and dimethylsulfide [71].

A number of neutral iron(II) bis(dicarbollides) based on 'charge-compensated' dicarbollide ligands of the general type $[LC_2B_9H_{10}]^-$, where L is a $2e^-$ function, e.g. SMe_2, NEt_3, pyridine, etc., have been prepared. The $[8,8'\text{-}(Me_2S)_2\text{-}3,3'\text{-Fe}(1,2\text{-C}_2B_9H_{10})_2]$ complex **51** was prepared based on the charge-compensated *nido*-$[10\text{-Me}_2S\text{-}7,8\text{-C}_2B_9H_{11}]$ and its structure was determined using the single-crystal X-ray diffraction method. The dicarbollide ligands in **51** were found to adopt *gauche* configuration [77]. The $[4,4'(7')\text{-}(Me_2S)_2\text{-}3,3'\text{-Fe}(1,2\text{-C}_2B_9H_{10})_2]$ complex was synthesized based on the charge-compensated *nido*-$[9\text{-Me}_2S\text{-}7,8\text{-C}_2B_9H_{10}]$. The mixture of $[4,4'\text{-}(Me_2S)_2\text{-}3,3'\text{-Fe}(1,2\text{-C}_2B_9H_{10})_2]$ (*meso*-form) (**52**) and $[4,7'\text{-}(Me_2S)_2\text{-}3,3'\text{-Fe}(1,2\text{-C}_2B_9H_{10})_2]$ (DL form) (**53**) was separated by fraction crystallization from acetone [78]. Structures of **52** [79] and **53** [78] have been determined by the single-crystal X-ray diffraction method. The dicarbollide ligands in the structure of **52** adopts a *transoid* conformation, whereas the C_2B_3 bonding faces of the dicarbollide ligands in **53** are staggered and in a *cisoid* configuration. The Me_2S substituents are oriented in a *gauche* configuration, corresponding to a rotation of ca. 104° of the C_2B_3 bonding faces about their centroid–centroid axis from the position in which the Me_2S groups are eclipsed [78].



46 **52** **54**

Fig. 3. B-bridged iron bis(1,2-dicarbollides).

Oxidation of **53** with *p*-benzoquinone results in the formation of the cationic iron(III) complex $[4,7'\text{-}(Me_2S)_2\text{-}3,3'\text{-}Fe(1,2\text{-}C_2B_9H_{10})_2]^+$ (**54**), which was isolated as the air- and moisture-stable hydrosulfate and *p*-tolylsulfate salts. Solutions of **54** are very sensitive, however, towards reduction by aqueous or alcoholic basic media and can be reduced even by heating in boiling methanol or ethanol [79]. Reaction of **53** with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone gives the 1:1 charge-transfer complex with the cationic metallacarborane part. The crystal structure of $[4,7'\text{-}(Me_2S)_2\text{-}3,3'\text{-}Fe(1,2\text{-}C_2B_9H_{10})_2]^+[ddq]^{\bullet -}$ was determined. The $[4,7'\text{-}(Me_2S)_2\text{-}3,3'\text{-}Fe(1,2\text{-}C_2B_9H_{10})_2]^+$ cation (**54**) adopts a staggered sandwich structure with the carbon atoms of the two dicarbollide cages in a *cisoid* arrangement. They are rotated by ca. 109° about their centroid-centroid axis from the position in which the Me_2S groups are eclipsed [78].

The neutral iron(II) complexes $[8,8'\text{-}(Et_3N)_2\text{-}3,3'\text{-}Fe(1,2\text{-}C_2B_9H_{10})_2]$ (**55**) and $[4,4'\text{-}(4\text{-}MeOC(O)C_5H_4N)_2\text{-}3,3'\text{-}Fe(1,2\text{-}C_2B_9H_{10})_2]$ (**56**) were synthesized based on the corresponding charge-compensated boron-substituted *nido*-C_2B_9 compounds. The crystal structure of **55** has been determined using the single-crystal X-ray diffraction method. The dicarbollide ligands in **55** were found to have gauche configuration. Since the triethylamine substituent apparently affects the geometry of the molecule, the bonding faces are not parallel to each other showing a dihedral angle of 14.0° [70].

The reaction of **30** with carbon disulfide in the presence of $AlCl_3$ and hydrogen chloride produces $[8,8'\text{-}\mu\text{-}(HCS_2)\text{-}3,3'\text{-}Fe(1,2\text{-}C_2B_9H_{10})_2]$ (**57**) (Fig. 3) [80].

The decomposition of unstable benzene diazonium salt $(PhN_2)[3,3'\text{-}Fe(1,2\text{-}C_2B_9H_{11})_2]$ in refluxed benzene results in the formation of the 1,2-phenylene-bridged derivative $[8,8'\text{-}\mu\text{-}(1,2\text{-}C_6H_4)\text{-}3,3'\text{-}Fe(1,2\text{-}C_2B_9H_{10})_2]^-$ (**59**) (Fig. 3) [81].

The $[6,6'(11')\text{-}(C_5H_5N)_2\text{-}2,2'\text{-}Fe(1,7\text{-}C_2B_9H_{10})_2]$ (**60**) [70] and $[6,11'\text{-}\mu\text{-}(pyrazol\text{-}1\text{-}yl\text{-}2\text{-}yliumyl)\text{-}2,2'\text{-}Fe(1,7\text{-}C_2B_9H_{10})_2]$ (DL-form) (**61**) (Fig. 2) [58] complexes were synthesized based on the corresponding boron-substituted charge-compensated *nido*-C_2B_9 compounds, which were prepared by the reductive addition of a nucleophile to [*closo*-1,8-$C_2B_9H_{11}$]. The crystal structure of **61** has been determined using the method of single-crystal X-ray diffraction. The angle between normals to the eclipsed bonding faces of the dicarbollide ligands was found to be 9.6(2)° [58].

4. Potential applications of nickel and cobalt bis(dicarbollides)

In spite of small knowledge on iron and nickel bis(dicarbollides), some of them demonstrated great potential as electron acceptor molecules and as building blocks for the synthesis of novel molecular materials, such as molecular conductors and ferromagnets [34,39,40,74], and as catalysts acting as weakly coordinating anions to stabilize highly reactive cationic intermediates [67]. Another possible area of practical application of iron and nickel bis(dicarbollides) is medicine, where they could be used as boron-rich elements for the design of agents for boron neutron capture therapy, and as carriers of radiometals for nuclear medicine.

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