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Synthesis and molecular structure of *closo*-3-(η^6-C_6H_6)-3,1,2-$FeC_2B_9H_{11}$ *

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Abstract

The mixed-sandwich complex, *closo*-3-(η^6-C_6H_6)-3,1,2-$FeC_2B_9H_{11}$ (**2**), has been prepared in high yield by the photolysis of *closo*-3,3,3-$(CO)_3$-3,1,2-$FeC_2B_9H_{11}$ (**1**) in benzene. The molecular structure of **2** has been determined by an X-ray diffraction study. Compound **2** crystallized in the orthorhombic space group *Pmcn* (standard setting *Pnma*) with *a* 7.693(1) Å, *b* 9.001(2) Å, *c* 18.420(3) Å, *V* 1276 Å^3, and $Z = 4$ (8 half molecules related by a mirror plane at $x = 1/4$). The structure was solved by heavy atom methods to a final discrepancy index of $R = 0.053$, $R_w = 0.067$ for 861 independent reflections.

Introduction

The recognition of the structural and electronic similarities between the dicarbollide anion and that of the cyclopentadienide anion [1] has resulted in the richly explored field of metallacarboranes. In the past decade, increasing interest has been expressed in the synthesis of (π-arene)metallacarboranes [2]. The reported routes to (η^6-arene) iron dicarbollide complexes [2a,b,g,n], have involved either reaction of an iron source with a carborane in the presence of an aromatic solvent, or the introduction of a bis(arene)iron salt to the dicarbollide anion. These methods are accompanied by low to moderate yields. Herein, we report the high yield synthesis and full structural characterization of a benzene-bound ferracarborane.

Results and discussion

Synthesis

Todd and co-workers [2b] reported the detection of a (π-arene) $FeC_2B_9H_{11}$ complex incorporating benzene from the reaction of a bis(benzene) iron salt with

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* This contribution is dedicated to Professor F.G.A. Stone, F.R.S., on the occasion of his sixty-fifth birthday and for his leadership in the development of organometallic chemistry.

$Tl^+[3,1,2\text{-}TlC_2B_9H_{11}]^-$ in THF. Since this benzene-complexed ferracarborane has also eluded isolation in the reaction of K[*nido*-7,8-$C_2B_9H_{12}$], ferric chloride, and triethylamine in benzene solution [2n], our strategy involved utilizing ligand substitution in a system containing a ferracarborane moiety in an effort to minimize the production of $[Fe^{III}(C_2B_9H_{11})_2]^-$ [1b], an undesired product formed using the methods described above.

Photolysis of *closo*-3,3,3-$(CO)_3$-3,1,2-$FeC_2B_9H_{11}$ (**1**) [3] in benzene resulted in the quantitative production of *closo*-3-(η^6-C_6H_6)-3,1,2-$FeC_2B_9H_{11}$ (**2**), as monitored by ^{11}B NMR. Compound **2** is a thermally stable neutral orange solid which can be easily isolated via removal of solvent. Although its solution showed color change and the presence of fine precipitates after exposure to air for one day, no signs of decomposition were observed in the solid state.

Prolonged refluxing of **1** in benzene resulted in the formation of trace amounts of **2**. Irradiation of **1** in tetrahydrofuran or diethyl ether in the presence of a three-fold excess of benzene afforded the known sandwich complex, $[Fe^{III}(C_2B_9H_{11})_2]^-$ which was identified by its paramagnetic ^{11}B NMR spectrum [1b].

The ^{11}B FT NMR spectrum of **2**, showing relative area ratios of 1 : 1 : 2 : 2 : 2 : 1, is consistent with an icosahedral geometry for the carborane cage found in other (η^6-arene)iron dicarbollide complexes [2b,n]. In the ^{1}H FT-NMR spectrum, the two singlets observed at δ 6.29 and 3.93 in an intensity ratio of 3 : 1 are assigned to the aromatic ring protons and the carboranyl CH, respectively. The exhibited upfield shift from free benzene is expected for the protons of a metal-complexed arene [4]. As an augmentation to this spectroscopic data, we also determined the molecular structure of **2**.

Structural analysis

The structure of **2**, displayed in Fig. 1, confirms the sandwich-type geometry with the iron atom flanked by an η^6-benzene ring and the open C_2B_3 face of the

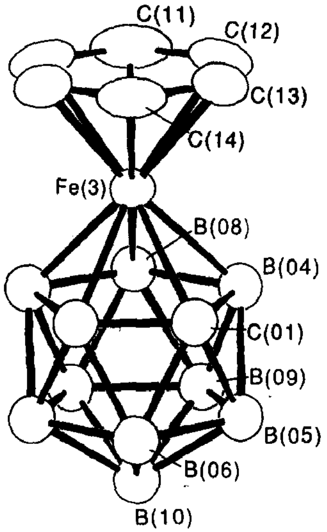

Fig. 1. Molecular structure of *closo*-3-(η^6-C_6H_6)-3,1,2-$FeC_2B_9H_{11}$ (**2**) showing the atom-labeling scheme. All hydrogen atoms have been omitted for clarity.

Table 1

Selected interatomic distances and angles for **2** [a]

*Distances/*Å			
Fe(3)–C(01)	2.037(5)	Fe(3–C(11)	2.085(8)
Fe(3)–C(12)	2.091(6)	Fe(3)–B(04)	2.106(6)
Fe(3)–C(13)	2.111(6)	Fe(3)–C(14)	2.112(8)
Fe(3)–B(08)	2.143(8)	B(08)–B(04)	1.783(8)
B(08)–B(09)	1.786(9)	C(11)–C(12)	1.399(8)
C(14)–C(13)	1.372(8)	B(10)–B(06)	1.753(13)
B(10)–B(05)	1.768(8)	B(10)–B(09)	1.782(9)
B(06)–C(01)	1.739(9)	B(06)–B(05)	1.753(8)
C(01)–C(01)*	1.602(10)	C(01)–B(05)	1.703(7)
C(01)–B(04)	1.717(7)	C(12)–C(13)	1.409(9)
B(09)–B(05)	1.764(8)	B(09)–B(09)*	1.771(12)
B(09)–B(04)	1.785(8)	B(04)–B(05)	1.801(8)
*Bond angles/*deg			
C(01)–Fe(3)–C(01)*	46.31(28)	C(01)–Fe(3)–C(11)	156.07(15)
C(01)–Fe(3)–C(12)	164.02(26)	C(01)–Fe(3)–C(12)*	120.49(26)
C(01)–Fe(3)–B(04)	48.95(20)	C(01)–Fe(3)–B(04)*	83.14(21)
C(01)–Fe(3)–C(13)	126.77(24)	C(01)–Fe(3)–C(13)*	98.77(22)
C(01)–Fe(3)–C(14)	102.03(25)	C(01)–Fe(3)–B)08)	82.82(26)
C(11)–Fe(3)–B(04)	110.79(23)	C(11)–Fe(3)–C(13)	70.82(25)
C(11)–Fe(3)–C(14)	83.13(33)	C(11)–Fe(3)–B(08)	91.58(33)
C(12)–Fe(3)–C(12)*	70.53(40)	C(12)–Fe(3)–B(04)	146.37(28)
C(12)–Fe(3)–B(04)*	92.51(24)	C(12)–Fe(3)–C(13)*	83.11(24)
C(12)–Fe(3)–C(14)	69.75(26)	C(12)–Fe(3)–B(08)	106.05(27)
C(12)–Fe(3)–B(04)	146.37(28)	C(12)–Fe(3)–C(14)	69.75(26)
B(04)–Fe(3)–B(04)*	86.19(32)	B(04)–Fe(3)–C(13)	170.43(26)
B(04)–Fe(3)–C(13)*	102.18(25)	B(04)–Fe(3)–C(14)	132.53(19)
B(04)–Fe(3)–B(08)	49.63(19)	C(13)–Fe(3)–C(13)*	69.12(37)
C(13)–Fe(3)–B(08)	139.81(23)	C(14)–Fe(3)–B(08)	174.71(31)
B(04)–B(08)–B(04)*	107.54(57)	B(04)–B(08)–B(09)	107.47(50)
B(04)–B(08)–B(09)*	60.02(32)	B(04)–B(08)–Fe(3)	64.10(31)
B(09)–B(08)–B(09)*	59.45(46)	B(09)–B(08)–Fe(3)	116.69(42)
C(12)–C(11)–C(12)*	119.29(80)	C(12)–C(11)–Fe(3)	70.64(42)
C(13)–C(14)–C(13)*	121.68(83)	C(13)–C(14)–Fe(3)	71.03(41)
B(06)–B(10)–B(05)	59.70(33)	B(06)–B(10)–B(09)	107.82(53)
B(05)–B(10)–B(05)*	106.32(59)	B(05)–B(10)–B(09)	106.79(52)
B(05)–B(10)–B(09)	59.58(33)	B(09)–B(10)–B(09)*	59.58(46)
C(01)–B(06)–C(01)*	54.84(42)	C(01)–B(06)–B(05)	58.38(32)
C(01)–B(06)–B(05)*	102.66(51)	C(01)–B(06)–B(10)	104.76(53)
B(05)–B(06)–B(05)*	107.65(61)	B(05)–B(06)–B(10)	60.56(33)
C(01)*–C(01)–B(05)	111.13(27)	C(01)*–C(01)–B(04)	111.80(26)
C(01)*–C(01)–B(06)	62.58(21)	C(01)*–C(01)–Fe(3)	66.85(14)
B(05)–C(01)–B(04)	63.57(31)	B(05)–C(01)–B(06)	61.21(33)
B(05)–C(01)–Fe(3)	125.55(33)	B(04)–C(01)–B(06)	114.74(43)
B(04)–C(01)–Fe(3)	67.62(27)	B(06)–C(01)–Fe(3)	125.64(32)
C(11)–C(12)–C(13)	119.98(63)	C(11)–C(12)–Fe(3)	70.21(44)
C(13)–C(12)–Fe(3)	71.20(33)	C(14)–C(13)–C(12)	119.54(66)
C(14)–C(13)–Fe(3)	71.07(42)	C(12)–C(13)–Fe(3)	69.61(33)
B(05)*–B(09)–B(09)*	107.46(28)	B(05)*–B(09)–B(10)	59.80(33)
B(05)*–B(09)–B(04)*	61.00(32)	B(05)*–B(09)–B(08)	108.67(45)
B(09)*–B(09)–B(10)	60.21(23)	B(09)*–B(09)–B(04)*	108.05(27)
B(09)*–B(09)–B(08)	60.28(23)	B(10)–B(09)–B(04)*	109.36(44)
B(10)–B(09)–B(08)	109.31(43)	B(04)*–B(09)–B(08)	59.92(33)

Table 1 (Continued)

C(01)–B(04)–B(08)	104.37(42)	C(01)–B(04)–B(09)	103.09(39)
C(01)–B(04)–B(05)	57.82(31)	C(01)–B(04)–Fe(3)	63.43(25)
B(08)–B(04)–B(09)	60.06(37)	B(08)–B(04)–B(05)	107.12(45)
B(08)–B(04)–Fe(3)	66.27(32)	B(09)* –B(04)–B(05)	58.91(32)
B(09)* –B(04)–Fe(3)	118.59(36)	B(05)–B(04)–Fe(3)	116.63(36)
C(01)–B(05)–B(06)	60.41(39)	C(01)–B(05)–B(09)*	104.61(40)
C(01)–B(05)–B(10)	105.68(43)	C(01)–B(05)–B(04)	58.61(31)
B(06)–B(05)–B(09)*	108.68(44)	B(06)–B(05–B(10)	59.74(41)
B(06)–B(05)–B(04)	109.97(48)	B(09)* –B(05)–B(10)	60.62(38)
B(09)–B(05)–B(04)	60.09(31)	B(10)–B(05)–B(04)	109.29(47)

[a] Asterisks denote position related to tabulated positions by $1/2-x$, y, z.

carborane cage. Unlike the structurally characterized complexes of the (π-arene)$FeC_2B_9H_{11}$ (arene = toluene [2n], xylene [2n], mesitylene [2b]) series, **2** possesses mirror symmetry in which the cage atoms, Fe, B(06), B(08), and B(10), and the arene carbons, C(11) and C(14), lie on a crystallographic mirror plane. The C_2B_3 bonding face and the benzene ring are essentially planar with no deviation from the least-squares plane by more than 0.026 Å and 0.001 Å, respectively. The iron atom bonds symmetrically to the C_2B_3 plane with a Fe–C_2B_3 face (centroid) distance [5] of 1.487 Å. The iron atom is also centered over the arene ring at a distance of 1.571 Å from the C_6 plane [6]. The C_2B_3 and C_6 planes are almost parallel with an dihedral angle [7] of 2.1°. The average Fe–C (arene) distance of 2.100 Å is similar to other *closo*-FeC_2B_9 arene complexes [8]. Selected interatomic distances and angles are listed in Table 1.

An interesting feature of this structure is the orientation of the C_6 ring with respect to the carborane ligand. Figure 2, the projection of the benzene ring and the Fe onto the carborane C_2B_3 plane, shows the rings oriented in a symmetrical fashion relative to each other. The C_6 ring is staggered with respect to the carboranyl carbon–carbon edge and nearly eclipsed to the boron edges (B(04)–B(08)). The other possible symmetrical arrangement calls for the benzene ring to be

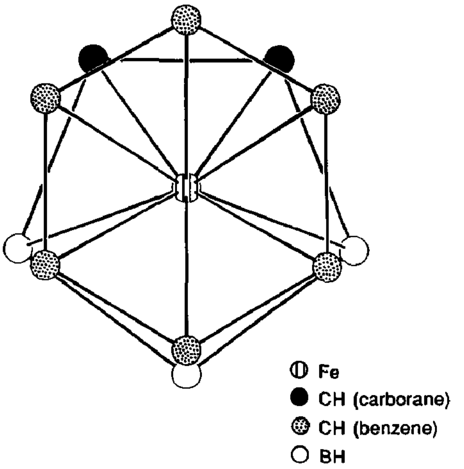

Fig. 2. Projection of benzene ring onto carborane C_2B_3 plane.

eclipsed with respect to the carboranyl C–C edge. Since **2** is found to crystallize only in the staggered geometry, it appears that this conformation is favored by offering a means of minimizing the energy of interaction.

Experimental section

All manipulations were carried out under an argon or dinitrogen atmosphere employing standard Schlenk techniques [9]. All solvents were reagent grade and distilled from appropriate drying agents [10]. Details of the preparation of *closo*-3,3,3-$(CO)_3$-3,1,2-$FeC_2B_9H_{11}$ (**1**) and related chemistry will be reported separately [3].

Photochemical experiments were carried out using a Hanovia 550 W medium pressure mercury lamp. Solutions to be irradiated were placed in pyrex Schlenk tubes supported four inches away from the light source.

^1H FT NMR spectra were recorded on a Bruker AF-200 (200.133 MHz) spectrometer. ^{11}B NMR spectra were obtained on a Bruker AM-500 FT-NMR spectrometer at 160.463 MHz. Proton and boron chemical shifts were referenced to residual solvent protons (CD_2Cl_2, 5.32 ppm) and external $BF_3 \cdot OEt_2$, respectively. All chemical shifts downfield of the reference are designated as positive. Infrared spectra were recorded as nujol mulls (NaCl) on a Beckman FT-1100 instrument. Elemental analyses were performed by Analytische Laboratorien, Gummersbach, F.R.G.

Preparation of closo-3-(η^6-C_6H_6)-3,1,2-$FeC_2B_9H_{11}$ (2)

A yellow solution of 0.150 g of **1** (0.55 mmol) in 45 mL of benzene was photolyzed (using the light source described above) for 17 h. The solution was reduced in volume and the resultant orange precipitate was collected, dried and recrystallized from CH_2Cl_2 by addition of heptane to yield 0.130 g of **2** (0.49 mmol, 89% yield). Anal. Calcd for $C_8H_{17}B_9Fe$: C, 36.07; H, 6.45; B, 36.52; Fe, 20.97. Found: C, 35.92; H, 6.30; B, 36.25; Fe, 20.70. IR (cm^{-1}): 2547 (B–H). ^1H NMR (ppm, CD_2Cl_2): 6.29 (s, 6H, aromatic protons), 3.93 (s, 2H, carboranyl CH). $^{11}B\{^1H\}$ NMR (ppm, THF): 2.7, 0.4, −7.0, −9.6, −18.9, −24.6 (1 : 1 : 2 : 2 : 2 : 1).

Collection and reduction of X-ray data for 2

An amber-brown air-stable crystal, obtained from the slow cooling of a hot benzene solution containing **2**, was mounted on a thin glass fiber on Picker FACS-1 diffractometer modified by Professor C.E. Strouse of this department. Systematic absences were found for $h0l$ reflections for which $l \neq 2n$ and for $hk0$ reflections for which $h + k \neq 2n$. Unit cell parameters were determined from a least-squares fit of 23 accurately centered reflections ($9.6° < 2\theta < 20.0°$). These dimensions and other parameters, including conditions of data collection, are summarized in Table 2. Data were collected at 25 °C in the θ–2θ scan mode. Three intense reflections (2 −2 0), (2 3 −1), and (0 1 −8) were monitored every 97 reflections to check stability. Intensities of these reflections decayed less than 1% during the course of the experiment (15.4 hours). Of the 1207 unique reflections measured, 861 were considered observed ($I > 3\sigma(I)$) and were used in the subsequent structure analysis. Data were corrected for Lorentz, polarization, and absorption effects. Programs used in this work include locally modified versions of the programs listed in the reference section [11].

Table 2

Details of the crystallographic data collection for **2**

Temperature/C	25
Crystal size/mm	$0.16 \times 0.32 \times 0.16$
Normal to faces	010 100 $01-1$
Appearance	Amber-brown fragment
Radiation (graphite monochromator)	Mo-K_α
Wavelength/Å	0.7107
Space group	*Pmcn* (standard setting *Pnma*)
a/Å	7.693(1)
b/Å	9.001(2)
c/Å	18.420(3)
V/Å^3	1276
Z	4
ρ(calcd)/g cm^{-3}	1.39
μ/cm^{-1}	11.4 [a]
Scan width, below K_{α_1}	1.3
above K_{α_2}	1.6
Scan rate/deg min^{-1}	4.5
Number of unique reflections	1207
Number of observed ($I > 3\sigma(I)$) reflections	861
2θ max/deg	50
Data collected	$+h$, $+k$, $+l$
Number of parameters refined	62
R, R_w, GOF	0.053, 0.067, 1.97

[a] Psiscan correction used.

Solution and refinement of the structure of 2

Atoms were located by use of the heavy atom method. All calculations were performed on the VAX 11/750 crystallographic computer. Hydrogen atoms were included in located positions with isotropic B assigned to be 4.0 Å^2. Anisotropic thermal parameters were refined for Fe and arene C. Scattering factors for H were

Table 3

Positional and equivalent isotropic thermal parameters for 2 [a]

Atom	x	y	z	$10^4\ U$/Å^2
Fe(3)	0.2500	0.2901(1)	0.4029(1)	332(6)
B(08)	0.2500	0.5275(9)	0.4116(5)	380(20)
C(11)	0.2500	0.2664(9)	0.5155(5)	661(62)
C(14)	0.2500	0.0555(9)	0.4049(5)	572(53)
B(10)	0.2500	0.6136(10)	0.2593(5)	404(20)
B(06)	0.2500	0.4264(10)	0.2330(5)	427(21)
C(01)	0.1459(6)	0.3337(5)	0.3035(3)	397(13)
C(12)	0.4069(9)	0.2127(7)	0.4875(3)	674(42)
C(13)	0.4057(9)	0.1060(7)	0.4315(3)	608(39)
B(09)	0.3651(8)	0.6274(6)	0.3430(3)	397(13)
B(04)	0.0630(8)	0.4471(6)	0.3700(3)	393(14)
B(05)	0.0661(8)	0.5008(6)	0.2758(3)	401(14)

[a] $U_{eq} = [1/(6\pi^2)] \times \Sigma\Sigma\beta_{ij}a_ia_j$. The complete temperature factor is: $\exp[-U8\pi^2\sin^2\theta/\lambda^2)]$ or $\exp[-B\sin^2\theta/\lambda^2)]$ where $B = U8\pi^2$.

obtained from Stewart et al. [12] and for other atoms were taken from ref. [13]. Anomalous dispersion terms were applied to the scattering of Fe. The largest peak on a final difference electron density map was 0.5 e/Å^{-3}. Final positional and thermal parameters for nonhydrogen atoms are given in Table 3.

Supplementary material available

Tables of positional and thermal parameters, anisotropic thermal parameters, interatomic distances, and bond angles (5 pages); listings of observed and calculated structure factors (4 pages) [14*].

Acknowledgment

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5 Fe–C_2B_3 plane distances: (a) 1.494 Å in $[(CH_3)C_6H_5]FeC_2B_9H_{11}$ and 1.480 Å in $[(CH_3)_2C_6H_4]FeC_2B_9H_{11}$ [2n]; (b) 1.480 Å in $[(CH_3)_3C_6H_3]$ $FeC_2B_9H_{11}$ [2b]; (c) 1.49 Å in $(C_5H_5)FeC_2B_9H_{11}$ [A. Zalkin, D.H. Templeton and T.E. Hopkins, J. Am. Chem. Soc., 87 (1965) 3988]; (d) 1.58 Å in $Cs_2[(C_2B_9H_{11})_2Fe_2(CO)_4]\cdot(CH_3)_2CO\cdot H_2O$ [P.T. Greene and R.F. Bryan, Inorg. Chem., 9 (1970) 1464]; (e) 1.606 Å in $(C_{10}H_8)Fe[(C_2H_5)_2C_2B_4H_4]$ and 1.73 Å in $(C_{14}H_{10})Fe[(C_2H_5)_2C_2B_4H_4]$ [2j].

6 Fe–C_6 plane distances: (a) 1.566 Å in $[(CH_3)C_6H_5]FeC_2B_9H_{11}$ and 1.575 Å in $[(CH_3)_2C_6H_4]FeC_2B_9H_{11}$ [2n]; (b) 1.60 Å in $[(CH_3)_3C_6H_3]FeC_2B_9H_{11}$ [2b]; (c) 1.58 Å in $[C_6(CH_3)_6]Fe(C_5H_5)$ [D. Astruc, J.R. Hamon, G. Althoff, E. Roman, P. Batail, P. Michand, J.P. Mariot, R. Varret and D. Cozak, J. Am. Chem. Soc., 101 (1979) 5445]; (d) 1.59 Å in $[Fe\{n\text{-}C_5H_4\text{-}CH_2)_3\text{-}\eta\text{-}C_6H_5\}][PF_6]$ [A.N. Nesmeyanov, M.V. Tolstaya, M.I. Rybinskaya, G.B. Shulpin, N.G. Bokii, A.S. Batsanov and Y.T. Struchkov, J. Organomet. Chem., 142 (1977) 89]; (e) 1.548 Å in $(C_6H_6)Fe[(C_2H_5)_2C_2B_4H_4]$, 1.539 Å in $[(CH_3)C_6H_3]Fe[(C_2H_5)_2C_2B_4H_4]$, and 1.554 Å in $[(CH_3)_6C_6]Fe[(C_2H_5)_2C_2B_4H_4]$ [2d]; (f) 1.559 Å in $(C_{10}H_8)Fe[(C_2H_5)_2C_2B_4H_4]$ and 1.47 Å in $(C_{14}H_{10})Fe[(C_2H_5)_2C_2B_4H_4]$ [2j]; (g) 1.564 Å in $[(CH_3)_3C_6H_3]FeC_2B_7H_9$ and 1.566 Å in $[(CH_3)_3C_6H_3]FeC_2B_7H_{11}$ [2k].

7 C_2B_3 plane–C_6 plane dihedral angles: (a) 1.8° in $[(CH_3)C_6H_5]FeC_2B_9H_{11}$ and 2.2° in

$[(CH_3)_2C_6H_4]FeC_2B_9H_{11}$ [2n]; (b) 2.9° in $[(CH_3)_3C_6H_3]FeC_2B_9H_{11}$ [2b]; (c) 2.5° in $[(CH_3)C_6H_5]Fe[(CH_3)_2C_2B_9H_9]$ [2a]; (d) 3.30° in $(C_5H_5)FeC_2B_9H_{10}(OCOCF_3\text{-}8)$ [L.J. Zakharkin, V.V. Kobak, A.I. Kovredov, N.G. Furmanova and Y.T. Struchkov, IZV. Akad. Nauk S.S.R., Ser. Khim., (1979) 1097]; (e) 2.08° in $(C_6H_6)Fe[(C_2H_5)_2C_2B_4H_4]$ and 2.83° in $[(CH_3)_3C_6H_3]Fe[(C_2H_5)_2C_2B_4H_4]$ [2d]; (f) 1.2° in $[(CH_3)C_6H_5]Fe[(C_2H_5)_2C_2B_4H_4]$ [2e]; (g) 3.52° in $(C_{10}H_8)Fe[(C_2H_5)_2C_2B_4H_4]$ [2j].

8 Fe–C (arene) distances: (a) 2.098 Å in $[(CH_3)C_6H_5]FeC_2B_9H_{11}$ and 2.115 Å in $[(CH_3)_2C_6H_4]FeC_2B_9H_{11}$ [2n]; (b) 2.123 Å in $[(CH_3)_3C_6H_3]FeC_2B_9H_{11}$ [2b] (c) 2.116 Å in $[(CH_3)C_6H_5]Fe[(CH_3)_2C_2B_9H_9]$ [2g]; (d) 2.038 Å in $[(CH_3)C_6H_5]Fe[(C_2H_5)_2C_2B_4H_4]$ [2e]; (e) 2.099 Å in $[(CH_3)_3C_6H_3[FeC_2B_7H_9$ and 2.101 Å in $[(CH_3)_3C_6H_3]FeC_2B_7H_{11}$ [2k].

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