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Additive Character of Electron Donation by Methyl Substituents within a Complete Series of Polymethylated [1-(η^6-Me$_n$C$_6$H$_{6-n}$)-*closo*-1,2,3-FeC$_2$B$_9$H$_{11}$] Complexes. Linear Correlations of the NMR Parameters and Fe$^{II/III}$ Redox Potentials with the Number of Arene Methyls

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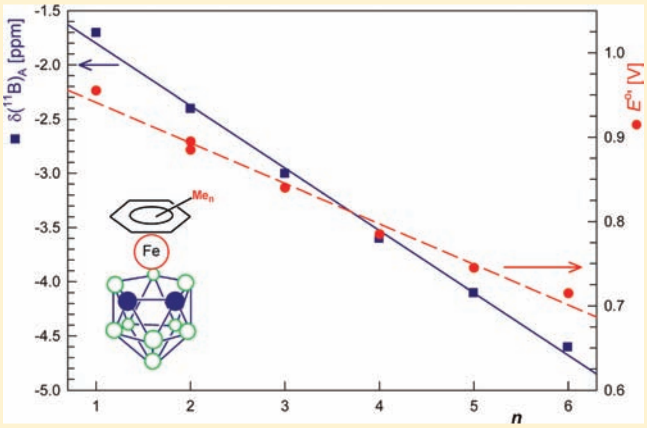

ABSTRACT: A systematic method for the incorporation of the {(η^6-Me$_n$C$_6$H$_{6-n}$)Fe} fragment into the dicarbollide cage was developed based on reactions between [(η^6-Me$_n$C$_6$H$_{6-n}$)$_2$Fe][PF$_6$]$_2$ salts (**1**) and Tl$_2$[*nido*-7,8-C$_2$B$_9$H$_{11}$]. These reactions proceed with elimination of one arene ligand to generate a complete series of the neutral [1-(η^6-Me$_n$C$_6$H$_{6-n}$)-*closo*-1,2,3-FeC$_2$B$_9$H$_{11}$] (**2**) complexes with $n = 1-6$ in yields ranging 15−70% depending on the arene. The structures of mesitylene and pentamethylbenzene complexes were established by X-ray diffraction analyses. All compounds were characterized by ^{11}B and ^{1}H NMR measurements, mass spectra, melting points and elemental analyses. Correlations between selected ^{1}H and ^{11}B NMR parameters and the Fe$^{II/III}$ redox potentials and the number of arene methyls for complexes **2** are linear. These facts establish direct evidence for a strictly additive character of electron donation by the methyl substituents to the arene ring and further to the Fe center and the second (dicarbollide) ligand. Correlations between the number of arene methyls (n) and selected ^{1}H and ^{11}B NMR parameters or the Fe$^{II/III}$ redox potentials for complexes [1-(η^6-MenC$_6$H$_{6-n}$)-*closo*-1,2,3-FeC$_2$B$_9$H$_{11}$] are of strictly linear character.

■ INTRODUCTION

Owing to the lack of representative sets of π-ring-coordinated metal-sandwich complexes [(η^x-Me$_n$C$_x$H$_{x-n}$)ML$_y$]^c (where x = number of ring atoms, n = number of ring-methyl substituents, M = metal atom, L = an auxiliary ligand, and c = charge) with varying numbers of n, there are only a few examples of correlations between the number of ring-methyl substituents (n) and physicochemical characteristics of either M or the second ligand L. The relatively recent studies include a linear correlation between n and ^{57}Fe−Mössbauer quadrupole splittings for the cationic complexes [Fe(η^6-C$_6$H$_n$Me$_{6-n}$)(η^5-C$_5$H$_4$X)]PF$_6$ ($n = 0-6$, X = H, Me, or COPh),[1] a linear relationship between n or λ_{max} and ^{49,47}Ti NMR shifts for complexes [(η^5-C$_5$H$_{5-n}$Me$_n$)TiCl$_3$] ($n = 0-5$),[2] a linear correlation between Ru$^{II/III}$ redox potentials within an incomplete series of the cationic complexes [(η^6-arene)Ru(SC$_5$H$_4$NH)$_3$]$^{2+}$ (arene = C$_6$H$_6$, MeC$_6$H$_5$, *p*-cymene, and C$_6$Me$_6$),[3] a correlation including n and spin−lattice relaxation times in the ^{95}Mo NMR spectra of the [Mo(CO)$_3$(η^6-C$_6$H$_{6-n}$Me$_n$)] complexes.[4] In the chemistry of boron-cluster compounds, a correlation between the Co$^{II/III}$ redox potentials in the Cs[3,3′-Co(C$_2$B$_9$H$_{11-n}$Cl$_n$)] series and the number of chlorine substituents (n) has been published just recently.[5]

The aim of this study is to define relationships between the number of arene-methyl substituents and significant molecular characteristics for the contiguous series of all possible polymethylated arene-iron complexes [1-(η^6-Me$_n$C$_6$H$_{6-n}$)-*closo*-1,2,3-FeC$_2$B$_9$H$_{11}$].[6] Synthetic work in this area was initiated by Todd et al.[7] who isolated in low-yield (9%) the mesitylene complex [1-(η^6-1,3,5-C$_6$H$_3$)-1,2,3-FeC$_2$B$_9$H$_{11}$] from a room-temperature reaction between Tl$_2$[*nido*-7,8-C$_2$B$_9$H$_{11}$] and [(η^6-1,3,5-C$_6$H$_3$)$_2$Fe][PF$_6$]$_2$ in tetrahydrofuran (THF). Using different procedures, Hawthorne et al.[8] prepared the toluene and *p*-xylene analogues, [1-(η^6-Me-C$_6$H$_5$)-1,2,3-FeC$_2$B$_9$H$_{11}$] and [1-(η^6-1,4-Me$_2$-C$_6$H$_4$)-1,2,3-FeC$_2$B$_9$H$_{11}$], in yields of 3 and 5%, respectively. The same group also prepared the parent

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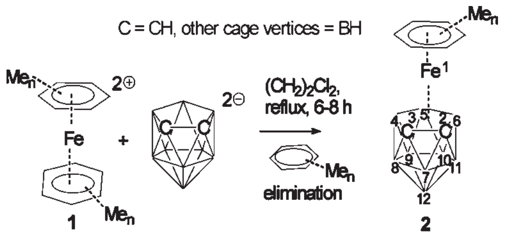
Scheme 1. Insertion of the $\{(\eta^6\text{-arene})Fe\}$ Fragment into the Dicarbollide Cage via Displacement of One Arene Ligand[a]



arene	compd	%
tol	**2a**	48
m-xyl	**2b**	56
p-xyl	**2c**	58
mes	**2d**	70
dur	**2e**	60
pmb	**2f**	20
hmb	**2g**	15

[a] tol = toluene, xyl = xylene, mes = mesitylene, dur = durene, pmb = pentamethylbenzene, and hmb = hexamethylbenzene.

benzene complex $[1\text{-}(\eta^6\text{-}C_6H_6)\text{-}1,2,3\text{-}FeC_2B_9H_{11}]$, which was isolated from photochemical reaction of $[1\text{-}(CO)_3\text{-}1,2,3\text{-}FeC_2B_9H_{11}]$ with benzene.[9] In a preliminary communication,[10] we have extended and highly improved the original Todd's "cationic" approach to arene ferradicarbollides[7] by efficient syntheses of further representatives of the $[1\text{-}(\eta^6\text{-}Me_nC_6H_{6-n})\text{-}closo\text{-}1,2,3\text{-}FeC_2B_9H_{11}]$ family with $n = 3{-}6$. Herein we wish to report full experimental details on the syntheses of a representative set of complexes of this series possessing 1−6 arene methyls and further structural work in this area. The complete set of derivatives was used to examine relations between the number of arene-methyl substituents (n) and significant NMR parameters or $Fe^{II/III}$ redox potentials in these compounds.

RESULTS AND DISCUSSION

Syntheses. Some time ago it was demonstrated that the benzene ligand in the $[CpFe(\eta^6\text{-}C_6H_6)]^+$ cation[11] (Cp = η^5-cyclopentadienyl) can be replaced photochemically by a number of cluster borane monoanions to generate ferradicarbaboranes,[12] ferratricarbaboranes,[13] and thiacarbaboranes[14] incorporating the {CpFe} fragment in the borane cage. Despite the low yield of the same arene-replacement type is the aforementioned reaction involving the $[(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)_2Fe]^{2+}$ dication,[7] which led us to consider that such reactions might be of general character provided that optimum reaction conditions are found. In general, at least one of the arene ligands in $[(\eta^6\text{-arene})_2Fe]^{2+}$ might be conveniently displaced by an arbitrary dicarbaborane dianion $[nido\text{-}C_2B_{n\text{-}2}H_n]^{2-}$ (n indicates the total number of cage vertices) to form *closo*-η^6-arene-iron dicarbaboranes,[15] in which the $\{(\eta^6\text{-arene})Fe\}^{2+}$ vertex, isolobal with the BH group, would constitute an inherent part of the borane cluster:

$$[(\eta^6\text{-arene})_2Fe]^{2+} + [nido\text{-}C_2B_{n-2}H_n]^{2-}$$

$$\rightarrow \text{arene} + [(\eta^6\text{-arene})\text{-}closo\text{-}FeC_2B_{n-2}H_n] \qquad (1)$$

In this work we demonstrate that this synthetic approach is viable at least for the dicarbollide dianion $[nido\text{-}7,8\text{-}C_2B_9H_{11}]^{2-}$ (Scheme 1). The scheme shows optimum reaction conditions found to effect the arene-ligand replacement and demonstrates that reactions between the $[(\eta^6\text{-}Me_nC_6H_{6-n})_2Fe][PF_6]_2$ ([**1a**−**g**]$[PF_6]_2$) salts bearing 1−6 arene methyls and $Tl_2[nido\text{-}7,8\text{-}C_2B_9H_{11}]$[16] in refluxing 1,2-dichloroethane for 6−8 h provides a straightforward access to the twelve-vertex arene ferradicarbaboranes $[1\text{-}(\eta^6\text{-}Me_nC_6H_{6-n})\text{-}closo\text{-}1,2,3,\text{-}FeC_2B_9H_{11}]$ (**2**) in yields ranging 15−70%. Note the lower yields (Scheme 1) for the pmb and hmb derivatives, which can be explained by a stronger Fe-arene bond in the highly methylated cations **1**. Complexes **2** were purified by LC combined with preparative TLC on silica gel in CH_2Cl_2 to isolate the front brown-orange fraction of R_f ∼0.50−0.60. All compounds **2** are air stable and can be easily crystallized from CH_2Cl_2−hexane mixtures. Their melting

Table 1. ^{11}B and ^1H NMR Chemical Shifts ($CDCl_3$) for BH Vertexes in Complexes 2[a]

comp	BH5	BH12	BH4/6	BH9/10	BH8/11	BH7
2a	1.3	−1.7	−8.9	−10.3	−20.2	−25.4
	134	146	∼160	∼170	156	162
	[2.87]	[2.84]	[1.60]	[2.55]	[1.38]	[1.45]
2b	1.5	−2.4	−9.1	−10.1	−20.3	−25.5
	137	141	∼140	∼140	156	168
	[2.67]	[2.81]	[1.58]	[2.43]	[1.37]	[1.45]
2c	1.6	−2.4	−9.2	−10.1	−20.3	−25.5
	136	131	∼140	∼140	153	167
	[2.64]	[2.81]	[1.58]	[2.41]	[1.35]	[1.44]
2d	2.2	−3.0	−9.2	−9.9	−20.3	−25.6
	135	134	∼130	∼130	153	161
	[∼2.20]	[2.79]	[∼2.20]	[2.40]	[1.37]	[1.42]
2e	+1.9	−3.6	−9.3	−9.3	−20.6	−25.6
	134	143	144	144	155	167
	[2.52]	[2.76]	[2.23]	[2.23]	[1.34]	[1.43]
2f	+2.6	−4.1	−9.3	−9.3	−20.7	−25.8
	138	137	135	135	156	168
	[2.40]	[2.73]	[2.10]	[1.53]	[1.32]	[1.41]
2g	+2.9	−4.6	−8.4	−9.4	−20.8	−25.7
	137	141	∼130	∼135	153	165
	[2.23]	[2.70]	[1.96]	[1.51]	[1.29]	[1.41]

[a] Ordered as $\delta(^{11}B)$ (in ppm relative to $BF_3 \cdot OEt_2$), $^1J(BH)$ (in Hz), and $[\delta(^1H)]$ (in ppm relative to tetramethylsilane).

Table 2. Additional ^1H NMR Data for **2a**−**g** ($CDCl_3$)

complex	arene H	arene Me	cage CH
2a	6.18(3)[a] 6.01(2)	2.50(3)	3.74(2)
2b	6.13 5.96(2) 5.70	2.44(6)	3.57(2)
2c	5.86(4)	2.32(6)	3.58(2)
2d	5.69(3)	2.42(9)	3.42(2)
2e	5.63(2)	2.30(12)	3.22(2)
2f	5.64	2.32(6)[c] 2.26(3) 2.24(6)	3.05(2)
2g		2.28(18)	2.84(2)

[a] Intensities other than 1 are given in parentheses.

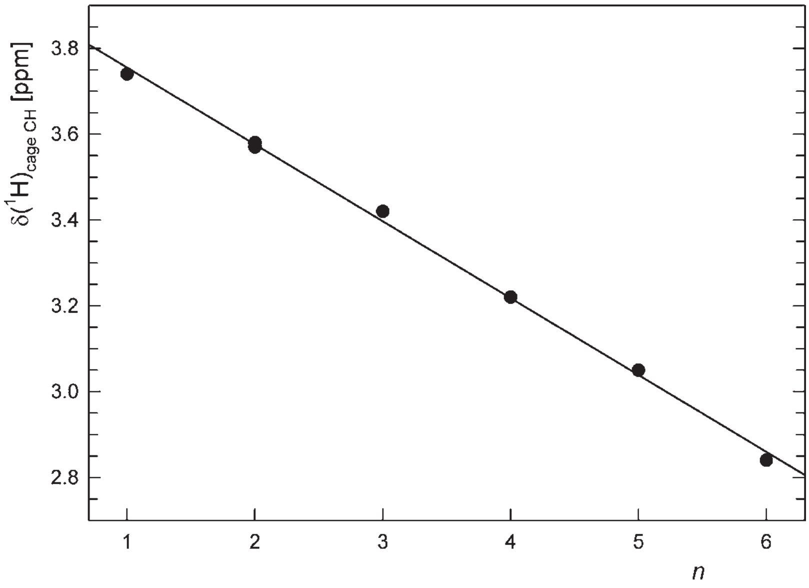


Figure 1. Linear correlation between $\delta(^{1}H)$ chemical shifts for the CH cage hydrogen atoms and the number of arene methyls (n) for complexes **2**.

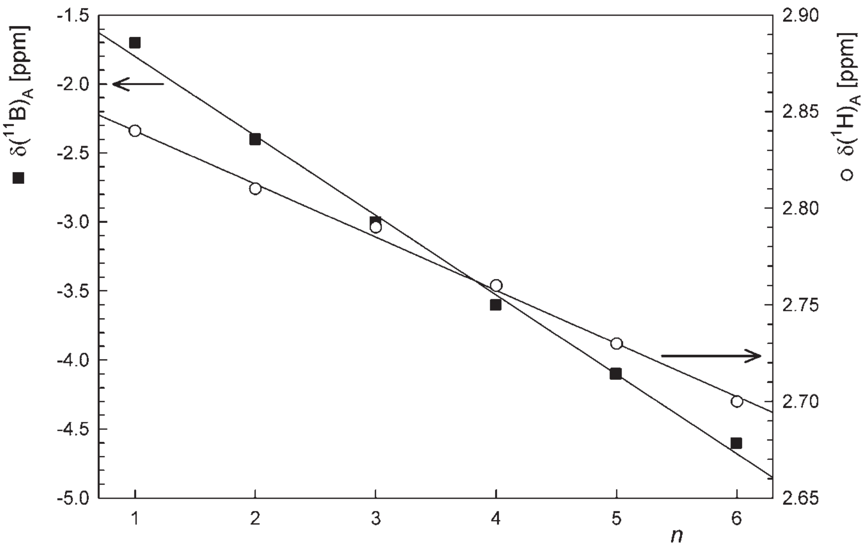


Figure 2. Linear correlation between the number of arene methyls (n) and antipodal $\delta(^{11}B)_A$ (■, B12), and $\delta(^{1}H)_A$ (○, H12) shifts for complexes **2**.

points fall within the range of 248−282 °C; no cluster isomerization at these temperatures was observed.

Structural Studies. *NMR Spectroscopy.* The constitution of the neutral complexes of type **2** is in agreement with the results of ^{1}H and ^{11}B NMR spectroscopic measurements and mass spectrometry. The ^{11}B NMR spectra of compounds **2a**−**g** (Table 1) consist of 1:1:2:2:2:1 patterns of doublets (assigned by [^{11}B-^{11}B]-COSY experiments[17] to B5, B12, B4/6, B9/10, B8/11, and B7 atoms, respectively), which is consistent with a symmetry plane passing through the Fe, B5, B7, and B12 atoms. The ^{1}H NMR spectra (Table 2) clearly show the expected resonances due to aromatic (except for **2d**) and methyl hydrogens. The ^{1}H-{^{11}B(selective)} experiments[18] also allowed for assignments of all resonances due to cluster BH units (values in square brackets in Table 1). Figures 1 and 2 demonstrate that there is an excellent linear correlation between selected NMR parameters and the number of arene methyls (n), which indicates that the arene substituents proportionally affect the diamagnetic shielding at individual cluster vertexes of the dicarbollide ligand. For example, Figure 1 shows that shielding of the cluster CH2/3 protons linearly grows with increasing n. Exactly the same trend is seen in Figure 2 for antipodal (A)[19] ^{11}B and ^{1}H NMR shieldings in the BH12 cage positions. All these correlations suggest additive character of the electron donating (I^{+}) effect of arene methyl substituents to the Fe center and transmission of this effect further onto the dicarbollide ligand.

X-ray Diffraction Analyses. Thus far, the structures of type-**2** complexes with the benzene,[9] toluene,[8] *p*-xylene,[8] and mesitylene (with a disordered borane cluster)[7] ligands have been reported by other laboratories. Recently we have published crystallographic studies on the durene and hexamethylbenzene compounds **2e** and **2g**. Additional two structures (Figures 3 and 4)

Table 3. Melting Points, Mass Spectra, Elemental Analyses, and $Fe^{II/III}$ Redox Potentials for **2a**−**g**

comp	mp (°C)	$m/z_{calc/exp}$[a]	analysis calc/found[b]	$E^{\circ\prime}$ (V)[c]
2a	248	283.17(6)/283.17(6)	38.54/38.62	0.955
		281.17(100)/281.17(100)	6.89/6.73	
2b	253	297.19(8)/297.20(7)	40.78/41.01	0.895
		295.19(100)/295.19(100)	7.19/7.14	
2c	252	297.19(8)/297.20(7)	40.78/42.03	0.885
		295.19(100)/295.19(100)	7.19/7.22	
2d	260	311.20(8)/ 311.20(6)	42.82/43.03	0.840
		309.20(100)/309.20(100)	7.51/7.68	
2e	275	325.22(8)/3.25.22(7)	44.68/45.03	0.785
		323.22(100)/323.22(100)	7.81/7.69	
2f	280	339.23(8)/ 339.26(8)	46.39/46.63	0.745
		337.23(100)/337.23(100)	8.09/8.16	
2g	282	353.25(8)/353(7)	47.96/48.13	0.715
		351.25(100)/351.25(100)	8.34/8.42	

[a] Molecular peaks (relative abundances in parentheses). [b] % C followed by % H. [c] Recorded at Pt disk electrode on about 0.5 mM solutions in 1,2-dichloroethane in the presence of 0.1 M $Bu_4N[PF_6]$ supporting electrolyte. The potentials are given relative to ferrocene/ferrocenium reference. $E^{\circ\prime} = {}^1/_2(E_{pa} + E_{pc})$, where E_{pa} (E_{pc}) is the anodic (cathodic) peak potential in cyclic voltammetry.

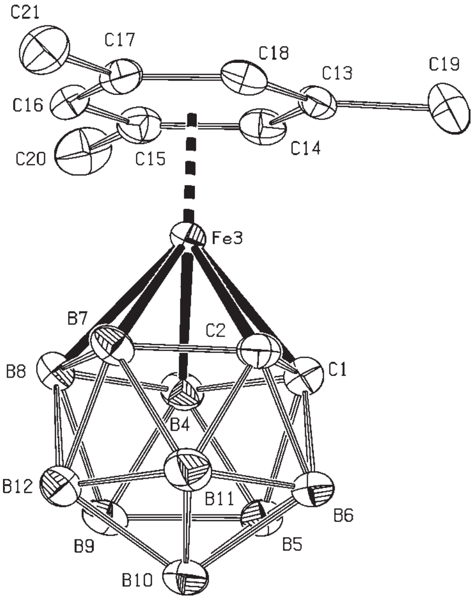


Figure 3. ORTEP representation of **2d** at 50% probability level. The hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): C1−C2 1.649(5), Fe3−C1 2.053(3), C1−B4 1.735(6), C1−B5 1.731(5), C2−B6 1.717(5), Fe−arene (ring centroid) 1.574(2), Fe−C_2B_3 (ring centroid) 1.480(2), mean Fe−C(arene ring) 2.112(1), Fe3−B4 2.118(3), Fe3−B7 2.083(3), Fe3−B8 2.137(3), mean C−CH_3 1.5035(11), C2−C1−Fe3 65.90(15), B4−C1−Fe3 67.38(15), B4−C1−B5 62.3(2), B5−C1−B6 61.2(2), C2−C1−B4 109.2(2), C2−Fe3−C1 47.49(13), C1−Fe3−B4 49.13(16), B4−Fe3−B8 49.75(13).

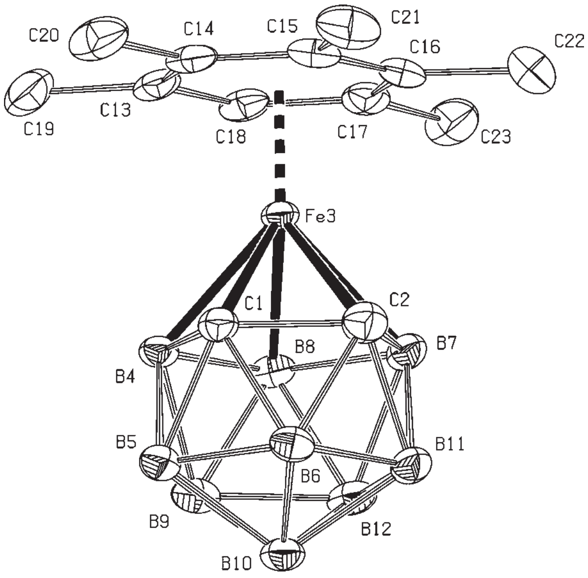


Figure 4. ORTEP representation of **2f**·$^1/_2CHCl_3$ at 50% probability level. The hydrogen atoms and the solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): C1−C2 1.659(3), Fe3−C1 2.0345(19), C1−B4 1.655(3), C1−B5 1.715(3), C1−B6 1.715(3), Fe−arene (ring centroid) 1.579(3), Fe−C2B3 (ring centroid) 1.481(3), mean Fe−C(arene ring) 2.118(3), Fe3−B4 2.060(2), mean C−CH_3 1.5048(12) C1−Fe3−B4 47.67(9), B4−C1−Fe3 66.98(10), B4−C1−B5 62.72(13), B4−C1−B6 112.93(16), C2−C1−B4 111.16(16), C2−Fe3−C1 47.75(8), C1−Fe3−B8 83.37(8), B4−Fe3−B8 49.39(9).

determined now comprise those of the mesitylene (undisordered) and pentamethylbenzene complexes **2d** and **2f**·$^1/_2CHCl_3$. Molecular parameters of **2d** and **2f**·$^1/_2CHCl_3$ do not differ much from structural data reported earlier for the analogous compounds. However, the solvent in the structure of **2f**·$^1/_2CHCl_3$ was disordered, and all attempts at modeling this disorder met with no success. The contribution of the solvent molecule to scattering was therefore subtracted. The iron atoms in complexes **2d** and **2f**·$^1/_2CHCl_3$ are symmetrically located between the arene and dicarbollide ligands with the Fe-arene(ring centroid) bond vectors being in average ∼0.1 Å longer than the Fe−C_2B_9(ring centroid) distances. The CCC bond angles in the arene ring approximate the hexagonal angle (120°), while the CCB and BBB angles in the C_2B_3 ring are close to the pentagonal angle (106°). However, the FeC_2B_3 pentagonal pyramid is slightly distorted because of unequal Fe−C and Fe−B bond lengths.

Electrochemistry. The electrochemical behavior of ferradicarbaboranes **2** has been studied by cyclic voltammetry (CV) at the platinum disk electrode in 1,2-dichloroethane. In the potential window provided by the solvent (ca. −2.2 to 1.3 V vs ferrocene/ferrocenium reference), the compounds displayed one electrochemically reversible redox change attributable to oxidation of the Fe^{II} center (Table 3). In all cases, the redox waves corresponded to a one-electron exchange as suggested by a comparison of the CV peak parameters to those of ferrocene at the same concentration, and were diffusion-controlled with the anodic peak current (i_{pa}) being proportional to the square root of the scan rate over the scan rates used (0.05−1 V s^{-1}). From Figure 8, it is readily seen that the $Fe^{II/III}$ redox potential decreases linearly with increasing number of methyl groups on the η^6-arene ring (ca. 40 mV per one methyl group; Figure 5) which is entirely consistent with the linear dependence of the NMR parameters shown in Figures 1−3. The easier oxidation of compounds with a

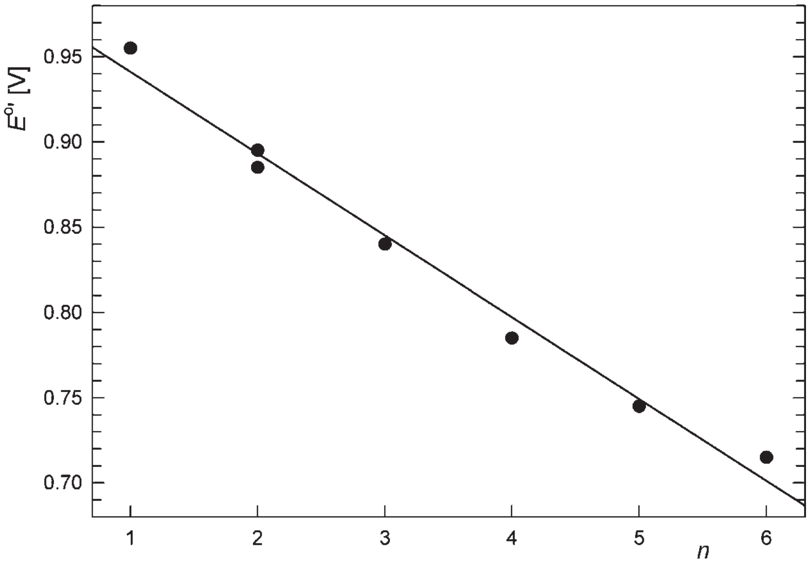


Figure 5. Variation of the Fe^{II}/Fe^{III} redox potential for compounds **2** with the number of methyl substituents (n) on the η^6-arene ring.

higher number of arene-methyl substituents obviously reflects their stronger electron-donating (I^+) ability.

CONCLUSIONS

It was clearly demontrated that the electronic effect of the Me substituents on the arene ring is undoubtedly of electron-donating (I^+) character and of strictly additive character. This finding, however, sharply contrasts with conlusions of the theoretical work by Teixidor's group[20] on electron-withdrawing (I^-) effects of Me substituents in boron positions of the *o*-caborane cage. The electron-donating effect by arene-methyl substituents to the iron center was demonstrated in this work for the first time in metalacarborane chemistry on a contiguous series (n = 1−6) of seven methyl-arene iron-dicarbollide complexes [1-(η^6-$Me_nC_6H_{6-n}$)-*closo*-1,2,3,-$FeC_2B_9H_{11}$] (**2**) by linear correlations between the selected ^1H and ^{11}B NMR parameters and the $Fe^{II/III}$ redox potentials, and the number of arene methyls. The data show that the Me-I^+ effect is transmitted not only to the Fe center but also further onto the dicarbollide ligand of the sandwich molecule. Especially the possibility of fine-tuning of the metal redox potentials in sandwiched metallaboranes or carboranes by placing suitable substituents onto the ligands may sometimes find interesting technical applications in material chemistry. In connection with this study, we have remarkably improved the previous preparative procedure[7] for the synthesis of compounds **2** by developing a generally applicable method for the incorporation of the {(η^6-arene)Fe^{II}} moiety into a carborane cage based on reactions between arene salts [(η^6-$Me_nC_6H_{6-n}$)$_2$Fe]-$[PF_6]_2$ and the [*nido*-7,8-$C_2B_9H_{11}$]$^{2-}$ anion. It is expected that this method will allow for structural modifications in both the arene and the cluster subsections of complexes **2**. These might be achieved either by direct substitution or by synthesis from presubstituted starting components. This derivatization would lead to compounds of biological activity or to syntheses of metallacarborane building blocks of designed constitution. Further efforts to expand the scope of arene-iron carborane chemistry to other arenes and carborane anions are currently underway in our laboratories.

EXPERIMENTAL SECTION

General Procedures. All reactions were carried out with use of standard vacuum or inert-atmosphere techniques as described by Shriver,[21] although some operations, such as column liquid chromatography (LC), were carried out in air. The starting $Tl_2[7,8\text{-}C_2B_9H_{11}]$ and dications of type **1** were prepared according to the literature.[10] Dichloromethane and hexane were dried over CaH_2 and freshly distilled before use. Other chemicals were of reagent or analytical grade and were used as purchased. Analytical TLC was carried out on Silufol (silica gel on aluminum foil; detection by I_2 vapor, followed by 2% aqueous $AgNO_3$ spray). Column chromatography was performed on silica gel (Aldrich, 250−350 mesh). Mass spectra were recorded on a Thermo Finnigan LCQ Fleet Ion Trap mass spectrometer. ^1H and ^{11}B, NMR spectroscopy was performed on a Varian Mercury 400 instrument. The [^{11}B-^{11}B]-COSY[17] and ^1H-{^{11}B(selective)}[18] NMR experiments were made essentially as described earlier.[22] Electrochemical measurements were carried out with a computer-controlled potentiostat μAUTOLAB III (Eco Chemie, The Netherlands) at room temperature using a standard three-electrode cell with a platinum disk electrode (AUTOLAB RDE, 3 mm diameter) as the working electrode, platinum sheet auxiliary electrode, and saturated calomel reference electrode (SCE) which was separated from the analyzed solution by a salt-bridge (0.1 M $Bu_4N[PF_6]$ in 1,2-dichloroethane). The analyzed compounds were dissolved in 1,2-dichloroethane (anhydrous, Sigma-Aldrich) to give a solution containing about 5 × 10^{-4} M of the analyzed compound and 0.1 M $Bu_4N[PF_6]$ (Fluka, purissimum for electrochemistry) as the supporting electrolyte. The solutions were degassed with argon before the measurement and then kept under an argon blanket. The redox potentials are given relative to the ferrocene/ferrocenium reference.

[1-(η^6-Arene)-*closo*-1,2,3-$FeC_2B_9H_{11}$] (2a−2g) Complexes. In a typical experiment, a mixture of the dicationic compounds [**1a**−**g**]$[PF_6]_2$ (reaction scale ca. 1 mmol) and 1,2-dichloroethane (30 mL) was treated with $Tl_2[7,8\text{-}C_2B_9H_{11}]$ (540 mg, 1 mmol). The mixture was heated at reflux under stirring for 6−8 h. Upon cooling to ambient temperature, silica gel (~ 5 g) was added, the solvent was evaporated, and the remaining solid residue was mounted onto a silica gel column (2.5 × 35 cm), which was eluted with 100% CH_2Cl_2 to collect the front orange-brown band of R_f (anal.) = ~0.60. The eluted solutions were evaporated to dryness, and the residual crude products washed by hexane, which was then removed by a syringe. Crystals of all compounds of structure **2** were grown from concentrated CH_2Cl_2 or $CHCl_3$ solutions, onto the top of which a layer of hexane of equal volume was carefully added. This crystallization yielded unsolvated products, except for **2f** which was isolated as **2f**$\cdot{}^1/_2CHCl_3$. Compounds **2** can be also purified by vacuum sublimation at about 150 °C (**2f**$\cdot{}^1/_2CHCl_3$ is desolvated under these conditions) without detection of any cage isomerization. Yields of compounds **2** range 15−70% (see Scheme 1). NMR, MS, and other selected data are summarized in Tables 1−3.

X-ray Crystallography. The X-ray data for orange-brown crystals of compounds **2d** and **2f**$\cdot{}^1/_2CHCl_3$ were obtained at 150 K using an Oxford Cryostream low-temperature device and a Nonius KappaCCD diffractometer with Mo K_α radiation (λ = 0.71073 Å), a graphite monochromator, and the ϕ and χ scan mode. Data reductions were performed with DENZO-SMN.[23] The absorption was corrected by integration methods.[24] Structures were solved by direct methods (Sir92)[25] and refined by full matrix least-squares based on F^2 (SHELXL97).[26] Hydrogen atoms could be mostly localized on a difference Fourier map. However, to ensure uniformity of treatment of crystal structures, they were recalculated into idealized positions (riding model) and assigned temperature factors $U_{iso}(H) = 1.2U_{eq}$(pivot atom) or of $1.5U_{eq}$ for the methyl moieties with C−H = 0.96 Å, 0.97, and 0.93 Å for the methyl, methylene, and aromatic hydrogen atoms, respectively, and 1.1 Å for B−H and C−H bonds in the carborane cage.

The solvent in the structure of **2f**$\cdot{}^1/_2CHCl_3$ was disordered. Since all attempts to model this disorder met with no success, the contribution of the solvent molecule to scattering was subtracted using the PLATON/SQUEZZE[27] routine. A potential solvent volume of 166 Å^3 was found with 56 electrons per the unit cell, which correspond with 58 electrons per unit cell expected for a 1:1 solvate.

Crystalographic data for **2d**: $C_{11}H_{23}B_9Fe$, M = 308.43, orthorhombic, $Pna2_1$, red block, a = 12.6502(4), b = 9.7061(11), c = 12.4388(14) Å, V = 1527.3(2) Å^3, Z = 4, T = 150(1) K, 13267 total reflections, 3360 independent (R_{int} = 0.0463), $R1$ (obs. data) = 0.0373, w$R2$ (all data) = 0.0876, GOF = 1.060. For **2f**$\cdot{}^1/_2CHCl_3$: $C_{13}H_{27}B_9Fe\cdot{}^1/_2CHCl_3$, M = 396.17, triclinic, $P\bar{1}$, red block, a = 9.5070(6), b = 9.8140(7), c = 12.2810(6) Å, α = 98.024(6), β = 97.341(5), γ = 117.782(5)°, V = 979.21(10) Å^3, Z = 2, T = 150(1) K, 17211 total reflections, 4452 independent (R_{int} = 0.0448), $R1$ (obs. data) = 0.0416, w$R2$ (all data) 0.0965, GOF = 1.040.

Crystallographic data for structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC deposition nos. 789926 and 789925 for **2d** and **2f**$\cdot{}^1/_2CHCl_3$, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EY, U.K. (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http:// www.ccdc.cam.ac.uk.

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■ REFERENCES

(1) Brown, R. A.; Houlton, A.; Howe, S. D.; Roberts, R.M. G.; Silver, J. *J. Chem. Soc., Dalton Trans.* **1993**, 3329.

(2) Pinkas, J.; Lyčka, A.; Šindelář, P.; Gyepes, R.; Varga, V.; Kubišta, J.; Horáček, M.; Mach, K. *J. Mol. Catal. A: Chem.* **2006**, *257*, 14.

(3) Gras, M.; Therrien, B.; Suess-Fink, G.; Štěpnička, P.; Renfrew, A. K.; Dyson, P. J. *J. Organomet. Chem.* **2008**, *693*, 3419.

(4) Brownlee, R. T. C.; O'Connor, M. J.; Shehan, P. B.; Wedd, A. G. *Aust. J. Chem.* **1986**, *39*, 931.

(5) Gonzáles-Cardoso, P.; Stoica, A.-I.; Farràs, P.; Pepiol, A.; Viñas, C.; Teixidor, F. *Chem.—Eur. J.* **2010**, *16*, 6660.

(6) Note that a more convenient numbering in which the metal atom bears number 1 will be used throughout instead of the misleading IUPAC carbon-preference system.

(7) Hanusa, T. P.; Huffman, J. C.; Todd, L. J. *Polyhedron* **1982**, *1*, 77.

(8) Kang, H. C.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1987**, *26*, 3409.

(9) Lee, S. S.; Knobler, C. B.; Hawthorne, M. F. *J. Organomet. Chem.* **1990**, *394*, 29.

(10) Štíbr, B.; Bakardjiev, M.; Holub, J.; Růžička, A.; Kvíčalová, M. *Inorg. Chem.* **2009**, *48*, 10904.

(11) (a) Nesmeyanov, A. N.; Vol'kenau, N. A.; Bolesova, I. N. *Tetrahedron Lett.* **1963**, *4*, 1725. (b) Nesmeyanov, A. N.; Vol'kenau, N. A.; Bolesova, I. N.; Polkovnikova, L. S. *Koord. Khim.* **1975**, *1*, 1252.

(12) Kudinov, A. R.; Meshcheryakov, V. I.; Petrovskii, P. V.; Rybinskaya, M. I. *Izv. Akad. Nauk, Ser. Khim.* **1999**, 177; *Russ. Chem. Bull.*48, 176 (Engl. Transl.).

(13) (a) Holub, J.; Grüner, B.; Perekalin, D. S.; Golovanov, D. G.; Lyssenko, K. A.; Petrovskii, P. V.; Kudinov, A. R.; Štíbr, B. *Inorg. Chem.* **2005**, *44*, 1655. (b) Perekalin, D. S.; Lyssenko, K. A.; Petrovskii, P. V.; Holub, J.; Štíbr, B.; Kudinov, A. R. *J. Organomet. Chem.* **2005**, *690*, 2775. (c) Štíbr, B. *J. Organomet. Chem.* **2005**, *690*, 2694. (d) Perekalin, D. S.; Holub, J.; Golovanov, D. G.; Lyssenko, K. A.; Petrovskii, P. V.; Štíbr, B.; Kudinov, A. R. *Organometallics* **2005**, *24*, 4387. (e) Perekalin, D. S.; Glukhov, I. V.; Štíbr, B.; Kudinov, A. R. *Inorg. Chim. Acta* **2006**, *359*, 3264.

(14) Perekalin, D. S.; Glukhov, I. V.; Holub, J.; Císařová, I.; Štíbr, B.; Kudinov, A. R. *Organometallics* **2008**, *27*, 5273.

(15) For other arene-iron dicarbaboranes see, for example: (a) Swisher, R. G.; Sinn, E.; Grimes, R. N. *Organometallics* **1983**, *2*, 506. (b) Swisher, R. G.; Sinn, E.; Butcher, R. J.; Grimes, R. N. *Organometallics* **1985**, *4*, 882. (c) Swisher, R. G.; Sinn, E.; Grimes, R. N. *Organometallics* **1985**, *4*, 890. (d) Swisher, R. G.; Sinn, E.; Grimes, R. N. *Organometallics* **1985**, *4*, 896. (e) Briguglio, J. J.; Sneddon, L. G. *Organometallics* **1986**, *5*, 327. (f) Grimes, R. N. *Pure Appl. Chem.* **1987**, *59*, 847. (g) Davis, J. H.; Sinn, E.; Grimes, R. N. *J. Am. Chem. Soc.* **1989**, *111*, 4776. (h) Merkert, J. W.; Geiger, W. E.; Attwood, M. D.; Grimes, R. N. *Organometallics* **1991**, *10*, 3545. (i) de Biani, F. F.; Fontani, M.; Ruiz, E.; Zanello, P.; Russell, J. M.; Grimes, R. N. *Organometallics* **2002**, *21*, 4129. (j) Loginov, D. A.; Vinogradov, M. M.; Shul'pina, L. S.; Vologzhanina, A. V.; Petrovskii, P. V.; Kudinov, A. R. *Russ. Chem. Bull.* **2007**, *56*, 2118.

(16) Spencer, J. L.; Green, M.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1972**, 1178.

(17) Hutton, W. C.; Venable, T. L.; Grimes, R. N. *J. Am. Chem. Soc.* **1984**, *106*, 29.

(18) Fontaine, X. L. R.; Kennedy, J. D. *J. Chem. Soc., Dalton Trans.* **1987**, 1573.

(19) Heřmánek, S. *Chem. Rev.* **1992**, *92*, 325, and refs therein.

(20) Teixidor, F.; Barbera, G.; Vaca, A.; Kivekäs, R.; Sillanpää, R.; Oliva, J.; Viñas, C. *J. Am. Chem. Soc.* **2005**, *127*, 10158.

(21) Shriver, D. F.; Drezdzon, M. A. *Manipulation of Air Sensitive Compounds*, 2nd ed.; Wiley: New York, 1986.

(22) See, for example: Grűner, B.; Štíbr, B.; Holub, J.; Cisařová, I. *Eur. J. Inorg. Chem.* **2003**, 1533.

(23) Otwinowski, Z.; Minor, W. *Method Enzymol.* **1997**, *276*, 307.

(24) Coppens, P. In *Crystallographic Computing*; Ahmed, F. R., Hall, S. R., Huber, C. P., Eds.; Munksgaard: Copenhagen, 1970; pp 255− 270.

(25) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Crystallogr.* **1993**, *26*, 343.

(26) Sheldrick, G. M. *SHELXL-97*; University of Göttingen: Göttinge, Germany, 1997.

(27) Spek, A. L. *Acta Crystalllogr., Sect. A* **1990**, *46*, C34.