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Communication

Systematic Method for the Incorporation of the $\{(\eta^6\text{-Arene})\text{Fe}\}$ Fragment into Carborane Cages via $[(\eta^6\text{-Arene})\text{Fe}]^{2+}$ Dications. A Series of $[3\text{-}(\eta^6\text{-Arene})\text{-}closo\text{-}3,1,2\text{-FeC}_2\text{B}_9\text{H}_{11}]$ Complexes. Reliable Synthesis of Polymethylated $[(\eta^6\text{-Arene})_2\text{Fe}]^{2+}$ Cations

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Developed was a systematic method for the incorporation of the $\{(\eta^6\text{-arene})\text{Fe}\}$ fragment into a carborane cage. Reactions between $[(\eta^6\text{-arene})_2\text{Fe}](\text{PF}_6)_2$ salts and $\text{Tl}_2[nido\text{-}7,8\text{-C}_2\text{B}_9\text{H}_{11}]$ in refluxing $(\text{CH}_2)_2\text{Cl}_2$ generated a series of $[3\text{-}(\eta^6\text{-arene})\text{-}closo\text{-}3,1,2\text{-FeC}_2\text{B}_9\text{H}_{11}]$ neutral complexes with variable types of polymethylated arene ligands in the structure. The structures of durene and hexamethylbenzene complexes were established by X-ray diffraction analyses. The work also shows that the original high-temperature method for the preparation of the $[(\eta^6\text{-arene})_2\text{Fe}]^{2+}$ dications fails for mesitylene and durene compounds, which was overcome by a reliable room-temperature modification.

The iron bis(arene) dications, $[(\eta^6\text{-arene})_2\text{Fe}]^{2+}$ (**1**), are usually prepared via reactions between anhydrous FeCl_2 or FeCl_3 and the corresponding arene in the presence of 2 equiv of anhydrous AlCl_3:[1]

$$\text{arene} + \text{FeCl}_2 + 2\text{AlCl}_3 \rightarrow [(\eta^6\text{-arene})_2\text{Fe}](\text{AlCl}_4)_2 \qquad (1)$$

Of this series of sandwich complexes, the $[(\eta^6\text{-mes})_2\text{Fe}]^{2+}$ dication (where mes = mesitylene = $1,3,5\text{-Me}_3\text{C}_6\text{H}_3$), has always been taken as the most important member of the $[(\eta^6\text{-arene})_2\text{Fe}]^{2+}$ family because of its addition reactions with strong nucleophiles, leading to derivatization of the arene rings via cyclohexadienyl (pseudoferrocene) complexes.[1c,f,2] Some time ago, it was clearly demonstrated that the benzene ligand in the structurally related $[\text{CpFe}(\eta^6\text{-C}_6\text{H}_6)]^+$ cation[3] can be replaced photochemically by a number of cluster borane monoanions to generate whole families of ferradicarbaboranes,[4] ferratricarbaboranes,[5] and thiacarbaboranes,[6] incorporating the {CpFe} fragment as a part of the borane cage. These arene ligand-exchange reactions prompted us to consider that at least one of the arene ligands in $[(\eta^6\text{-arene})_2\text{Fe}]^{2+}$ might be conveniently displaced by an arbitrary dicarbaborane dianion $[nido\text{-C}_2\text{B}_{n-2}\text{H}_n]^{2-}$ (where n = number of cage vertices) to form the still very rare[7] $closo\text{-}\eta^6$-arene iron dicarbaboranes, in which the $\{(\eta^6\text{-arene})\text{Fe}\}^{2+}$ vertex, isolobal with the BH^{2+} group, would constitute an inherent part of the borane cluster:

$$[(\eta^6\text{-arene})_2\text{Fe}]^{2+} + [nido\text{-C}_2\text{B}_{n-2}\text{H}_n]^{2-} \rightarrow \text{arene} + [(\eta^6\text{-arene})\text{-}closo\text{-FeC}_2\text{B}_{n-2}\text{H}_n] \qquad (2)$$

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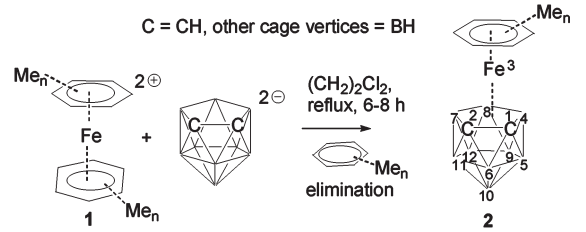
Scheme 1. Insertion of the $\{(\eta^6\text{-Arene})\text{Fe}\}$ Fragment into the Dicarbollide Cage via Displacement of One Arene Ligand



arene	compd	%
mes	**2a**	70
dur	**2b**	60
pmb	**2c**	20
hmb	**2d**	5

In this Communication, we demonstrate that this synthetic approach is viable at least for the dicarbollide dianion $[nido\text{-}7,8\text{-}C_2B_9H_{11}]^{2-}$ (see Scheme 1). Previous work in the area of arene iron dicarbollide complexes includes a low-yield synthesis of $[3\text{-}(\eta^6\text{-}1,3,5\text{-}C_6H_3)\text{-}3,1,2\text{-}FeC_2B_9H_{11}]$ by Todd et al.[8] in a procedure similar to that of reaction (2). Using different procedures, Hawthorne et al. prepared the toluene and *p*-xylene analogues (yields 3 and 5%, respectively).[9] The same group prepared the benzene complex, which was isolated in high yield from the photochemical reaction between $[3\text{-}(CO)_3\text{-}3,1,2\text{-}FeC_2B_9H_{11}]$[10] and benzene.

To avoid major arene−ligand isomerization and disproportionation problems encountered in the preparation of the starting $[(\eta^6\text{-arene})_2Fe]^{2+}$ dications containing polymethylated arenes (see the Supporting Information), when using the well-known and highly cited procedure,[1c] we have employed a room-temperature modification of reaction (1): In a typical experiment, arene, $FeCl_2$ and $AlCl_3$ powder, and heptane in the mole ratio 3:1:3:3 were stirred vigorously under nitrogen at ambient temperature for 36 h. A further workup procedure, such as that in ref [1c], gave good yields of the PF_6^- salts of the polymethylated $[(\eta^6\text{-arene})_2Fe]^{2+}$ dications, $[\mathbf{1}](PF_6)_2$ (arene = mes, **1a**, 65% ; dur, **1b**, 69%; pmb, **1c**, 65%; hmb = Me_6C_6, **1d**, 71%; where mes = mesitylene, dur = durene, pmb = pentamethylbenzene, and hmb = hexamethylbenzene).

Scheme 1 shows that reactions between the $[\mathbf{1a}-\mathbf{1d}](PF_6)_2$ salts (with 3−6 arene methyls) and $Tl_2[nido\text{-}7,8\text{-}C_2B_9H_{11}]$[11] in refluxing $(CH_2)_2Cl_2$ for 6−8 h provided reasonable access to the 12-vertex arene ferradicarbaboranes of the general structure $[3\text{-}(\eta^6\text{-arene})\text{-}closo\text{-}3,1,2\text{-}FeC_2B_9H_{11}]$ [**2**, where arene = mes (**2a**), dur (**2b**), pmb (**2c**), and hmb **2d**] in yields of 5−70% (unoptimized), dropping with the number of arene methyls. The complexes were isolated by liquid chromatography combined with preparative thin-layer chromatography on silica gel in CH_2Cl_2 to isolate the front brown-orange fraction of $R_f \sim 0.60$. All of the compounds of type **2** are air-stable and can be easily crystallized from CH_2Cl_2−hexane mixtures. Their melting points fall within the range of 260−282 °C, and no cluster isomerization at these temperatures was observed.

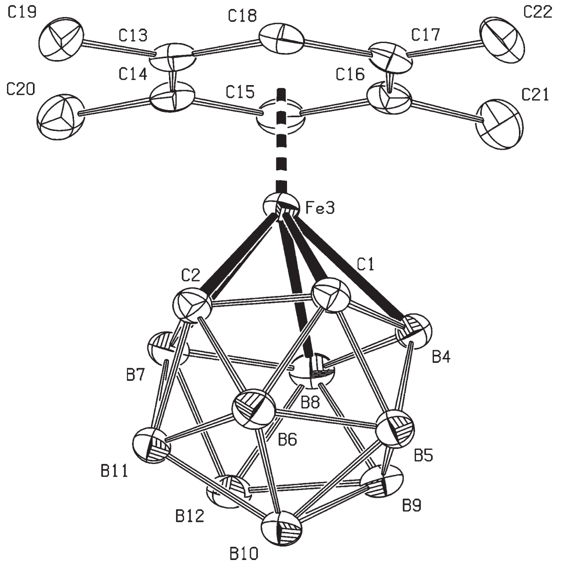


Figure 1. ORTEP representation of the crystallographically determined molecular structure of $[3\text{-}(\eta^6\text{-dur})\text{-}closo\text{-}3,1,2\text{-}FeC_2B_9H_{11}]$ (**2b**). Selected bond lengths (Å) and angles (deg): C1−C2 1.619(3), Fe3−C1 2.043(2), C1−B4 1.696(4), C1−B5 1.702(4), C1−B6 1.723(4), Fe−arene(ring centroid) 1.352(1), Fe−C_2B_3(ring centroid) 1.483(1), mean Fe−C(arene ring) 2.117(1), Fe−B4 2.104(3), Fe3−B7 2.099(3), Fe3−B8 2.135(3), mean C−CH_3 1.502(4); C2−C1−Fe3 66.21(12), B4−C1−Fe3 67.77(12), B4−C1−B5 63.60(16), B5−C1−B6 61.62(16), C2−C1−B4 111.21(19), C2−Fe3−C1 46.83(9), C1−Fe3−B4 48.23(10), B4−Fe3−B8 49.82(11).

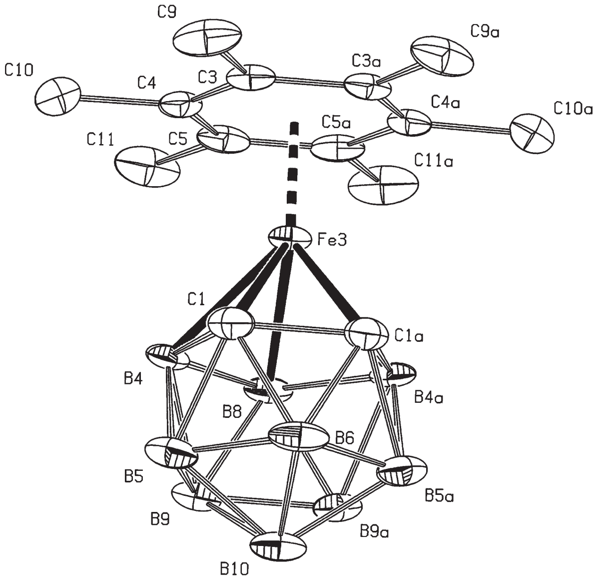


Figure 2. ORTEP representation of the crystallographically determined molecular structure of $[3\text{-}(\eta^6\text{-hmb})\text{-}closo\text{-}3,1,2\text{-}FeC_2B_9H_{11}]$ (**2d**). Selected bond lengths (Å) and angles (deg) (crystallographic numbering, symmetry $-x, y, z$): C1−C1a 1.665(8), Fe3−C1 2.051(3), C1−B4 1.693(5), C1−B5 1.737(5), C1−B6 1.745(5), Fe−arene(ring centroid) 1.366(2), Fe−C2B3-(ring centroid) 1.485(3), mean Fe−C(arene ring) 2.133(3), Fe3−B8 2.100(5), mean C−CH3 1.505(4) C1−Fe3 66.05(11); B4−C1−Fe3 66.80(17), B4−C1−B5 62.3(2), B4−C1−B6 111.5(3), C1a−C1−B4 109.2(2), C1a−Fe3−C1 47.9(2), C1−Fe3−B4 48.35(15), B4−Fe3−B8 48.81(13).

The suggested constitution of all neutral complexes of type **2** is in agreement with the results of ^1H and ^{11}B NMR

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spectroscopy and mass spectrometry. The ^{11}B NMR spectra of compounds **2a**−**2d** consist of 1:1:2:2:2:1 patterns of doublets (assigned by [^{11}B−^{11}B] COSY experiments[12] to B8, B10, B4,7, B9,12, B5,11, and B6 atoms, respectively), which is consistent with the symmetry plane intersecting the Fe, B6, B8, and B10 vertexes. The ^{1}H NMR spectra clearly show the expected resonances of arene H (except for **2d**) and methyl H atoms, and the ^{1}H{^{11}B(selective)} NMR experiments[13] also allowed for assignments of all resonances due to cluster BH units. The cluster CH1,2 resonances vary in the range 2.83−3.42 ppm, depending on the type of arene.

Thus far, the structures of the benzene,[10] toluene,[9] *p*-xylene,[9] and mesitylene[8] (with a disordered borane cluster) compounds have been determined by X-ray diffraction analysis. In this work, we report the structures of **2b** and **2d** shown in Figures 1 and 2. Both compounds **2b** and **2d** exhibit similar structural features and adopt the expected structures in which the Fe atom is sandwiched between arene and dicarbollide ligands. For instance, the Fe−arene(ring centroid) bond vectors are on average ~0.12 Å shorter than the Fe−C_2B_9(ring centroid) distances. The C−C−C bond angles in the arene ring approximate the hexagonal angle (120°), and the C−C−B and B−B−B angles of the (Fe)C_2B_3 ring are close to the pentagonal angle (106°). The FeC_2B_3 pentagonal pyramid is slightly deformed because of unequal Fe−C and Fe−B bond lengths.

In summary, we have remarkably improved previous procedures[8−10] by developing a systematic method for the incorporation of the {(η^6-arene)Fe^{II}} unit into a carborane cage. It was demonstrated that reactions between arene salts [(η^6-Me$_n$C$_6$H$_{6-n}$)$_2$Fe](PF$_6$)$_2$ (for n = 3−6) and the [*nido*-7,8-C$_2$B$_9$H$_{11}$]$^{2-}$ dianion give a series of 12-vertex arene *closo*-ferradicarbaboranes of the general structure [3-(η^6-Me$_n$C$_6$H$_{6\text{-}n}$)-*closo*-3,1,2-FeC$_2$B$_9$H$_{11}$] in which the {(η^6-arene)Fe} fragment is isolobal with the BH^{2+} cluster vertex. We have also shown that the structure of the polymethylated [(η^6-arene)$_2$Fe]$^{2+}$ cations prepared at elevated temperatures[1c] must be taken with caution and the relevant work in this area may be worthy of reconsideration. The synthetic method outlined above allows for structural modifications in both the arene and cluster subsections of complex **2**. These might be achieved either by direct substitution or by synthesis from presubstituted starting components. It is expected that this derivatization would lead to compounds of biological activity or to designed syntheses of metallacarborane building blocks. Further efforts to expand the scope of arene−iron carborane chemistry to other arenes and carborane anions and to optimize the yields are currently underway in our laboratories. In progress are also electrochemical investigations (cyclic voltammetry) of these types of compounds.

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Supporting Information Available: Experimental procedures, spectroscopic data for new compounds, and CIF files for **2b** and **2d**. This material is available free of charge via the Internet at http://pubs.acs.org.

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