

Hexaferrocenylbenzene†

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Received (in Berkeley, CA, USA) 4th April 2006, Accepted 5th May 2006

First published as an Advance Article on the web 23rd May 2006

DOI: 10.1039/b604844g

Hexaferrocenylbenzene has been synthesized by six-fold Negishi type ferrocenylation of hexabromo- or hexaiodobenzene.

Hexaferrocenylbenzene **1** has been sought for decades.¹ The molecule is of great interest as a metalated hexakis(cyclopentadienyldiene)radialene,² an electronically tunable dendritic substructure,³ a radial oligocyclopentadienylmetal⁴ with potential in electronic, magnetic, optical, and catalytic applications,⁵ a super-crowded arene that may function as a molecular gear,⁶ a starting point for the construction of cyclic hexa-decker “Ferris-wheel” ferrocenes,⁷ and an annealing precursor to the unknown hexacyclopentacoronene, C₃₆H₁₂.⁸ The most highly ferrocenylated benzenes are dimethyl 1,2,3,4-tetraferrocenylphthalate^{1a} and 1,2,4,5-tetraferrocenylbenzene,⁹ neither one of which has been structurally characterized, although a cycloheptatrienylvanadium analog of the latter has.¹⁰ We have reported recently the five-fold metallacyclopentadienylation of C₅I₅Mn(CO)₃ using Negishi conditions,¹¹ the success of which encouraged us to extend this method to the synthesis of the title compound, despite the anticipated considerably increased steric crowding around the six-fold symmetric benzene core.

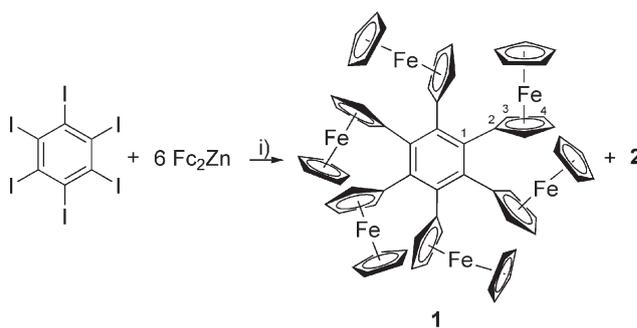
Indeed, when hexaiodobenzene was treated with six equivalents of diferrocenylzinc,^{11,12} prepared from iodoferrocene¹³ by lithiation with BuLi followed by zincation with ZnBr₂, complex **1** was obtained (4%), in addition to pentaferrocenylbenzene **2** (56%; Scheme 1, Fig. 1), separated by repeated chromatography on silica.‡ The observation of substantial quantities of **2** is evidence for the reluctance of the final system or its precursors to incorporate six bulky substituents around the benzene core, although the origin of the proton is obscure.¹⁴ Prolonged reaction times or using excess Fc₂Zn did not improve yields. Switching the substrate to C₆Br₆ slowed conversion and allowed the isolation of **1** (1%), **2** (4%), and, in addition, products **3–5** (Fig. 1), as described in the Supplementary Information†. The structures of complexes **1–4** were ascertained by X-ray crystallographic analysis.§ HPLC of crude reaction mixtures showed a plethora of other compounds, presumably variously ferrocenylated benzenes bearing varying amounts of residual bromines, therefore the products reported are not representative of the entire spectrum of complexes generated.

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† Electronic supplementary information (ESI) available: Experimental and X-ray structural data. See DOI: 10.1039/b604844g



Scheme 1 Synthesis of hexaferrocenylbenzene **1**. Reagents and conditions: (i) Pd₂(dba)₃ (30%), THF, 68 °C, 63 h.

The title compound is remarkably stable, but sensitive to air, especially in solution. The crowded nature of the molecule notwithstanding, the NMR spectra indicate considerable flexibility and average symmetry at room temperature. However, VTNMR reveals decoalescence of the signals due to H3 and H4 at –60 °C to four peaks in the ratio 1 : 1 : 1 : 1 at $\delta = 3.96$ (C3), 4.26 (C4), 4.35 (C4'), and 4.57 (C3') ppm, while the remote CpH absorptions remain as a singlet, signaling (at least local) chirality around C1–C4. Quantification of the data by EXSY provides $\Delta H^\ddagger = 10.5$ (± 0.6) kcal mol⁻¹ and $\Delta S^\ddagger = -0.6$ e.u. (± 3). Thus, as expected, symmetrization is more energetic than that in the pentaferrocenylcyclopentadienyl (Fc₅Cp) scaffold,¹¹ but not by much. On the basis of the X-ray structural features (*vide infra*), we propose a static, chiral, propeller-like structure with alternating “up-down” Fe atoms, all oriented in the same sense around the periphery, the

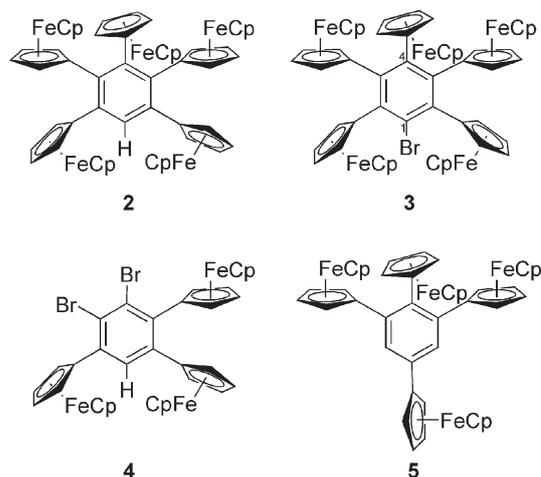


Fig. 1 Products of incomplete ferrocenylation of C₆X₆.

NMR dynamics originating from enantiomerization by a presumably ungeared⁶ substituent motion that leaves the facial disposition of the metals unchanged. The ¹³C resonance for the central C₆ fragment is surprisingly normal.¹⁵ Effective electronic communication is apparent in the UV spectrum, which displays bathochromic shifts relative to that of ferrocene ($\lambda_{\max} = 325, 440 \text{ nm}$)¹⁶ and 1,3,5-triferrocenylbenzene ($\lambda_{\max} = 330, 450 \text{ nm}$).^{1b} Similarly, and in contrast to various Fc_nbenzenes ($n = 2-4$),^{9,17} the voltammogram (see Supplementary Information†) exhibits clearly separated redox waves, $E_{1/2} = -162.8$ (1 e wave), -32.3 (2 e wave), and 222.4 (3 e wave) mV (CH₂Cl₂, NBu₄PF₆, versus [Cp₂Fe]⁰/[Cp₂Fe]⁺).

The extraordinary steric encumbrance in **1** is evident in its X-ray structural details (Fig. 2). The molecule has been characterized as two different solid-state solvates, and the conformation of **1** is indistinguishable in the two cases. In the following analysis, the corresponding geometric values found in the structure of the parent ferrocenylbenzene¹⁸ are given in italics. The molecule is arranged roughly as assumed above for the low-temperature NMR species, in this way minimizing steric and angle strain. The radial C₅H₄ substituents deviate substantially from coplanarity with the benzene frame. Thus, the dihedral angles of the respective benzene ring bonds with their proximal C₅H₄ counterparts (*e.g.*, C1–C2–C17–C18, C2–C3–C27–C31, *etc.*) fall into two alternating groups averaging 30.8 and -81.9° , respectively (10.6°). As in Fc₅CpMn(CO)₃,¹¹ but to a significantly attenuated degree, there appear to be elongated C₅H₄_{quat}–Fe bonds in the direction of η^1, η^4 -bonding [average bond lengths (long/short, Å): 2.09 (2.05)/2.04 (2.03)], and bent ferrocenyls, average value 177.2 (179.9°). The quaternary C₅H₄ carbons are pyramidalized, such as to minimize interference of the appended CpFe unit with the neighboring Fc substituent, quantified by the nonlinear C₅H₄_{centroid}–C₅H₄_{quat}–C_{arom} linkages, average value 170.1 (179.9°). Further strain relief appears derived from elongated C₅H₄_{quat}–C_{arom} distances, average value 1.50 [$1.469(5)$] Å.

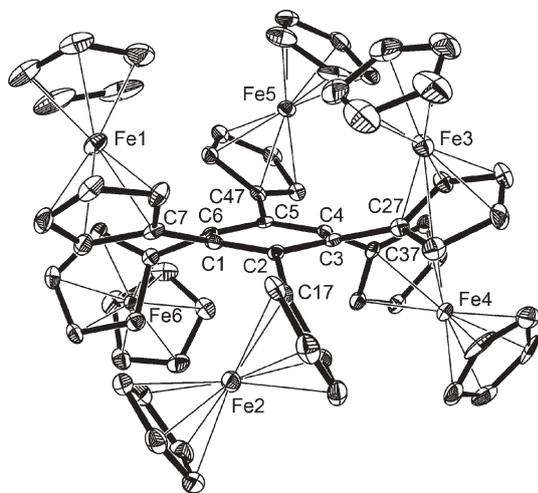


Fig. 2 Hexaferrocenylbenzene **1** in the solid **1**·C₆H₆, showing displacement ellipsoids at 50% probability. The H atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): C1–C2 1.413(6), C2–C3 1.431(5), C3–C4 1.409(5), C4–C5 1.431(5), C5–C6 1.415(5), C6–C1 1.419(5), C1–C7 1.498(5); C1–C2–C3 119.1(4), C₅H₄Fe1_{centroid}–C7–C1 172.7, C1–C2–C3–C4 $-13.7(6)$, C1–C2–C17–C18 $-75.8(6)$, C7–C1–C2–C17 39.1(5).

Most obvious are the distortions of the central ring caused by perferrocenylation. Thus, the benzene ring adopts a chair conformation, evidenced by alternating dihedral angles along the carbon sequence (*e.g.*, C1–C2–C3–C4, *etc.*), average ± 14.0 (0.25°), large torsion angles C₅H₄_{quat}–C_{arom}–C_{arom}–C₅H₄_{quat}, absolute values ranging from 37.5(5) to 40.5(6)[°] [average 38.9 (1.8 for C₅H₄_{quat}–C_{arom}–C_{arom}–H)], and elongated bonds, average 1.42 (1.37) Å. In addition, there is noticeable bond alternation with long/short bonds averaging 1.427/1.411 Å. The bond angles deviate minimally from 120° (average 119.5°). Taking the plane C1–C2–C4–C5 (rms. deviation 0.001 Å) as a reference, C3 lies 0.148(6) Å above this plane and C6 lies 0.152(6) Å below it. These deformations are larger than those in the current record C₆(SiMe₃)₆ (comparable deviations from the C1–C2–C4–C5 plane $+0.13$ and -0.08 Å)¹⁹ and other symmetrically hexasubstituted benzenes.²⁰

Comparison of the structure of **1** with that of the pentaferrocenyl derivative **2** (Fig. 3) is revealing. Thus, the space supplied by removing one Fc substituent generates a much less ordered overall geometry, with Fc1 aligned roughly perpendicular to the benzene core [C6–C1–C7–C11 $86.2(6)^\circ$], the remaining Fcs arranged in an up–down manner, but varying in the extent to which they are not coplanar and in their sense of direction [corresponding dihedral angles Fc2–Fc5: 31.1(7), $-28.2(7)$, 15.8(6), 37.6(7)[°]]. As one might expect, the C₆ core is more deformed from expected geometry around C6 than around C3. For example, the C1–C6 and C5–C6 bonds [both 1.392(6) Å] are close to that expected for a benzene ring, while the other four bonds (average 1.426 Å) are significantly elongated; the four C_{arom} dihedrals incorporating C6 are smaller (average 8.6°) than the remaining two (average 27.0°); the C47–C5–C6–H6A–C1–C7 fragment is basically flat (rms deviation 0.002 Å), whereas the torsions C₅H₄_{quat}–C_{arom}–C_{arom}–C₅H₄_{quat} range from $-14.0(6)^\circ$ (C7–C1–C2–C17) to $-47.9(5)^\circ$ (C27–C3–C4–C37). Taking the near-plane C1–C2–C4–C5 (rms deviation 0.026 Å) as a reference, C6 is only slightly displaced from it [0.075(6) Å], but C3 acutely so [0.294(6) Å], and both in the same direction, thus describing a halfboat-like center ring.

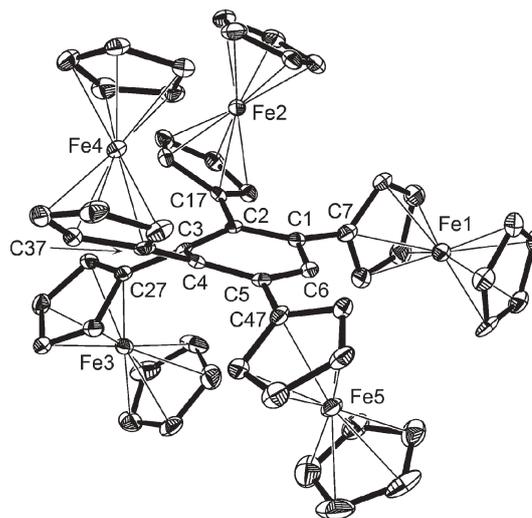


Fig. 3 Pentaferrocenylbenzene **2** in the solid, showing displacement ellipsoids at 50% probability. The H atoms have been omitted for clarity. For selected features, see text.

Interestingly, in the structure of **3** (see Supplementary Information†), the sizeable Br atom serves to symmetrize the molecule substantially, with a pseudo-mirror plane passing through Br, C1, and C4 (for numbering, see Fig. 1), and the Fcs arranged in a regular up–down sequence. Taking the plane C2–C3–C5–C6 (rms deviation 0.006 Å) as a reference, C1 lies essentially in it [displacement 0.011(8) Å], while C4 is displaced substantially [0.272(7) Å] from it. The other features of **3** are similar to those of **2**.

Finally, the structure of **4** deviates much less from expectation than the preceding molecules, most notable being a small dihedral angle of 3.8(6)° between the two *ortho*-ferrocenyls, and two elongated C_{arom}–C_{arom} bonds, one separating the two Fcs [1.439(6) Å], and one between one of these Fcs and the adjacent Br atom [1.431(6) Å]. The benzene ring is fairly flat (rms deviation of all six C atoms 0.025 Å, average C_{arom}–C_{arom}–C_{arom} = 3.5°).

In summary, we have shown that hexaferrocenylbenzene **1** can be made, despite its considerably encumbered structure, and that it shows remarkable conformational mobility in solution. Current efforts are directed at improving yields and exploring the chemistry of this molecule along the lines described in the introduction.

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division, of the US Department of Energy, under Contract DE-AC02-05CH11231 (KPCV) and MRI/NSF 0420863 (TVT). PWL was an NSF Fellow, GDW was supported by NSF and Bayer-Miles predoctoral fellowships, and UL is grateful for a German National Academic Foundation Scholarship. We thank Dr Alex Shafir for expert assistance with the CV measurements and Professor J. Arnold for illuminating discussions.

Notes and references

† **1**: Yellow-orange crystals. Mp: 270 °C (decomp.). Anal.: Calc. for C₆₆H₅₄Fe₆: C, 67.05; H, 4.60%. Found: C, 66.99; H, 4.87%. HRMS (*m/z*): Calc. for C₆₆H₅₄Fe₆: 1182.0322. Found: 1182.0345. ¹H NMR (300 MHz, CD₂Cl₂, δ/ppm): 4.35 (BB'm, 12H, H4), 4.32 (AA'm, 12H, H3), 3.99 (s, 30H, CpH). ¹³C{¹H} NMR (100 MHz, CD₂Cl₂, δ/ppm): 137.6 (C1), 93.0 (C2), 75.0 (C3), 70.0 (Cp), 67.8 (C4). IR (KBr, cm⁻¹): 3100, 1655, 1638, 1459, 1108, 817. UV/VIS (CH₂Cl₂, nm/ε): 274sh (11400), 312 (11400), 370 (5850), 462 (1620). **2**: Orange-red powder. Mp: 166–168 °C (decomp.). Anal.: Calc. for C₅₆H₄₆Fe₅: C, 67.38; H, 4.64%. Found: C, 67.61; H, 4.89%. HRMS (*m/z*): Calc. for C₅₆H₄₆Fe₅: 998.0346. Found: 998.0326. ¹H NMR (300 MHz, CD₂Cl₂, δ/ppm): 8.29 (s, 1H), 4.85 (t, *J* = 1.8 Hz, 4H), 4.47 (t, *J* = 1.8 Hz, 4H), 4.38 (s, 10H), 4.32 (t, *J* = 1.8 Hz, 4H), 4.19 (t, *J* = 1.8 Hz, 4H), 3.90 (m, 4H), 3.88 (s, 5H), 3.85 (s, 10H). ¹³C{¹H} NMR (100 MHz, CD₂Cl₂, δ/ppm): 143.3, 136.7, 133.0, 132.2 (CH), 92.8, 91.5, 88.9, 73.7, 72.2, 71.9, 69.9, 69.6 (2Cp), 69.5 (Cp), 67.4, 67.39, 67.30, 67.26. IR (KBr, cm⁻¹): 3100, 1655, 1638, 1459, 1107, 817. UV/VIS (CH₂Cl₂, nm/ε): 296sh (18800), 354sh (11000), 466 (2840).

§ Crystallographic data. **1**: C₆H₆ (from C₆H₆): C₇₂H₆₀Fe₆, *M* = 1260.3, *T* = 100(2) K, crystal size 0.30 × 0.10 × 0.02 mm³, monoclinic, space group C2/c, *a* = 39.8230(12), *b* = 11.4629(3), *c* = 22.8543(6) Å, α = 90, β = 90.923(1), γ = 90°, *V* = 10431.3(5) Å³, *Z* = 8, *D*_{calc} = 1.605 g cm⁻³, μ(Mo Kα) = 1.672 mm⁻¹, 9210 unique reflections, of which 6409 were taken as observed [*I* > 2σ(*I*)], *R*1 = 0.041, *wR*2 = 0.104 (all data), *S* = 1.01. **1**·½C₆H₄Cl₂ (from MeOH–C₆H₄Cl₂): C₆₉H₅₆ClF₆, *M* = 1255.7, *T* = 220(2) K, crystal size 0.14 × 0.10 × 0.01 mm³, monoclinic, space group I2/a, *a* = 44.218(11), *b* = 11.535(2), *c* = 22.898(5) Å, α = 90, μ = 93.960(9), γ = 90°, *V* = 11651(4) Å³, *Z* = 8, *D*_{calc} = 1.432 g cm⁻³, μ(synchrotron, λ = 0.6850 Å) = 1.541 mm⁻¹, 8218 unique reflections, of

which 5820 were taken as observed [*I* > 2σ(*I*)], *R*1 = 0.105, *wR*2 = 0.291 (all data), *S* = 1.04. **2** (from MeOH–CH₂Cl₂): C₅₆H₄₆Fe₅, *M* = 998.2, *T* = 130(2) K, crystal size 0.50 × 0.20 × 0.18 mm³, triclinic, space group P $\bar{1}$, *a* = 11.9387(7), *b* = 12.4181(7), *c* = 15.7154(9) Å, α = 99.808(1), β = 100.205(1), γ = 115.062(1)°, *V* = 1996.9(2) Å³, *Z* = 2, *D*_{calc} = 1.660 g cm⁻³, μ(Mo Kα) = 1.815 mm⁻¹, 6443 unique reflections, of which 5410 were taken as observed [*I* > 2σ(*I*)], *R*1 = 0.050, *wR*2 = 0.133 (all data), *S* = 1.03. The data for **3** and **4** are included in the Supplementary Information. CCDC 603715–603719. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b604844g

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