

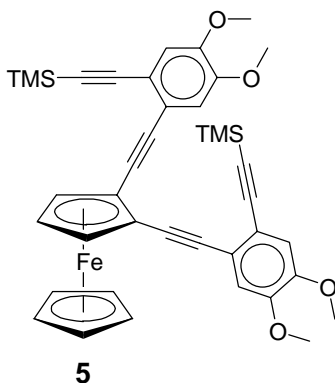
Is ferrocene more aromatic than benzene?

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Supplementary Material

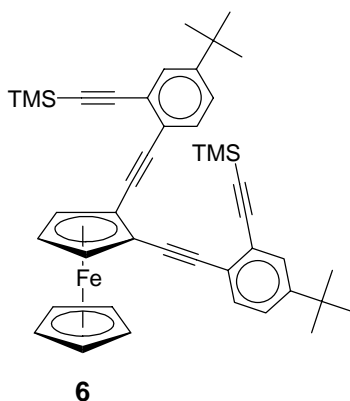
General All reagents were of commercial grade and used as obtained. ^1H - and ^{13}C -NMR spectra were recorded in CDCl_3 on a Bruker AM 300 or a Varian Mercury 400 spectrometer. The mass spectra were measured on a VG 70SQ. IR spectra were obtained using a Perkin Elmer FTIR 1600 on NaCl plates. X-Ray structure analysis of all were measured at 293 K using a Bruker SMART APEX CCD-based diffractometer system equipped with a Mo target x-ray tube. 1-chloro-2-(trimethylsilylethynyl) ethylene was prepared by the Pd/Cu catalyzed reaction of *cis*-1,2-dichloroethylene and trimethylsilylacetylene in piperidine.



[1,2-Di(ethynyl-1,2-(2'-(trimethylsilylethynyl)-4',5'-dimethoxyphenyl)-ferrocene (5)

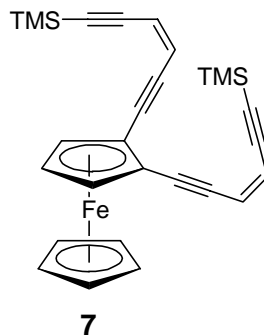
A round bottom flask was charged with 1,2-diethynylferrocene (**1**)ⁱ (0.140 g, 0.60 mmol), 1,2-dimethoxy-4-trimethylsilylethynyl-5-iodobenzene (**2**) (0.491 g, 1.36 mmol), $(\text{PPh}_3)_2\text{PdCl}_2$ (9 mg, 0.01 mmol), CuI (6 mg, 0.03 mmol) and piperidine (10 ml). After

purging the reaction vessel with N₂, the reaction was stirred at room temperature for 18 h. After aqueous workup with hexanes, the brown mixture was chromatographed on silica gel with CH₂Cl₂:hexane (1:1) to yield pure **5** (0.130 g, 30%) as an orange oil. IR (neat): ν 2972, 2144, 1695, 1511, 1365, 1183 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 6.98 (s, 2H), 6.91 (s, 2H), 4.57-4.65 (d, 2H), 4.32 (s, 5H), 4.31-4.29 (t, 1H), 3.87 (s, 6H), 3.80 (s, 6H), 0.24 (s, 18H). ¹³C NMR (100 MHz, CDCl₃): δ 149.07, 148.44, 119.94, 117.78, 114.49, 114.29 (12C), 103.56, 96.63, 89.54, 87.32 (8C), 72.05, 71.31, 68.96, 68.87 (10C), 55.91, 55.87 (4C), 0.11 (6C). MS (EI) *m/z*. Calc. For M⁺ (C₄₅H₅₇CoO₄Si₄) 689.9171, Found 698.1988 (E = 2.6 ppm).

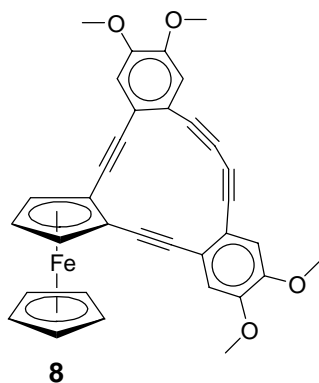


[1,2-Di(ethynyl-1,2-(2'-(trimethylsilylethynyl)-4'-tert-butylphenyl)-ferrocene (6) A round bottom flask was charged with **1** (0.200 g, 0.85 mmol), 4-iodo-3-(trimethylsilylethynyl)-*tert*-butylbenzeneⁱⁱ (**3**) (0.581 g, 1.63 mmol), (PPh₃)₂PdCl₂ (11 mg, 0.02 mmol), CuI (7.2 mg, 0.04 mmol) and piperidine (10 ml). After purging the reaction vessel with N₂, the reaction was stirred at room temperature for 18 h. After aqueous workup with hexanes, the brown mixture was chromatographed on silica gel with CH₂Cl₂:hexane (9:1) to yield pure **6** (0.511 g, 96%) as an orange oil. IR (neat): ν 2966, 2187, 1700, 1361, 1183, 844 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 7.49-7.45 (d, 2H),

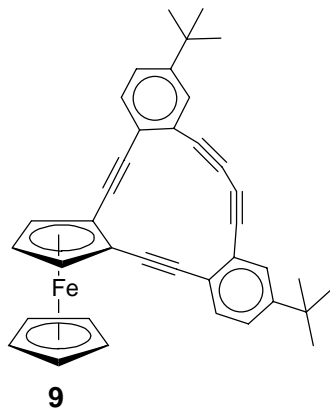
7.29 (s, 2H), 7.27-7.26 (d, 2H), 4.58-4.57 (d, 2H), 4.30-4.29 (t, 1H), 4.29 (s, 5H), 1.29 (s, 18H), 0.26 (s, 18H). ^{13}C NMR (100 MHz, CDCl_3): δ 150.53, 132.05, 129.27, 125.61, 124.42, 123.89 (12C), 104.50, 97.25, 90.14, 87.32 (8C), 72.19, 72.16, 71.71, 68.88 (10C), 34.65, 31.02 (8C), 0.21 (6C). MS (EI) m/z Calc. For M^+ ($\text{C}_{44}\text{H}_{50}\text{FeSi}_2$) 690.2800, Found 690.2774 (E = 2.1 ppm).



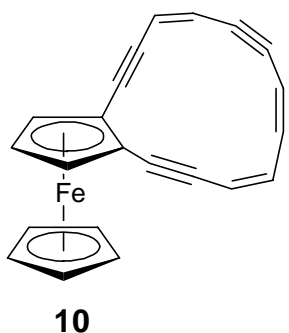
[1,2-Di(ethynyl-1,2-(2'-(trimethylsilylethynyl)-ethylene)]-ferrocene (7) A round bottom flask was charged with **1** (0.200 g, 0.85 mmol), 1-chloro-2-(trimethylsilylethynyl) ethylene (**4**) (0.342 g, 2.14 mmol), $(\text{PPh}_3)_2\text{PdCl}_2$ (12 mg, 0.02 mmol), CuI (8 mg, 0.04 mmol) and piperidine (10 ml). After purging the reaction vessel with N_2 , the reaction was stirred at room temperature for 18 h. After aqueous workup with hexanes, the brown mixture was chromatographed on silica gel with CH_2Cl_2 :hexane (8:2) to yield pure **7** (0.320 g, 77 %) as an red-orange oil. IR (neat): ν 2958, 2339, 2196, 1642, 843 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 6.00-5.96 (d, 2H), 5.83-5.80 (d, 2H), 4.52-4.51 (d, 2H), 4.30-4.29 (t, 1H), 4.25 (s, 5H), 0.22 (s, 18H). ^{13}C NMR (100 MHz, CDCl_3): δ 121.23, 117.90 (4C), 102.58, 102.56, 95.33, 86.04 (8C), 72.32, 72.29, 69.65, 67.88 (10C), 0.05 (6C). MS (EI) m/z Calc. For M^+ ($\text{C}_{28}\text{H}_{30}\text{FeSi}_2$) 478.1235, Found 478.1223 (E = 2.5 ppm).



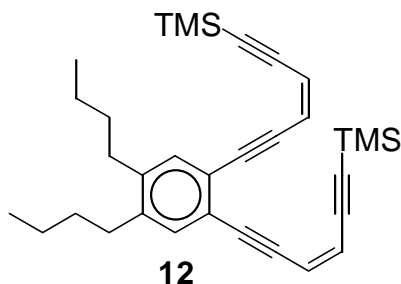
Dimethoxy Ferrocene Cycle (8) A round bottom flask was charged with **5** (0.130 g, 0.19 mmol), Bu₄NF (1 M in THF) (0.55 ml, 0.57 mmol), THF (3 ml) and diethyl ether (10 ml). The resulting mixture was stirred at 25°C for 2 hr. Aqueous workup with diethyl ether followed by removal of the solvent *in vacuo* yields a dark red oil. Then Cu(OAc)₂ (2.60 g, 14.31 mmol) and CH₃CN (50 ml) was added to the oil and the reaction mixture was then heated to 80°C for 6 hr. After which the mixture was washed with water and extracted with ethyl acetate. Chromatography on silica gel with ethyl acetate:hexanes (1:1) yields pure **8** (30 mg, 49 %) as a orange solid. Mp: >230°C (dec.). IR (neat): ν 2967, 1698, 1500, 1365, 1216, 1183 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 7.18 (s, 2H), 6.98 (s, 2H), 4.79-4.78 (d, 2H), 4.41-4.40 (t, 1H), 4.27 (s, 1H), 4.00 (s, 6H), 3.94 (s, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 149.76, 148.34, 123.66, 115.90, 114.18, 111.49 (12C), 90.90, 87.12, 85.15, 78.76 (8C), 73.89, 71.92, 69.41, 67.28 (10C), 56.11, 56.06 (4C). UVVis (CHCl₃): λ 274 ($\epsilon = 7856 \text{ cm}^{-1} \text{ M}^{-1}$), 314 ($\epsilon = 12028 \text{ cm}^{-1} \text{ M}^{-1}$), 371 ($\epsilon = 2873 \text{ cm}^{-1} \text{ M}^{-1}$). UVVis (Solid State): λ 212, 278, 326 nm. MS (EI) *m/z* Calc. For M⁺ (C₃₉H₃₉CoO₄Si₂) 552.1024, Found 552.1009 (E = 2.7 ppm).



tert-Butyl Ferrocene Cycle (9) A round bottom flask was charged with **6** (0.341 g, 0.62 mmol), Cu(OAc)₂ (2.60 g, 13.64 mmol) and CH₃CN (50 ml). The reaction mixture was then heated to 80°C for 6 hr. After which the mixture was washed with water and extracted with hexanes. Chromatography on silica gel with hexanes yields pure **9** (170 mg, 50 %) as a bright orange solid. Mp: 152°C (dec.). IR (neat): ν 2967, 2189, 1700, 1360, 1183 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 7.62-7.59 (d, 2H), 7.51 (s, 2H), 7.42-7.39 (d, 2H), 4.75-4.74 (d, 2H), 4.40-4.38 (t, 1H), 4.23 (s, 5H), 1.32 (s, 18H). ¹³C NMR (100 MHz, CDCl₃): δ 150.33, 131.48, 127.24, 126.39, 126.08, 122.53 (12C), 91.69, 87.10, 85.23, 79.21 (8C), 74.22, 71.93, 69.61, 67.14 (10C), 34.72, 30.99 (8C). UVVis (CHCl₃): λ 303 ($\epsilon = 114671 \text{ cm}^{-1} \text{ M}^{-1}$), 352 ($\epsilon = 29002 \text{ cm}^{-1} \text{ M}^{-1}$). UVVis (Solid State): λ 238, 322, 370 nm. MS (EI) m/z Calc. For M⁺ (C₃₈H₃₂Fe) 544.1853, Found 544.1854 (E = 0.2 ppm).

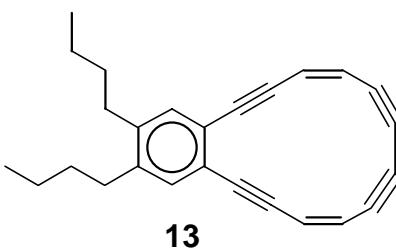


Dialkene Ferrocene Cycle (10) A round bottom flask was charged with **7** (0.30 g, 0.63 mmol), K₂CO₃ (0.26 g, 1.88 mmol), THF (3 ml) and methanol (10 ml). The resulting mixture was stirred at 25°C for 6 hr. Aqueous workup with diethyl ether followed by removal of the solvent *in vacuo* yields a dark red oil. Then Cu(OAc)₂ (2.50 g, 13.76 mmol) and CH₃CN (70 ml) was added to the oil and the reaction mixture was then heated to 80°C for 4 hr. After which the mixture was washed with water and extracted with diethyl ether. Chromatography on silica gel with CH₂Cl₂:hexanes (8:2) yields pure **10** (131 mg, 63 %) as a dark red solid. Mp: 56° C (dec.). IR (neat): ν 2933, 2356, 2144, 1628, 739 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 6.77-6.23 (d, 2H), 6.23-6.20 (d, 2H), 4.88-4.87 (d, 2H), 4.42-4.41 (t, 1H), 4.16 (s, 5H). ¹³C NMR (100 MHz, CDCl₃): δ 126.69, 115.17 (4C), 99.10, 88.45, 88.01, 83.50 (8C), 73.97, 72.42, 70.37, 67.68 (10C). UVVis (CHCl₃): λ 265 ($\epsilon = 2639 \text{ cm}^{-1} \text{ M}^{-1}$), 308 ($\epsilon = 5359 \text{ cm}^{-1} \text{ M}^{-1}$). UVVis (Solid State): λ 215, 267, 315 nm. MS (EI) *m/z* Calc. For M⁺ (C₂₂H₁₂Fe) 332.0288, Found 332.0280 (E = 2.4 ppm).



[1,2-Di(ethynyl-1,2-(2'-(trimethylsilylethynyl)-ethylene)]-4,5-dibutylbenzene (12) A round bottom flask was charged with 1,2-diethynyl-4,5-dibutylbenzene (**11**) (0.460 g, 1.93 mmol), 1-chloro-2-(trimethylsilylethynyl)ethylene (0.711 g, 4.48 mmol), (PPh₃)₂PdCl₂ (15 mg, 0.02 mmol), CuI (18 mg, 0.09 mmol) and piperidine (10 ml). After

purging the reaction vessel with N₂, the reaction was stirred at room temperature for 18 h. After aqueous workup with hexanes, the brown mixture was chromatographed on silica gel with CH₂Cl₂:hexane (8:2) to yield pure **12** (0.692 g, 74 %) as a red-brown oily solid. IR (neat): ν 2955, 2862, 2184, 2142, 1671, 1564, 1487, 1464, 1407, 1249, 1051, 1025, 848, 760 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 7.28 (s, 2H), 6.11-6.08 (d, 2H), 5.87-5.83 (d, 2H), 2.58-2.52 (t, 4H), 1.52-1.50 (m, 4H), 1.52-1.50 (m, 4H), 0.90-0.95 (t, 6H), 0.22 (s, 18H). ¹³C NMR (100 MHz, CDCl₃): δ 141.49, 133.14, 122.66 (6C), 121.01, 118.95 (4C), 102.96, 102.37, 96.50, 89.96 (4C), 33.03, 32.11, 22.72, 13.93 (8C), -0.12 (6C). MS (EI) *m/z*. Calc. For M⁺ (C₃₂H₄₂Si₂) 482.2825, Found 482.2907 (E = 2.7 ppm).



Dehydroannulene (13) A round bottom flask was charged with **12** (0.530 g, 1.10 mmol), K₂CO₃ (0.450 g, 3.26 mmol), THF (5 ml) and methanol (2 ml). The resulting mixture was stirred at 25°C for 18 hr. Aqueous workup with diethyl ether followed by removal of the solvent *in vacuo* yields a dark brown oil. Then Cu(OAc)₂ (4.37 g, 24.06 mmol) and CH₃CN (20 ml) was added to the oil and the reaction mixture was then heated to 80°C for 12 hr. After which the mixture was washed with water and extracted with diethyl ether. Chromatography on silica gel with hexanes yields pure **13** (266 mg, 72 %) as a yellow oily solid. IR (neat): ν 2955, 2925, 2855, 2111, 1641, 1377, 1049, 844, 733 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 8.01 (s, 2H), 7.34-7.31 (d, 2H), 6.65-6.62 (d, 2H), 2.80-2.75 (t, 4H), 1.70-1.65 (m, 4H), 1.49-1.41 (m, 4H), 0.98-0.94 (t, 6H). ¹³C NMR (100 MHz,

CDCl₃): δ 141.77, 135.77, 125.99 (6C), 120.03, 115.64 (4C), 100.28, 92.38, 89.86, 84.65 (4C), 33.26, 32.30, 22.81, 13.99 (8C). UVVis (CHCl₃): λ 313 ($\epsilon = 2322 \text{ cm}^{-1} \text{ M}^{-1}$), 371 ($\epsilon = 254 \text{ cm}^{-1} \text{ M}^{-1}$), 390 ($\epsilon = 181 \text{ cm}^{-1} \text{ M}^{-1}$). UVVis (Solid State): λ 200, 223, 319, 375, 396 nm. MS (EI) decomposition occurred before M⁺ could be determined.

References:

ⁱ Bunz, UHF. *J. Organomet. Chem.* **1995**, 498, C8.

ⁱⁱ Wan, W.B., Brand, S.C., Pak, J.J., Haley, M.M. *Chem. Eur. J.* **2000**, 6(11), 2044-2052.