

## Tentacled Aromatics: from Central-ring to Outer-ring Iron Sandwich Complexes

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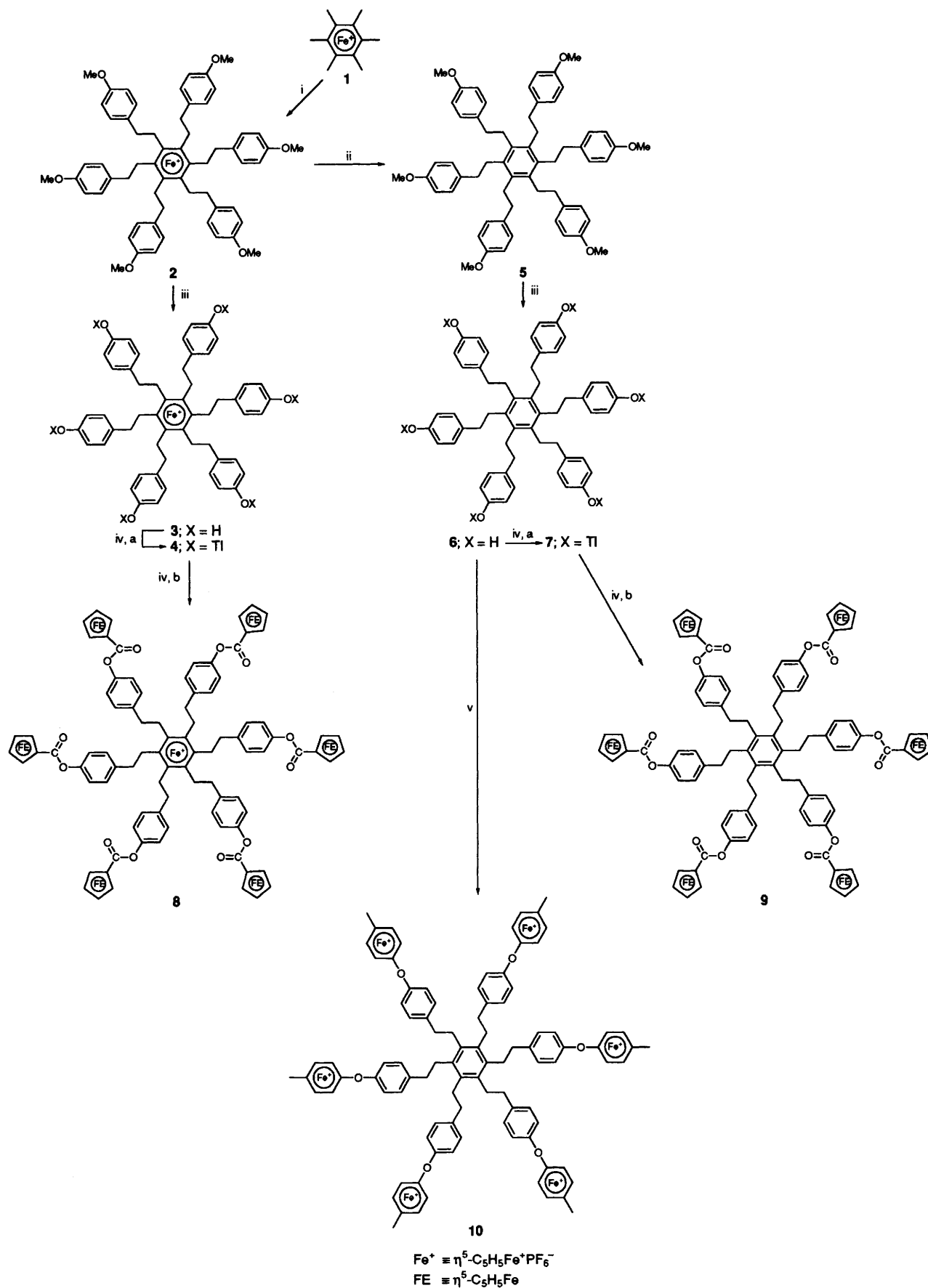
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Hexamethoxyphenylethylbenzenes synthesized by hexaalkoxybenzylation of  $C_6Me_6$  via their complexation to the  $Fe(C_5H_5)^+$  electron-withdrawing group are readily cleaved by  $BBr_3$  to yield hexaphenols, leading to hexa- and hepta-iron sandwich complexes with six equivalent redox centres.

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$\pi$ -Complexation of aromatic compounds by transition metal groups is a powerful way to reverse their polarity and thus facilitate nucleophilic reactions.<sup>1,2</sup> Since it has been found that this principle could lead to polyalkylation and polyfunctionalization of methylated aromatic compounds via their  $FeCp^+$  ( $Cp = C_5H_5$ ) complexes,<sup>2</sup> we envisaged that a new

area of molecular materials could be investigated, given the variety of accessible topologies. Unlike allylic functionalization,<sup>3a</sup> benzylation of  $[FeCp(C_6Me_6)][PF_6]$  **1** exclusively leads to single branching<sup>3b,c</sup> (Scheme 1). Based on this strategy we now report the synthesis of hexaphenoxide synthons and hexa- and hepta-iron sandwich complexes. Sandwich frameworks



**Scheme 1** Reagents and conditions: i, Bu<sup>t</sup>OK, BrCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>OMe-*p*, DME, 40°C, 24 h; ii, *hν*, PPh<sub>3</sub> (1 equiv.), MeCN, room temp., 8 h; iii, a, BBr<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, -78°C to room temp., 20 h; b, H<sub>2</sub>O, 0°C; iv, a, TiOEt, 7 equiv.; b, CpFe(C<sub>5</sub>H<sub>4</sub>COCl), 12 equiv., room temp., 20 h; v, [CpFeClC<sub>6</sub>H<sub>4</sub>Me][PF<sub>6</sub>], K<sub>2</sub>CO<sub>3</sub>, THF, 40°C, 4 days

are excellent geometries for stabilizing redox forms associated with fast heterogeneous electron transfers.<sup>4</sup> Thus, systems with several redox centres are excellent candidates for multielectron redox catalysis.<sup>5</sup> Moreover, the introduction of [FeCp(arene)]<sup>+</sup> units with *p*-methyl substituents on the branches potentially provides the possibility to iterate the polybenzylolation reaction (Scheme 1) for the build-up of organometallic molecular trees.<sup>6</sup>

The reaction of **1** with *p*-methoxybenzyl bromide and Bu<sup>t</sup>OK in 1,2-dimethoxyethane (DME) at 40 °C gives the hexakis(*p*-methoxyphenylethyl)benzene complex **2**.<sup>3c</sup> Reaction of **2** with BBr<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub> (-78 → 20 °C) yields (98%) the hexaphenol derivative **3**. Its thallium(I) salt **4** is readily prepared in quantitative yield by addition of 6.6 equiv. of thallium ethoxide to a solution of the phenol in tetrahydrofuran (THF). Analogous reactions can be performed without the FeCp<sup>+</sup> group if **2** is photolysed by visible light giving **5**. The organic hexaphenol **6** and the thallium(I) hexaphenoxide **7** are obtained by using the above procedures. We have found that treatment of a suspension of the unisolated phenol salts in anhydrous THF **4** or diethyl ether **7**, with 12 equiv. of ferrocenecarbonyl chloride for 20 h at room temperature, affords the pure phenol esters of ferrocenes **8** and **9** in good yields. The reaction of [FeCp(η<sup>6</sup>-*p*-MeC<sub>6</sub>H<sub>4</sub>Cl)]<sup>+</sup>PF<sub>6</sub><sup>-</sup> with **7** under mild conditions (THF, 40 °C, 4 days) in the presence of K<sub>2</sub>CO<sub>3</sub> results in the displacement of the halogen<sup>7</sup> and gives the hexacation **10**. In these ways (Scheme 1) a series of hexa- and hepta-iron complexes **8**–**10** are obtained as powders in 60–77% yields after aqueous work-up, extraction with nitromethane **10** or chromatographic purification on silica gel (Et<sub>2</sub>O and CH<sub>2</sub>Cl<sub>2</sub> as eluents) (**8** and **9**).

All isolated new compounds were satisfactorily characterized by elemental analysis and by NMR spectroscopy.† For instance, the perfect equivalence of the six branches observed by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy is consistent with the expected highly symmetrical structures of the hexa- and hepta-iron complexes. The hexakis [FeCp(arene)]<sup>+</sup> derivative **10** exhibits a single (reversible) wave in cyclic voltammetry [*E*<sup>o</sup> = -1.30 V, DMF (dimethylformamide), Bu<sub>4</sub>N<sup>+</sup>BF<sub>4</sub><sup>-</sup> (0.1 mol dm<sup>-3</sup>), Δ*E*<sub>p</sub> = 80 mV]. Comparison of its CV peak intensity using ferrocene as an internal reference gives the number of electrons *n* = 6 ± 1 corresponding to the six Fe<sup>II/I</sup> redox systems. For **9**, only one oxidation wave is observed, in which all six ferrocene units are oxidized at the same potential [+0.78 V vs. standard calomel electrode (SCE), DMF, room

temp., Δ*E*<sub>p</sub> = 60 mV]. As expected for **8**, one cathodic wave at *E*<sup>o</sup> = -1.34 V vs. SCE (DMF, -30 °C, Δ*E*<sub>p</sub> = 60 mV) is observed for the one-electron reduction of the central (cyclopentadienyl)(arene)iron cationic unit. In addition, one oxidation wave is observed at +0.88 V vs. SCE (DMF, room temp., Δ*E*<sub>p</sub> = 120 mV) corresponding, as in the case of **9**, to the oxidation of the peripheral ferrocenes. The direct comparison of this wave with the intensity of the CV peak due to the central [FeCp(arene)]<sup>+</sup> shows that the oxidation waves observed for **8** and **9** involved the transfer of six electrons at a same potential. It is noteworthy that for **8**, by comparison with **9**, the observed *E*<sup>o</sup> and Δ*E*<sub>p</sub> values signify an interaction between the iron centres.

In summary, this route to novel hexaphenol species opens attractive synthetic possibilities of molecular materials. The build up of larger molecular trees with various redox centres on the branches is in progress as well as the study of their physical and chemical properties.‡

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† **3**: <sup>1</sup>H NMR (CD<sub>3</sub>COCD<sub>3</sub>) δ 3.01 and 3.28 [br m, 24 H, (CH<sub>2</sub>)<sub>2</sub>], 4.98 (s, 5 H, C<sub>5</sub>H<sub>5</sub>), 6.83 and 7.28 (m, 24 H, ArH), 7.03 (OH); <sup>13</sup>C NMR (CD<sub>3</sub>COCD<sub>3</sub>) δ 33.94 and 37.32 (CH<sub>2</sub>), 79.26 (C<sub>5</sub>H<sub>5</sub>), 104.03 (ArCC), 116.43 and 130.14 (ArCH), 132.49 (ArCC), 156.93 (ArCO).

**6**: <sup>1</sup>H NMR (250 MHz, CD<sub>3</sub>COCD<sub>3</sub>) δ 2.73 and 2.94 [br m, 24 H, (CH<sub>2</sub>)<sub>2</sub>], 6.79 and 7.06 (m, 24 H, ArH), 8.18 (br s, OH); <sup>13</sup>C NMR (62.9 MHz, CD<sub>3</sub>COCD<sub>3</sub>) δ 33.63 and 37.98 (CH<sub>2</sub>), 116.37 and 130.23 (ArCH), 134.26 and 137.48 (ArCC), 156.61 (ArCO).

**8**: IR (Nujol, KBr) ν<sub>CO</sub>: 1715 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 3.13 and 3.25 [br m, 24 H, (CH<sub>2</sub>)<sub>2</sub>], 4.29 (s, 5 H, C<sub>5</sub>H<sub>5</sub>), 4.49 and 4.92 (m, 24 H, C<sub>5</sub>H<sub>4</sub>), 4.69 (s, 5 H, C<sub>5</sub>H<sub>5</sub>), 7.17 and 7.29 (m, 24 H, ArH); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 32.84 and 36.95 (CH<sub>2</sub>), 70.07 (C<sub>5</sub>H<sub>5</sub>), 71.82 and 72.02 (C<sub>5</sub>H<sub>4</sub>), 77.29 (C<sub>5</sub>H<sub>4</sub>C), 78.09 (C<sub>5</sub>H<sub>5</sub>), 102.88 (ArCCH<sub>2</sub>), 122.47 and 129.17 (ArCH), 137.10 (ArCCH<sub>2</sub>), 149.85 (ArCO), 170.58 (CO<sub>2</sub>).

**9**: IR (Nujol, KBr) ν<sub>CO</sub>: 1725 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 2.95 and 3.10 [br m, 24 H, (CH<sub>2</sub>)<sub>2</sub>], 4.31 (s, 30 H, C<sub>5</sub>H<sub>5</sub>), 4.50 and 4.99 (m, 24 H, C<sub>5</sub>H<sub>4</sub>), 7.21 and 7.35 (m, ArH); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 32.61 and 37.41 (CH<sub>2</sub>), 70.02 (C<sub>5</sub>H<sub>5</sub>), 70.71 and 71.93 (C<sub>5</sub>H<sub>4</sub>), 77.09 (C<sub>5</sub>H<sub>4</sub>C), 78.08 (C<sub>5</sub>H<sub>5</sub>), 121.94 and 129.16 (ArCH), 136.65 and 139.44 (ArCC), 149.33 (ArCO), 170.26 (CO<sub>2</sub>).

**10**: <sup>1</sup>H NMR (CD<sub>3</sub>COCD<sub>3</sub>) δ 2.42 (s, CH<sub>3</sub>), 3.02 and 3.15 [br m, 24 H, (CH<sub>2</sub>)<sub>2</sub>], 5.12 (s, 30 H, C<sub>5</sub>H<sub>5</sub>), 6.21 (m, ArH), 7.30 and 7.47 (m, ArH); <sup>13</sup>C NMR (CD<sub>3</sub>COCD<sub>3</sub>) δ 19.86 (CH<sub>3</sub>), 32.27 and 37.81 (CH<sub>2</sub>), 76.85 and 87.78 (ArCH), 78.47 (C<sub>5</sub>H<sub>5</sub>), 101.44 (ArCCH<sub>3</sub>), 121.86 and 131.46 (ArCH), 133.60 (ArCCH<sub>2</sub>), 137.43 (ArCC), 141.40 (ArCO), 152.61 (ArCO).

Satisfactory elemental analyses were obtained.