

## Regioselective Chlorocarbonylation of Polybenzyl Cores and Functionalization Using Dendritic and Organometallic Nucleophiles

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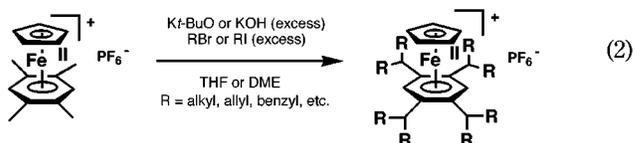
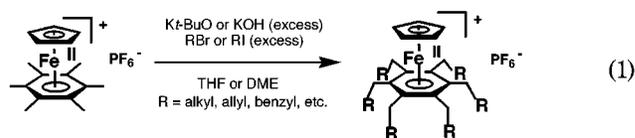
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Regiospecific chlorocarbonylation of the polybenzyl cores PhCH<sub>2</sub>CH<sub>2</sub>Ph, C<sub>6</sub>(CH<sub>2</sub>CH<sub>2</sub>Ph)<sub>6</sub>, **7**, and {CH(CH<sub>2</sub>Ph)<sub>2</sub>}<sub>4</sub>-1,2,4,5-C<sub>6</sub>H<sub>2</sub>, **8**, in the para position of the benzyl groups gives the chlorocarbonyl derivatives **2**, **9**, and **10**, respectively, in good yields. The octachlorocarbonyl derivative **10** reacts with Newkome's aminotripod NH<sub>2</sub>C(CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>CN)<sub>3</sub> to give the 24-nitrile dendrimer **13** which is characterized by its molecular peak in the MALDI TOF mass spectrum and with (5-aminopentyl)-1-ferrocene to give the octaferrocene complex **14**. Reactions of **2**, **9**, and **10** with sodium methanolate in methanol gives the methyl esters **3**, **15**, and **16** which are reduced by LiAlH<sub>4</sub> to the primary alcohols **4**, **17**, and **18**; reactions of these alcohols with NaI and BF<sub>3</sub>·Et<sub>2</sub>O yield the iodomethyl derivatives **5**, **19**, and **20**. The organoiron nucleophile [Fe<sup>II</sup>Cp(η<sup>5</sup>-C<sub>6</sub>Me<sub>5</sub>CH<sub>2</sub>)], **1**, reacts with **5**, **19**, and **20** leading to C–C bond formation and recovery of the aromatic structure of the ligand. This reaction with **5** yields a soluble complex, [Fe<sup>II</sup>Cp(η<sup>6</sup>-C<sub>6</sub>Me<sub>5</sub>CH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>)<sub>2</sub>], **6**, in which the two redox groups, separated by 14 carbon atoms, are independent, being reversibly reduced at approximately the same potential in an overall two-electron wave recorded by cyclic voltammetry. The analogous reaction with **19** and **20**, however, gave almost insoluble hexa- and octa-iron complexes **21** and **22** with mediocre purities.

### Introduction

Among the plethora of organotransition-metal activation types,<sup>1</sup> a number of them have now enriched the field of organic synthesis<sup>2</sup> and molecular engineering.<sup>3</sup> An efficient C–H activation/C–C bond formation system that we disclosed two decades ago was the CpFe<sup>+</sup>-induced hexamethylation of hexamethylbenzene using excess *t*-BuOK and CH<sub>3</sub>I,<sup>4a</sup> a reaction further extended to hexabenzylation, hexaalkylation, and hexaallylation<sup>4b</sup> (eq

1). Likewise, the CpFe<sup>+</sup>-induced octamethylation, octaallylation, and octabenzylation of durene were achieved selectively (eq 2).<sup>4</sup>



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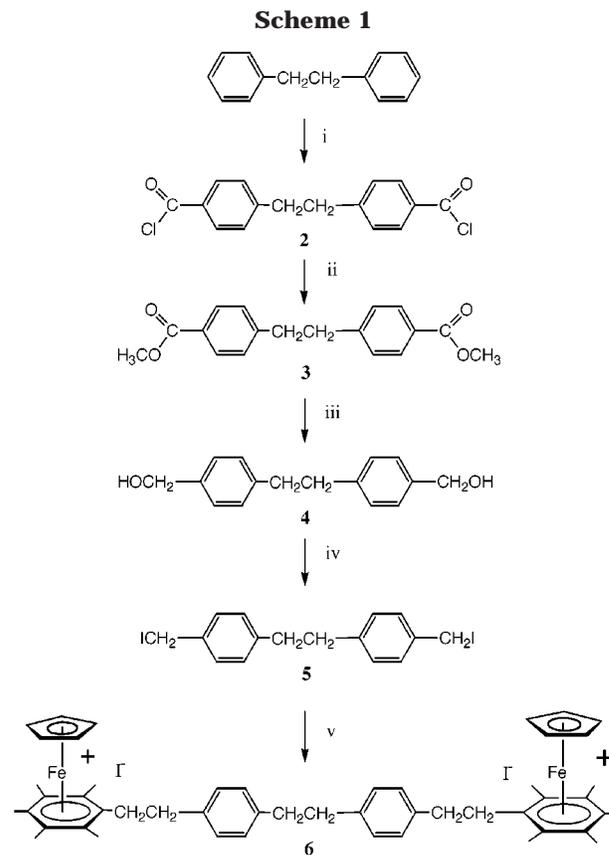
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These reactions are easy to carry out and proved useful to synthesize star cores, star polymers, and metallodendrimers.<sup>4b,c</sup> Thus, hexa- and octabenzyl cores are readily accessible by this method which may be attractive if subsequent functionalization can be achieved regiospecifically. In part of a preliminary communication, we disclosed the regiospecific chlorocarbonylation of an octabenzyl core resulting from the CpFe<sup>+</sup>-induced octabenzylation of durene.<sup>4c</sup> We now detail this reaction here with di-, hexa-, and octabenzyl cores,<sup>4f</sup> together with the reactions of these polychlorocarbonylated cores with amines and alcohol nucleophiles. We have chosen these nucleophiles as a function of their use either to introduce an organic dendron or a redox-active organometallic group. Direct reaction of the polychlorocarbonyl core with useful amines containing a dendron or a ferrocene termini is indeed achieved; alternatively, reaction with methanol followed by reduction and iodation introduces the iodomethyl function in benzylic position which allows

further reaction with the nucleophile  $[\text{Fe}^{\text{II}}\text{Cp}(\eta^5\text{-C}_6\text{Me}_5\text{-CH}_2)]$ , **1**.<sup>4d</sup> This nucleophile, isoelectronic to ferrocene, is obtained by the reaction of  $\text{O}_2$  with the 19-electron complex  $[\text{Fe}^{\text{I}}\text{Cp}(\text{C}_6\text{Me}_6)]$  or by deprotonation of the 18-electron cation  $[\text{Fe}^{\text{II}}\text{Cp}(\text{C}_6\text{Me}_6)]^+$ .<sup>4d</sup> It allows us to introduce iron sandwiches with a permethylated arene ring on the termini of star branches. The complex **1** is a good nucleophile, but also an excellent base (the  $\text{p}K_{\text{a}}$  of the acid  $[\text{Fe}^{\text{II}}\text{Cp}(\text{C}_6\text{Me}_6)][\text{PF}_6]$  is 28.2 in DMSO),<sup>4e</sup> so that it cannot be used in positions where dehydrohalogenation can occur such as the termini of alkyl chains. Organometallic stars and metal dendrimers are now a quickly growing area.<sup>5,6</sup> Various stars and dendritic structures are already known with ferrocene termini.<sup>7–12</sup>

## Results

We have carried out the Friedel–Crafts chlorocarbonylation of diphenyl-1,2-ethane, a commercial compound, as a model reaction. The aromatic Friedel–Crafts chlorocarbonylation is a known reaction<sup>13</sup> first reported by Neubert.<sup>13a</sup> The reaction product **2** was also published by Taramu using another route via the diacid.<sup>14</sup> It is an air-stable, white powder which is not very sensitive to hydrolysis in the solid state and was obtained in 94% yield from diphenyl-1,2-ethane. It was esterified with sodium methanolate in methanol which gave the diester **3** in 90% yield. Then, the diester was reduced to the diol **4** in 90% yield using  $\text{LiAlH}_4$  in ether/THF (12 h, 40 °C). This diol is a white hygroscopic powder which is soluble in THF and alcohols. The compound **4** was then treated with  $\text{NaI}/\text{BF}_3\cdot\text{Et}_2\text{O}$  in acetonitrile (12h, RT) to give the diiodomethyl compound **5** in 79% yield. The reaction of **5** with **1** was carried out in THF (12 h, RT) which gave a 31% yield of the air-stable, yellow dinuclear complex **6** after chromatographic purification. The complex **6** is well soluble in dichloromethane and acetonitrile. In cyclic voltammetry, it shows a single chemically- and electrochemically reversible two-electron wave at  $-1.88$  V vs  $\text{FeCp}_2^{0/+}$  in DMF, using ferrocene as internal standard.<sup>15</sup> These reactions are summarized in Scheme 1.



<sup>a</sup> (i)  $(\text{COCl})_2$ ,  $\text{AlCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ , 15 °C, 1 h; (ii)  $\text{CH}_3\text{OH}$ , 2 days, RT; (iii)  $\text{LiAlH}_4$ , 40 °C, ether/THF, 14 h; (iv)  $\text{NaI}$ ,  $\text{BF}_3\cdot\text{Et}_2\text{O}$ ,  $\text{CH}_3\text{CN}$ , RT, 12 h; (v)  $[\text{Fe}^{\text{II}}\text{Cp}(\eta^5\text{-C}_6\text{Me}_5\text{CH}_2)]$ , THF, 12 h.

Given the success of this scheme on the model diphenylethane, it was applied to the hexabenzyl and octabenzyl cores **7** and **8** available by the  $\text{CpFe}^+$ -induced hexabenzylation of hexamethylbenzene and octabenzylation of durene, respectively. The chlorocarbonylation proceeds well with **7** and **8**, and the hexa- and octachlorocarbonyl compounds **9** and **10** were both obtained in 86% yields. The polychlorocarbonyl derivatives **9** and **10** are white powders which are much more sensitive toward hydrolysis in air than **2**, however, so that great care must be taken during the workup (see Experimental Section). For instance, NMR spectra recorded in  $\text{DMSO-}d_6$  show resonances that are attributed to the presence of the polycarboxylic acids **11** and **12** due to fast hydrolysis by residual water in  $\text{DMSO-}d_6$ . Thus **9** and **10** must be quickly used for reactions with alcohol and amine nucleophiles.

To construct dendrimers rapidly, reaction of **10** was carried out with Newkome's aminotripod  $\text{NH}_2\text{C}(\text{CH}_2\text{-OCH}_2\text{CH}_2\text{CN})_3$ <sup>16</sup> in  $\text{CH}_2\text{Cl}_2$  in the presence of  $\text{NEt}_3$ . This reaction gave the 24-nitrile dendrimer **13** in 61% yield after chromatographic purification, which was characterized by its molecular peak in the MALDI-TOF mass spectrum ( $m/z = 3328.57$   $[\text{M} + \text{Na}^+]$ , see Figure 1). Similarly, reaction of **10** with (5-aminopentyl)-1-fer-

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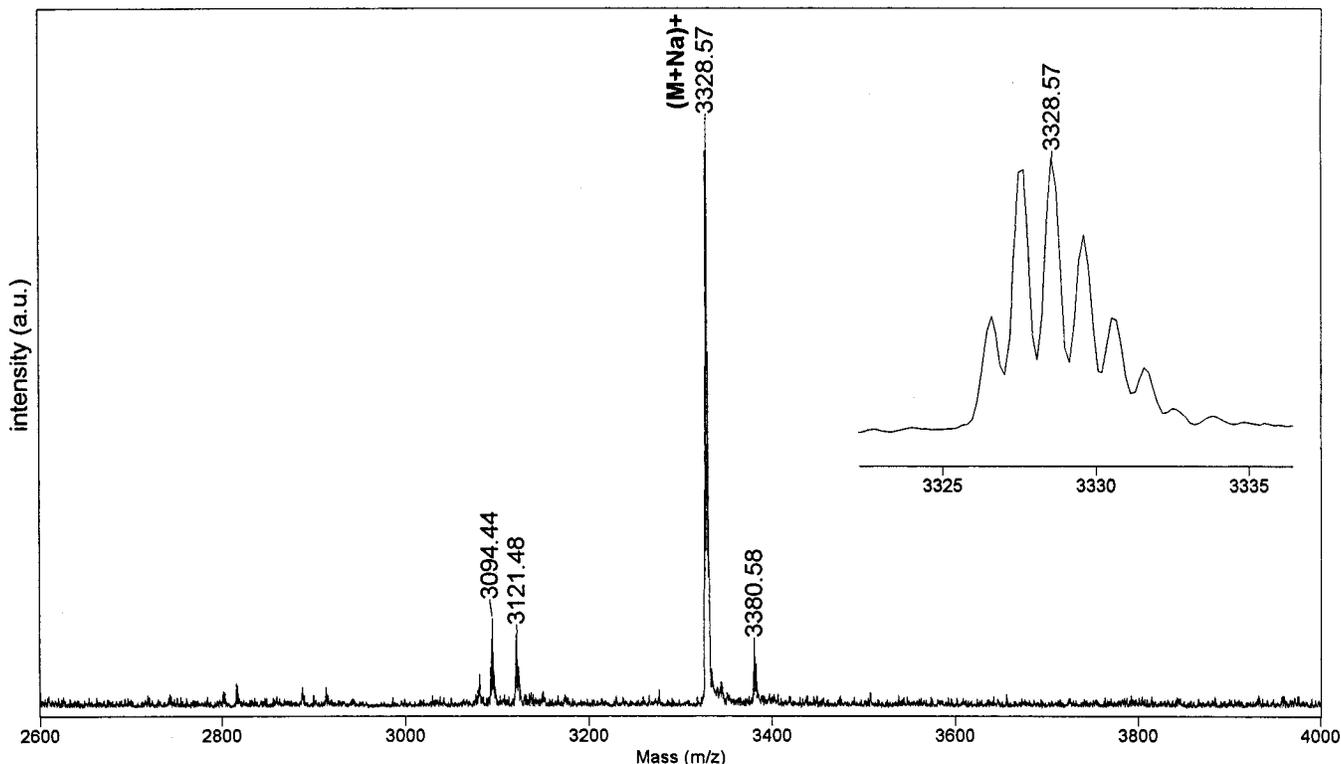
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**Figure 1.** MALDI TOF mass spectrum of the 24-CN dendrimer **13**. The molecular peak is  $M + Na^+$  at 3328.57 (isotopic distribution on the right).

rocene<sup>17</sup> gave the orange powdery octaferrocene derivative **14** in 81% yield (Scheme 2).<sup>1</sup>

Reactions of **9** and **10** with sodium methanolate in methanol gave the methyl esters **15** and **16** in 85 and 90% yields, respectively. These esters were reduced by  $LiAlH_4$  to the primary alcohols **17** and **18** which were obtained as white powders in 96 and 85% yields, respectively. Then, reactions of the alcohols **17** and **18** with  $NaI/BF_3 \cdot Et_2O$  gave, respectively, 85 and 55% yields of the hexa- and octaiodomethyl derivatives **19** and **20** as white powders. Finally, reactions between the polyiodo compounds **19** and **20** with **1** in THF gave yellowish powders which were almost completely insoluble in all solvents (Scheme 3). The introduction of an *n*-butyl substituent on the Cp ring of **1** did not provide a clear improvement of solubility. Their pale-yellow color and Mössbauer spectra ( $IS = 0.56 \text{ mm s}^{-1}$  vs iron;  $QS = 2.00 \text{ mm s}^{-1}$ ) are very characteristic of a  $[Fe^{II}Cp(\eta^6-C_6Me_5CH_2R)]^+$  structure. Cyclic voltammetry at 60 °C in DMF showed the classical reversible wave at  $E_{1/2} = -1.88 \text{ V}$  vs  $FeCp_2^{0/+}$  also characteristic of a  $[Fe^{II}Cp(\eta^6-C_6Me_5CH_2R)]^+$  structure. The number of electrons involved in the reduction could not be measured, however, because the amount of solubilized product was uncertain. Although the polynuclear complexes could not be purified otherwise than by washing the insoluble solids with solvents in order to remove all the soluble impurities, the elemental analyses were carried out. They indicate that the number of iron sandwich units is close to the expected number in the

proposed structures **21a** (Cp ring in **1**), **21b** (*n*-butylCp ring in **1b** instead of the Cp ring in **1**) and **22**. In **22** (Cp ring in **1**), the analysis shows that about 6% of iron sandwich is missing. These insoluble materials can be considered as polydisperse polymers, although it appears that, statistically, a weak proportion of the material must have the complete hexa- or octametalllic structure.

## Discussion

The chlorocarbonylation of polybenzyl stars is an excellent means of functionalization and further star or dendritic extension of the cores. What is remarkable and most useful is the complete regioselectivity in the para position obtained in all cases, contrary to other electrophilic aromatic reactions such as chloromethylation and iodination that have also been probed with **7**. It is known that the aromatic chloromethylation is not regioselective.<sup>19</sup> The selectivity of the bromomethylation reaction is good under certain conditions,<sup>20</sup> but attempts with **7** gave no reaction. All the organic reactions involved in the chemistry described here proceed under smooth conditions and high yields. Although the polychlorocarbonyl chlorides are air-sensitive toward hydrolysis, they are free of any

(18) The oxidation potential of the ferrocene center (0.39 V vs SCE) is shifted by 150 mV toward cathodic potentials upon addition of 1 equiv of  $[n\text{-Bu}_4\text{N}][H_2PO_4]$  and by 50 mV with 1 equiv of  $[n\text{-Bu}_4\text{N}][HSO_4]$  in  $CH_2Cl_2$  containing 0.1 M  $[n\text{-Bu}_4\text{N}][BF_4]$  on Pt electrode (auxiliary electrode: Pt, reference electrode: SCE, 20 °C, 100 mV/s). Compare with better dendritic sensors: Valério, C.; Fillaut, J.-L.; Ruiz, J.; Guittard, J.; Blais, J.-C.; Astruc, D. *J. Am. Chem. Soc.* **1997**, *119*, 2588.

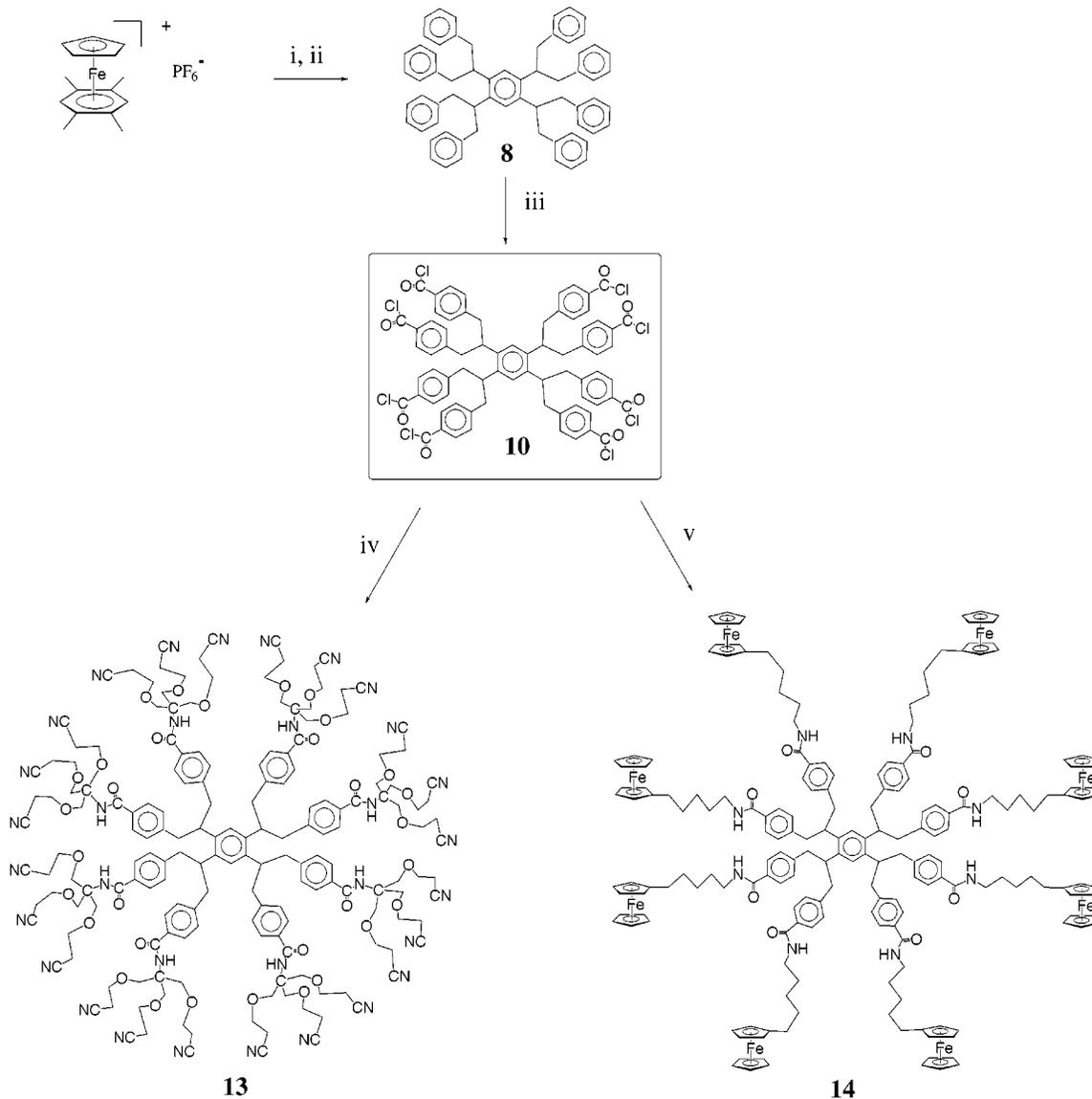
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(17) (a) (5-Aminopentyl)-1-ferrocene was synthesized from (4-iodopentyl)-1-ferrocene<sup>17b</sup> by reaction with KCN in DMF at room temperature followed by reduction of the nitrile by  $LiAlH_4$  in ether at room temperature.<sup>17c</sup> (b) Fillaut, Linares, J.; Astruc, D. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2460. (c) Ruiz, J.; Astruc, D. Unpublished results.

Scheme 2



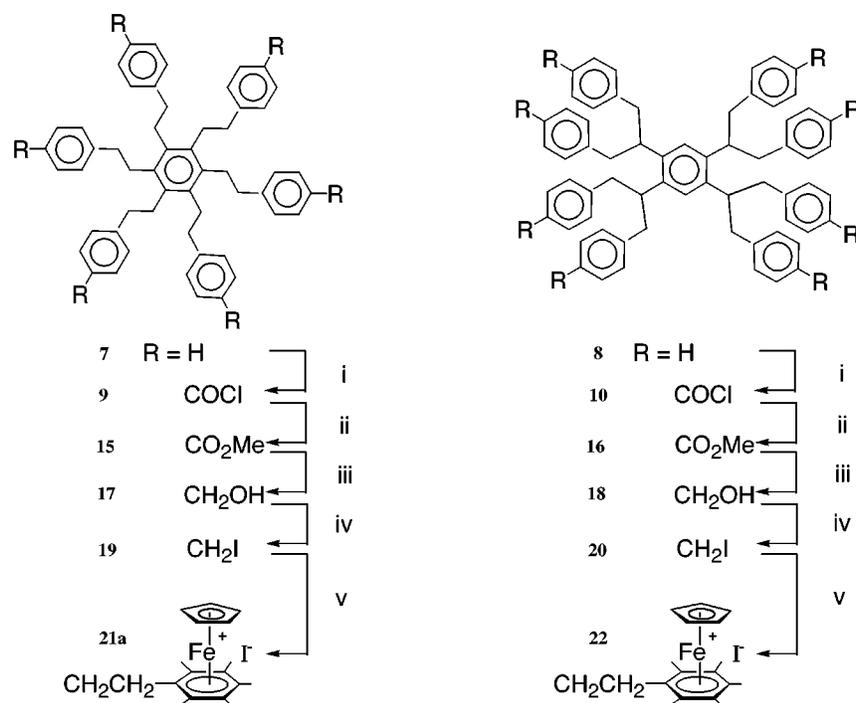
<sup>a</sup> (i)  $\text{PhCH}_2\text{Br}$ ,  $\text{KOH}$ , 10 d,  $40^\circ\text{C}$ ; (ii)  $h\nu_{\text{UV-vis}}$  (Hg lamp),  $\text{MeCN}$ , 12 h; (iii)  $(\text{COCl})_2$ ,  $\text{AlCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ ,  $15^\circ\text{C}$ , 1 h; (iv)  $\text{NH}_2\text{C}(\text{CH}_2\text{OCH}_2\text{CH}_2\text{CN})_3$ ,  $\text{NEt}_3$ ,  $\text{CH}_2\text{Cl}_2$ , 10 d, RT; (v)  $\text{NH}_2(\text{CH}_2)_5\text{Fc}$ ,  $\text{NEt}_3$ ,  $\text{CH}_2\text{Cl}_2$ , RT, 10 d.

impurity after the workup because acidic fractions eventually formed (even on a single branch) lead to insoluble products that are eliminated from the medium. The MALDI TOF mass spectrum of the 24-nitrile dendrimer **13** obtained indicates that it is remarkably free of defect. Thus the chlorocarbonylation is a key reaction toward rapid dendritic syntheses. We have already used it to synthesize 24-amidoferrere and 24- $[\text{Cp}^*\text{Fe}\eta^6\text{-}(N\text{-alkyl-aniline})]^+$  dendrimers which have outstanding properties of sensors for various anions with dramatic dendritic effects.<sup>4c</sup> The octaferrocene derivative **14** obtained by a similar reaction is another example of sensor. It can be used for the recognition of the dihydrogenophosphate and hydrogensulfate anions by cyclic voltammetry in DMF. Its sensitivity is not as good as those of 9- and 18-amidoferrere dendrimers that have already been reported, however, because the distance between the amido group and the ferrocene termini is larger than that in the amidoferrere dendrimers.<sup>15</sup>

The reaction of the organoiron nucleophile **1** with the diiodomethyl derivative is very satisfactory in terms of

yields and solubilities of the binuclear product **6** formed. The fact that only a single two-electron wave is observed in cyclic voltammetry shows that the two iron centers are far enough from each other to be completely independent (their benzene ligands are separated by 14 carbon atoms) even from the point of view of the electrostatic factor. Thus, this strategy was successful for the formation of C–C bonds between a core and the organometallic synthon. Further exploitation of this binuclear compound can be envisaged and pursued. A major drawback in this chemistry, however, is the insolubility of the hexa- and octametallic complexes **21** and **22** which prevents us from further use of these two compounds in dendritic chemistry. An initial goal was to perbenzylate **21** and **22** as in eq 1 in order to develop the dendritic structures, and this objective was obviously frustrated by the insolubility of these polymetallic stars. Fortunately, the reaction of the polychlorocarbonyl derivatives with nucleophiles are not marred by such problems and can lead to clean dendrimers as exemplified

Scheme 3



<sup>a</sup> (i) (COCl)<sub>2</sub>, AlCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, 15 °C, 1 h; (ii) CH<sub>3</sub>OH, 2 days, RT; (iii) LiAlH<sub>4</sub>, 40 °C, ether/THF, 14 h; (iv) NaI, BF<sub>3</sub>·Et<sub>2</sub>O, CH<sub>3</sub>CN, RT, 10 d (**19**) or 18 d (**20**); (v) [Fe<sup>II</sup>Cp(η<sup>5</sup>-C<sub>6</sub>Me<sub>5</sub>CH<sub>2</sub>)], THF, 3 d.

here by the reaction of **10** with Newkome's aminotripod to give the very useful dendrimer **13**.<sup>4c</sup>

### Conclusion

The chlorocarbonylation of di-, hexa-, and octabenzyl cores, a remarkably regiospecific reaction, has opened new synthetic routes toward molecular materials. It is especially useful as a complement to the well-established CpFe<sup>+</sup>-induced perbenzylation of polymethylbenzene derivatives. Examples of the direct use of the polychlorocarbonylated compounds with amines is provided by the syntheses of the 24-nitrile dendrimer **13** and the octaferrocene compound **14** using the octachlorocarbonyl derivative **10**. Dimetalation of the linear-chain dichlorocarbonyl compound **2** using the organoiron synthon **1** gives a stable, soluble complex **6** which is a reservoir of two electrons at two remote, independent redox centers. On the other hand, hexa- and octametalation with **1** of the iodomethylated hexa- and octabenzyl cores leads to almost insoluble hexa- and octametalated complexes with mediocre purities.

### Experimental Section

**General Data.** Reagent-grade tetrahydrofuran (THF), diethyl ether, and pentane were predried over Na foil and distilled from sodium-benzophenone ketyl under argon immediately prior to use. Acetonitrile (CH<sub>3</sub>CN) was stirred under argon overnight over phosphorus pentoxide, distilled from sodium carbonate, and stored under argon. Methylene chloride (CH<sub>2</sub>Cl<sub>2</sub>) was distilled from calcium hydride just before use. All other chemicals were used as received. The complex **1** was synthesized according to ref 4d. The hexa- and octabenzyl cores **7** and **8** were prepared according to ref 4f. All manipulations were carried out using Schlenk techniques or in a nitrogen-filled Vacuum Atmospheres drylab. Infrared spectra were recorded in solution (0.1 mm cells with NaCl windows), between NaCl disks in Nujol, or in KBr pellets. <sup>1</sup>H NMR

spectra were recorded with a Bruker AC 200 (200 MHz) spectrometer. <sup>13</sup>C NMR spectra were obtained at 50.327 MHz. Electronic spectra (UV and visible) were recorded at 20 °C with 10 or 1 mm quartz cells. Care was taken in the cyclic voltammetry experiments to minimize the effects of solution resistance on the measurements of peak potentials (the use of positive feedback *iR* compensation and dilute solution (≈10<sup>-3</sup> mol/L) maintained currents between 1 and 10 μA). The additional redox couple [FeCp<sub>2</sub>]/[FeCp<sub>2</sub>]<sup>+</sup> was used when possible as a control for *iR* compensation. Thermodynamic potentials were recorded with reference to an aqueous SCE in THF (0.1 M *n*-Bu<sub>4</sub>NBF<sub>4</sub>). The value of the [FeCp<sub>2</sub>]/[FeCp<sub>2</sub>]<sup>+</sup> redox couple was 0.382 V vs SCE on Pt in MeCN and 0.475 V vs SCE on Pt in CH<sub>2</sub>Cl<sub>2</sub>. The QRE potential was calibrated by adding the reference couple [FeCp<sub>2</sub>]/[FeCp<sub>2</sub>]<sup>+</sup>. The counter electrode was platinum. Mössbauer spectra were recorded with a 25 mCi <sup>57</sup>Co source on Rh, using a symmetric triangular sweep mode. Elemental analyses were performed by the Center of Microanalyses of the CNRS at Lyon-Villeurbanne, France.

**Synthesis of the Polycarbonyl Chloride Derivatives 2, 9, and 10 and Polycarboxylic Acids 11 and 12. General Procedure.** Aluminum chloride (2 equiv per branch) is introduced into a Schlenk flask and deaerated under vacuum. Dry, deaerated dichloromethane (6 mL) and then oxalyl chloride (3 equiv per branch) are added dropwise in 20 min at 15 °C. The polybenzyl derivative in 6 mL dry, deaerated dichloromethane is introduced dropwise in 1 h, and the reaction mixture is stirred at 15 °C. Rapid hydrolysis is carried out by adding a mixture of 120 g ice and 5 g calcium chloride to the reaction medium at 0 °C. The organic phase is quickly extracted using dichloromethane at 0 °C and dried over sodium sulfate, and the cold solvent is removed under vacuum. A white solid is obtained and stored in the freezer at -20 °C.

**Dicarbonyl chloride, 2:** from bibenzyl (1 g, 5.59 mmol), aluminum chloride (2.98 g, 22.4 mmol), and oxalyl chloride (2.9 mL, 33.5 mmol) is obtained 1.63 g (94% yield) of the known compound **2** (see ref 14). NMR (CDCl<sub>3</sub>, δ<sub>ppm</sub>): <sup>1</sup>H: 2.82 (s, 4H), 7.25–7.87 (AA'BB' system, 8H); <sup>13</sup>C: 37.79, 128.3, 128.1, 129.3, 135.9, 167.0. Infrared (NaCl plates, cm<sup>-1</sup>): 1770 (ν<sub>s</sub> C=O); 1740 (ν<sub>s</sub> C=O), 1600 (ν C=C Ar).

**Hexacarbonyl chloride, 9:** from hexaphenylethylbenzene, 7 (0.5 g, 0.711 mmol), aluminum chloride (1.14 g, 8.55 mmol), and oxalyl chloride (1.12 mL, 12.8 mmol) is obtained 0.661 g of **9** (86% yield). Infrared (NaCl plates): 1770 ( $\nu_{\text{as}} \text{C}=\text{O}$ ); 1740 ( $\nu_{\text{s}} \text{C}=\text{O}$ ), 1600 ( $\nu \text{C}=\text{C Ar}$ ). The compound **9** is then transformed into the hexaacid **11** for further characterization by dissolving into a saturated aqueous NaOH solution, washing this solution twice with dichloromethane, precipitation by addition of a concentrated chlorhydric acid solution, washing with water, and drying under vacuum. Analysis for **11**, calcd for  $\text{C}_{60}\text{H}_{54}\text{O}_{12}$ : C 74.52, H 5.63; found: C 74.24; H 5.60; NMR ( $\text{CD}_3\text{SOCD}_3$ ,  $\delta_{\text{ppm}}$ ):  $^1\text{H}$ : 2.82 (broad m, 24H), 7.26–7.87 (AA'BB' system, 24H), 13.52 (s, 6H);  $^{13}\text{C}$ : 31.15, 36.87, 128.35, 128.1, 129.3, 135.9, 146.8, 167.0. Infrared (NaCl plates,  $\nu$ ,  $\text{cm}^{-1}$ ): 3400 (OH), 1680 (C=O), 1600 (C=C<sub>Ar</sub>), 1280 (C–O).

**Octacarbonyl chloride 10 and octacarboxylic acid 12:** from tetrakis-1,2,3,4-(1-benzyl-2-phenylethyl)benzene, **8** (0.3035 g, 0.354 mmol), aluminum chloride (0.668 g, 4.26 mmol), and oxalyl chloride (0.75 mL, 6.39 mmol) is obtained 0.481 g of **10** (86% yield). Infrared (NaCl plates): 1770 ( $\nu_{\text{as}} \text{C}=\text{O}$ ), 1740 ( $\nu_{\text{s}} \text{C}=\text{O}$ ), 1600 ( $\nu \text{C}=\text{C Ar}$ ). The compound **10** is then transformed into the octaacid **12** as described above in the case of **9** for further characterization. Analysis for **12**, calcd for  $\text{C}_{74}\text{H}_{62}\text{O}_{16}$ : C 73.62, H 5.18; found: C 73.51, H 5.12. NMR ( $\text{CD}_3\text{SOCD}_3$ ,  $\delta_{\text{ppm}}$ ):  $^1\text{H}$ : 2.35–2.67 (two broad m, 16H), 3.26 (broad m), 6.92–7.75 (AA'BB' system, 32H), 7.05 (s, 2H), 13.40 (s, 8H,  $\text{CO}_2\text{H}$ );  $^{13}\text{C}$ : 40.90, 42.35, 125.69, 128.8, 129.1, 129.2, 138.4, 145.4, 167.0. Infrared (NaCl plates,  $\nu$ ,  $\text{cm}^{-1}$ ): 3400 (OH), 1680 (C=O), 1600 (C=C<sub>Ar</sub>), 1280 (C–O).

**Synthesis of the 24-Nitrile Dendrimer 13.** Newkome's amino-tripod  $\text{NH}_2\text{C}(\text{CH}_2\text{OCH}_2\text{CH}_2\text{CN})_3$ <sup>16</sup> (3.10 g, 10.80 mmol, 2 equiv per branch of **10**), synthesized according to ref 16, is dissolved under argon in 20 mL of dichloromethane in a Schlenk flask, triethylamine (4 mL, 54 mmol, 10 equiv per branch of **10**) is added, and then the octaacid chloride **10** (0.914 g, 0.675 mmol) is dissolved in 20 mL of dichloromethane and added to the flask. The reaction mixture is allowed to stir for 10 days at room temperature, the volatiles are removed under vacuum, and the solid residue is dissolved in dichloromethane. The organic solution is washed with water to remove triethylamine hydrochloride, dried over sodium sulfate, and filtered, and the solvent is removed under vacuum. The light-brown solid residue is chromatographed on an alumina column (activity II–III) using a dichloromethane/methanol 1/1 mixture, which gives 1.363 g (0.412 mmol, 61% yield) of **13** as an off-white hygroscopic powder. Analysis calcd for  $\text{C}_{178}\text{H}_{210}\text{O}_{34}\text{N}_{32}$ : C 63.89, H 6.36; found: C 63.77, H 6.48. NMR ( $\text{CDCl}_3$ ,  $\delta_{\text{ppm}}$ ):  $^1\text{H}$ : 1.92–2.45 (broad d,  $\text{CH}_2$ , 16H), 2.53 (broad t, 48H), 3.35 (broad m, 4H), 3.61 (broad t, 48H), 3.83 (s, 48H), 6.50 (broad s, 8H), 6.95 (broad s, 2H), 6.78–7.60 (AA'BB' system, 32H);  $^{13}\text{C}$ : 18.8, 41.45, 41.5, 50.0, 65.8, 69.0, 118.3, 120.0, 127.2, 129.5, 132.6, 138.5, 144.2, 167.9. Infrared (NaCl plates,  $\nu$ ,  $\text{cm}^{-1}$ ): 3410 (free amide NH), 3320 (bound amide NH), 3050 ( $\text{CH}_{\text{Ar}}$ ), 2920 ( $\nu_{\text{as}} \text{CH}_2$ ), 2880 ( $\nu_{\text{s}} \text{CH}_2$ ), 2250 (nitrile CN), 1650 (amide C=O), 1610 (C=C<sub>Ar</sub>), 1290 (amide C–N), 1100 (ether C–O).

**Synthesis of the Octaferrocene 14.** Under argon are introduced (5-amino-pentyl)-1-ferrocene<sup>17</sup> (1.01 g, 3.72 mmol, 2 equiv per branch) in 20 mL of dichloromethane and triethylamine (2.7 mL, 18.6 mmol, 10 equiv per branch) and **10** (0.315 g, 0.233 mmol) in 20 mL of dichloromethane into a Schlenk flask, and the reaction mixture is allowed to stir for 10 days at room temperature. Then, the volatiles are removed under vacuum, and the orange solid residue is dissolved in 20 mL of dichloromethane. This solution is washed with water to eliminate triethylamine hydrochloride and the excess amine and dried over sodium sulfate, and the solvent is removed under vacuum. The orange solid is dissolved in 10 mL of dichloromethane and 50 mL of pentane are added to precipitate **14** as an orange powder which is dried under vacuum (0.613 g, 0.190 mmol, 81% yield from **10**). Anal. Calcd for  $\text{C}_{194}\text{H}_{214}\text{O}_8\text{N}_8\text{Fe}_8$ : C 70.51, H 6.77, N 3.39, Fe 13.52. Found: C 70.41, H 6.73, N 3.57, Fe 13.26. NMR ( $\text{CDCl}_3$ ,  $\delta_{\text{ppm}}$ ):  $^1\text{H}$ : 1.28–1.41 (broad m, 48H), 2.24 5 (broad m, 16H), 2.21–2.61 (two complex m, 16H), 3.27 (broad m, 10H), 3.50 (broad m, 4H),

4.01 (broad m, 54H), 6.66–7.49 (broad s, 8H);  $^{13}\text{C}$ : 26.85, 29.4, 30.8, 40.0, 41.4, 41.45, 66.95, 67.9, 68.4, 77.2, 125.9, 127.0, 129.0, 132.4, 137.5, 143.0, 167.2. Infrared (KBr plates,  $\nu$ ,  $\text{cm}^{-1}$ ): 3310 (amide NH), 3070 ( $\text{CH}_{\text{Fc}}$ ), 2920 ( $\nu_{\text{as}} \text{CH}_2$ ), 2840 ( $\nu_{\text{s}} \text{CH}_2$ ), 2250 (nitrile CN), 1625 (amide C=O), 1610 (C=C<sub>Ar</sub>), 1540 ( $\text{CH}_2$ ), 1290 (amide C–N), 1100 (ether C–O).

**Syntheses of the Polymethyl Esters 3, 15, and 16. General Procedure.** Under argon is progressively introduced sodium metal (1.5 equiv per branch) into a Schlenk flask containing 30 mL of freshly distilled methanol. When all sodium has reacted, this solution is transferred into another Schlenk flask containing the polycarbonyl chloride derivative, and the reaction mixture is stirred for 2 days at room temperature. Methanol is removed under vacuum, the white solid residue is dissolved in methyl acetate, this solution is washed with an aqueous solution saturated with sodium chloride, the organic layer is dried over sodium sulfate and filtered, the solvent is removed under vacuum, and the off-white solid residue is dissolved in the minimum of dichloromethane and precipitated using excess pentane. After leaving the flask overnight at  $-20^\circ\text{C}$ , the ester is obtained as a white solid by filtration.

**Diester 3:** from **2** (1.9 g, 6.19 mmol) and Na (0.427 g, 6.19 mmol), a 90% yield of **3** is obtained (1.66 g, 5.57 mmol). NMR ( $\text{CDCl}_3$ ,  $\delta_{\text{ppm}}$ ):  $^1\text{H}$ : 2.78 (s, 4H), 3.96 (s, 6H), 7.25–8.02 (AA'BB' system, 8H);  $^{13}\text{C}$ : 37.4, 52.2, 128.1, 128.5, 130.1, 136.5, 168.7. Infrared (NaCl plates,  $\nu$ ,  $\text{cm}^{-1}$ ): 1720 (C=O), 1600 (C=C<sub>Ar</sub>), 1260 (C–O).

**Hexaester 15:** from **9** (0.5595 g, 0.52 mmol) and Na (0.107 g, 4.67 mmol) is obtained a 85% yield of **15** (0.461 g, 0.439 mmol). Anal. Calcd for  $\text{C}_{66}\text{H}_{66}\text{O}_{12}$ : C 75.41, H 6.33. Found: C 75.33, H 6.40. NMR ( $\text{CDCl}_3$ ,  $\delta_{\text{ppm}}$ ):  $^1\text{H}$ : 2.91–2.98 (two complex m, 24H), 3.95 (s, 18H), 7.26–8.03 (AA'BB' system, 24H);  $^{13}\text{C}$ : 32.4, 37.80, 52.15, 128.1, 128.5, 130.1, 136.5, 147.1, 168.8. Infrared (NaCl plates,  $\nu$ ,  $\text{cm}^{-1}$ ): 2920 ( $\text{CH}_{\text{Ar}}$ ), 1720 (C=O), 1610 (C=C<sub>Ar</sub>), 1270 (C–O).

**Octaester 16:** from **10** (0.4195 g, 0.309 mmol) and Na (0.071 g, 3.71 mmol) is obtained a 90% yield of **16** (0.371 g, 0.281 mmol). Anal. Calcd for  $\text{C}_{82}\text{H}_{78}\text{O}_{16}$ : C 74.63, H 5.96. Found: C 74.61, H 5.98. NMR ( $\text{CDCl}_3$ ,  $\delta_{\text{ppm}}$ ):  $^1\text{H}$ : 2.38–2.56 (two complex m, 16H), 3.26 (quintuplet, 4H), 3.74 (s, 24H), 6.75–7.82 (AA'BB' system, 32H), 7.19 (s, 27);  $^{13}\text{C}$ : 41.7, 41.9, 52.0, 125.9, 128.4, 129.2, 129.7, 138.95, 145.1, 166.7. Infrared (NaCl plates,  $\nu$ ,  $\text{cm}^{-1}$ ): 2920 ( $\text{CH}_{\text{Ar}}$ ), 1720 (C=O), 1600 (C=C<sub>Ar</sub>), 1260 (C–O).

**Syntheses of the Polyols. General Procedure.** Under argon, a suspension of  $\text{LiAlH}_4$  (2.5 equiv per branch ester) in 15 mL of freshly distilled ether is refluxed for 3 h in a Schlenk flask, and then the ester in 15 mL of freshly distilled THF is added by cannula at room temperature. The reaction mixture is refluxed for 2 h,  $\text{LiAlH}_4$  (2.5 equiv per branch ester) is added at room temperature to the reaction mixture which is then refluxed for 12 h, and  $\text{LiAlH}_4$  is hydrolyzed at room temperature by dropwise addition of an aqueous solution saturated with sodium sulfate. The white precipitates of  $\text{Al}(\text{OH})_3$  and  $\text{LiOH}$  are extracted using  $6 \times 50$  mL of a methanol/THF mixture. The solvent is removed under vacuum, leaving a white hygroscopic solid which is dissolved in a minimum of methanol and reprecipitated by addition of ether. After standing at  $-20^\circ\text{C}$  overnight, the polyol, a white powdery solid, is filtered.

**Diol 4:** from the ester **3** (1.37 g, 4.59 mmol) and  $\text{LiAlH}_4$  ( $2 \times 0.528$  g,  $2 \times 22.96$  mmol) is obtained the alcohol **4** (0.945 g, 3.90 mmol) in 85% yield. NMR ( $\text{CD}_3\text{COCD}_3$ ,  $\delta_{\text{ppm}}$ ):  $^1\text{H}$ : 2.78 (s, 4H), 4.57 (s, 6H), 7.11–7.24 (AA'BB' system, 8H);  $^{13}\text{C}$ : 37.4, 65.1, 128.4, 128.9, 138.8, 140.53. Infrared (NaCl plates,  $\nu$ ,  $\text{cm}^{-1}$ ): 3350 (free OH), 3380 (bound OH), 2900 ( $\text{CH}_{\text{Ar}}$ ), 2830 ( $\text{CH}_2$ ), 1610 (C=C<sub>Ar</sub>), 1010 (C–O).

**Hexol 17:** from the ester **15** (1.335 g, 1.27 mmol) and  $\text{LiAlH}_4$  ( $2 \times 0.438$  g,  $2 \times 19.04$  mmol) is obtained the hexol **17** (1.007 g, 1.14 mmol) in 90% yield. Anal. Calcd for  $\text{C}_{60}\text{H}_{66}\text{O}_6$ : C 81.60, H 7.53. Found: C 81.55, H 7.57. NMR ( $\text{CD}_3\text{OD}$ ,  $\delta_{\text{ppm}}$ ):  $^1\text{H}$ : 2.72–2.87 (two complex m, 24H), 4.57 (s, 18H), 7.11–7.24 (AA'BB' system, 24H);  $^{13}\text{C}$ : 33.7, 38.7, 65.2, 128.4, 129.3, 137.7,

140.5, 142.5. Infrared (NaCl plates,  $\nu$ ,  $\text{cm}^{-1}$ ): 3350 (free OH), 3380 (bound OH), 2900 ( $\text{CH}_{\text{Ar}}$ ), 1610 ( $\text{C}=\text{C}_{\text{Ar}}$ ), 1010 ( $\text{C}-\text{O}$ ).

**Octol 18:** from the ester **16** (0.904 g, 0.685 mmol) and  $\text{LiAlH}_4$  ( $2 \times 0.39$  g,  $2 \times 10.28$  mmol) is obtained the alcohol **17** (0.724 g, 0.661 mmol) in 96% yield. Anal. Calcd for  $\text{C}_{74}\text{H}_{78}\text{O}_8$ : C 81.14, H 7.18. Found: C 80.87, H 7.45. NMR ( $\text{CD}_3\text{-OD}$ ,  $\delta_{\text{ppm}}$ ),  $^1\text{H}$ : 2.42–2.61 (two complex m, 16H), 3.57 (quintuplet, 4H), 4.46 (s, 16H), 6.83–7.16 (AA'BB' system, 32H);  $^{13}\text{C}$ : 42.5, 44.18, 65.1, 126.2, 127.9, 130.6, 140.3, 140.7, 141.1. Infrared (NaCl plates,  $\nu$ ,  $\text{cm}^{-1}$ ): 3360 (free OH), 3370 (bound OH), 2910 ( $\text{CH}_{\text{Ar}}$ ), 1600 ( $\text{C}=\text{C}_{\text{Ar}}$ ), 1010 ( $\text{C}-\text{O}$ ).

**Syntheses of the Polyiodomethyl Derivatives 5, 19, and 20. General Procedure.** The polyol and sodium iodide (5 equiv per branch) are added into a flamed Schlenk flask under argon and deaerated under vacuum, 15 mL of dry acetonitrile are added, and a solution of  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  (5 equiv. per branch) in 5 mL of dry acetonitrile is added over 15 min. The reaction mixture is stirred in the dark at room-temperature all the longer, as the number of branches is higher (0.5 day for **5**, 10 days for **19**, 18 days for **20**). Then, the solvent is removed under vacuum, and the yellow solid residue is washed with  $4 \times 75$  mL of dichloromethane. This solution is treated with an aqueous solution saturated with sodium thiosulfate to remove iodine, washed with water, and dried over sodium sulfate, and the solvent is removed under vacuum. The remaining off-white solid residue is dissolved in the minimum of dichloromethane; then addition of pentane yields the polyiodomethyl derivative as a white powdery precipitate which is filtered.

**Diiodo 5:** from the diol **4** (0.874 g, 3.6 mmol) and NaI (5.41 g, 36 mmol) is obtained a 79% yield of **5** (1.31 g, 2.84 mmol). Anal. Calcd for  $\text{C}_{16}\text{H}_{16}\text{I}_2$ : C 41.59, H 3.49. Found: C 41.98, H 3.93. NMR ( $\text{CDCl}_3$ ,  $\delta_{\text{ppm}}$ ),  $^1\text{H}$ : 2.78 (s, 4H), 4.38 (s, 4H), 7.03–7.20 (AA'BB' system, 8H);  $^{13}\text{C}$ : 6.1, 37.4, 128.8, 129.0, 137.0, 141.5 (inner  $\text{C}_{\text{Ar}}$  q).

**Hexaiodo 19:** from the hexol **17** (0.150 g, 0.164 mmol) and NaI (0.75 g, 4.93 mmol) is obtained a 85% yield of **19** (0.22 g, 0.142 mmol). Anal. Calcd for  $\text{C}_{60}\text{H}_{60}\text{I}_6$ : C 48.35, H 4.37. Found: C 48.27, H 4.08. NMR ( $\text{CDCl}_3$ ,  $\delta_{\text{ppm}}$ ),  $^1\text{H}$ : 2.83–2.94 (two complex m, 24H), 4.51 (s, 12H), 7.25–7.36 (AA'BB' system, 24H);  $^{13}\text{C}$ : 6.15, 32.4, 37.5, 128.7, 129.1, 136.6, 137.3, 141.9, 142.5.

**Octaiodo 20:** from the octol **18** (0.724 g, 0.662 mmol) and NaI (3.968 g, 2.65 mmol) is obtained a 55% yield of **20** (0.722 g, 0.365 mmol). Anal. Calcd for  $\text{C}_{74}\text{H}_{70}\text{I}_8$ : C 45.01, H 3.57. Found: C 44.98, H 3.47. NMR ( $\text{CDCl}_3$ ,  $\delta_{\text{ppm}}$ ),  $^1\text{H}$ : 2.37–2.58 (two complex m, 16H), 3.29 (quintuplet, 4H), 4.29 (s, 16H), 6.73–7.17 (AA'BB' system, 32H), 6.81 (s, 2H);  $^{13}\text{C}$ : 6.9, 41.45, 41.8, 126.5, 128.6, 129.8, 137.0, 138.95, 140.0.

**Synthesis of the Polyiron Complexes 6, 21, and 22. General Procedure.** The iodo derivative is dissolved in 3 mL of freshly distilled THF, and this solution is introduced under argon into a Schlenk flask and deaerated. The deep-red complex  $[\text{Fe}^{\text{II}}\text{Cp}(\eta^5\text{-C}_6\text{Me}_5\text{CH}_2)]$ , **1**, is prepared under anhydrous conditions according to ref 4d in another Schlenk flask and dissolved in 4 mL of freshly distilled THF, and the THF solution of the polyiodo derivative is transferred dropwise into this flask by cannula. A yellow precipitate immediately appears. The reaction mixture is stirred for 12 h at room temperature, the solvent is removed under vacuum, the solid residue is washed with anhydrous pentane under argon to remove unreacted **1**, and dichloromethane is added. In the case of **6**, the solid residue is soluble, the solution is washed with

an aqueous solution saturated with potassium iodide and then with water, dried over sodium sulfate, and filtered, and the solvent is removed under vacuum. The yellow solid residue is chromatographed over a column of neutral activated alumina which gives **6** as a yellow solid. In the case of polyiron complexes **21** and **22**, these solids are insoluble in dichloromethane and almost insoluble in all the other organic solvents and water. They are very slightly soluble in DMF and DMSO upon sonification and warming to 60 °C. So, the solids are washed with  $3 \times 30$  mL of dichloromethane, filtered, and dried under vacuum.

**Diiron complex 6:** from **1** (0.660 g, 2.34 mmol) and **5** (0.300 g, 0.65 mmol) is obtained a 31% yield of **6** after chromatography and reprecipitation from a concentrated dichloromethane solution with ether. Anal. Calcd for  $\text{C}_{50}\text{H}_{60}\text{I}_2\text{-Fe}_2$ : C 58.50, H 5.89, Fe 10.88. Found: C 59.18, H 6.32, Fe 10.59. NMR ( $\text{CD}_3\text{CN}$ ,  $\delta_{\text{ppm}}$ ),  $^1\text{H}$ : 2.44 (s, 18H), 2.49 (s, 12H), 2.73–2.33 (complex m, 8H), 2.89 (s, 4H), 4.58 (s, 5H), 7.18 (s, 8H);  $^{13}\text{C}$ : 17.5, 18.1, 34.25, 35.5, 37.95, 79.2, 100.2, 100.3, 103.2, 129.55–129.75, 139.5, 140.5. Cyclic voltammetry: reversible wave (ia/ic = 1,  $E_{\text{pa}} - E_{\text{pc}} = 60$  mV at 20 °C ( $E_{\text{pa}} + E_{\text{pc}}$ )/2 = 1.88V vs ferrocene as internal standard in DMF on Pt. The number of electrons involved in this wave was determined vs the intensity of the ferrocene wave, corrected according to ref 18, which gave 2.00 electrons.

**Hexairon complex 21a:** from **19** (0.444 g, 0.288 mmol) and **1** (0.973 g, 3.45 mmol) is obtained a 44% yield of **6** (0.416 g, 0.128 mmol). Anal. Calcd for  $\text{C}_{162}\text{H}_{192}\text{I}_6\text{Fe}_6$ : C 60.13, H 5.98. Found: C 58.79, H 5.91. Cyclic voltammetry in DMF at 60 °C on Pt: reversible wave (ia/ic = 1,  $E_{\text{pa}} - E_{\text{pc}} = 60$  mV) at 20 °C, ( $E_{\text{pa}} + E_{\text{pc}}$ )/2 = 1.88V vs ferrocene as internal standard. Mössbauer spectrum: Isomer shift (IS) vs iron metal = 0.56 mm  $\text{s}^{-1}$ . Quadrupole splitting (QS) = 2.00 mm  $\text{s}^{-1}$ .

**Hexairon complex 21b:** from **19** (0.300 g, 0.65 mmol) and  $[\text{Fe}^{\text{II}}(\eta^5\text{-}i\text{-Bu-C}_5\text{H}_4)(\eta^5\text{-C}_6\text{Me}_5\text{CH}_2)]$ , **1b**, (0.660 g, 2.34 mmol) is obtained a 21% yield of **6** (0.500 g, 0.136 mmol) using the same procedure as above. Anal. Calcd for  $\text{C}_{186}\text{H}_{240}\text{I}_6\text{Fe}_6$ : C 62.54, H 6.77. Found: C 65.82, H 7.13, corresponding to 12% of iron sandwich missing. Cyclic voltammetry in DMF at 60 °C on Pt: reversible wave (ia/ic = 1,  $E_{\text{pa}} - E_{\text{pc}} = 60$  mV) at 20 °C, ( $E_{\text{pa}} + E_{\text{pc}}$ )/2 = 1.89 V vs ferrocene as internal standard.

**Octairon complex 22:** from **20** (0.486 g, 0.246 mmol) and **1** (1.666 g, 5.90 mmol) is obtained a 50.7% yield of **6** (0.528 g, 0.125 mmol). Anal. Calcd for  $\text{C}_{210}\text{H}_{246}\text{I}_8\text{Fe}_8$ : C 59.57, H 5.86. Found: C 61.56, H 6.38, corresponding to 6.5% of iron sandwich missing. Cyclic voltammetry in DMF at 60 °C on Pt: reversible wave (ia/ic = 1,  $E_{\text{pa}} - E_{\text{pc}} = 60$  mV) at 20 °C, ( $E_{\text{pa}} + E_{\text{pc}}$ )/2 = 1.88 V vs ferrocene as internal standard. Mössbauer spectrum: IS vs iron metal = 0.56 mm  $\text{s}^{-1}$ ; QS = 2.00 mm  $\text{s}^{-1}$ .

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**Supporting Information Available:** NMR peak assignments for the new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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