Controlled Design of Oligomeric Ethers with Pendant Cyclopentadienyliron Moieties†

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Synthetic strategies for the design of oligomeric ethers with pendant cyclopentadienyliron moieties have been developed. A wide range of these materials have been prepared *via* nucleophilic aromatic substitution reactions of a mono- or di-hydroxyaromatic nucleophiles and a variety of chloroarene complexes under mild experimental conditions. The mono- and bis-(cyclopentadienyliron) arene complexes were used as building blocks for the larger systems. The crystal stuctures of three bis(cyclopentadienyliron) arene dications, $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}C_6H_5)\text{-}o\text{-}XC_6H_4X\text{-}(\eta^6\text{-}C_6H_5)Fe(\eta^5\text{-}C_5H_5)]^{2+}$ (X = O or S) and $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}C_6H_5)\text{-}m\text{-}OC_6H_4O\text{-}(\eta^6\text{-}C_6H_5)Fe(\eta^5\text{-}C_5H_5)]^{2+}$, have been determined by X-ray crystal structure analysis. A number of routes to the synthesis of the oligomeric species (tri-, tetra- and hexa-iron moieties) have been investigated to determine the flexibility and efficiency of the proposed strategies, and these materials have been fully characterized using spectroscopic and analytical techniques. To prove further the structures of these complexes, some of them have been prepared using different starting materials, giving the same proposed products. A series of polyiron complexes containing terminal hydroxy groups have also been prepared and used as dinucleophiles. The systematic increase in the number of rings and iron moieties allowed full characterization by monitoring the changes in the NMR spectra. Furthermore, the possibility of preparing homo- and mixed-polyaromatic ethers where the number of cyclopentadienyliron moieties varied from two to thirty-five has been demonstrated.

Interest in the development of new synthetic routes to polyaromatic ethers and thioethers is due to their characteristic chemical and physical properties.[1–9] These polymers belong to a class of materials known as engineering thermoplastics,[10–14] which are known to have many desirable characteristics such as exceptional thermooxidative and dimensional stability, good mechanical properties, and resistance against high energy radiation.[15–19] These materials are also known to be tough, creep resistant, and to exhibit good flexural, and tensile properties.[4,20,21] Such polymers usually find their application in the form of mouldings, coatings, adhesives, membranes and composite matrices.[22]

Over the past two decades, there have been numerous reports dealing with the preparation of both large and small aromatic ethers.[1–22] Although there is a large interest in these materials, there are only a few general routes available which may be employed for their preparation. These include the Ullmann ether synthesis,[23,24] the Scholl reaction,[25] nickel-catalysed homocoupling,[26,27] conventional nucleophilic aromatic substitution,[28–32] and polycondensation.[33–35] While these methodological approaches provide the polyaromatic materials, there is still a tremendous demand to develop more efficient synthetic strategies. There are a number of drawbacks with the reported synthetic routes. These include the use of elevated temperatures, copper salts or oxides as catalysts, and in some cases electron-withdrawing groups are required to force the reaction to take place.[23–25,28–32] These factors along with the low reaction yields (in most cases) intrigued us to search for an alternative route to the synthesis of these materials, using relatively inexpensive starting materials. Recent developments in this field have also focused on the synthesis and physical properties of a number of polymers such as poly(ether ether ketone), which is the most widely used engineering thermoplastic to date. Others such as poly(ether ketone)s and poly(ether sulfone)s have also been under investigation.[36–40] The polyaromatic ethers suffer from poor solubility, while the poly(aryl ether sulfone)s are amorphous in nature and show good solubilities. Poor solubility may be overcome by the introduction of bulky substituents,[11,13] or by co-ordination to a metal moiety,[41] which may aid in increasing polymer solubility or decreasing crystallinity. The introduction of functionalities that are able to undergo crosslinking reactions into the poly(aryl ether sulfones) may effectively yield better solvent resistance and thermal stability.[13] It is also known that the orientation of the polymers may play a role in the toughness which is exhibited.[12] From this one can see that many factors must be overcome to yield a 'perfect' system.

The complexation of chloroarenes to a metal moiety such as $Cr(CO)_3$, $Fe^+(cp)$, $Ru^+(cp)$ ($cp = C_5H_5$) or $Mn^+(CO)_3$ could activate the ring towards nucleophilic aromatic substitution reactions.[42–54] A number of aryl ethers have been prepared using the above metal moieties, with varying degrees of success.[55–60] A report by Percec and Okita[61] describes the preparation of aryl ethers using the $Cr(C_6H_4Cl_2\text{-}1,4)(CO)_3$ moiety and mono- or di-phenoxides. However, in most cases the mixture of products obtained had to be separated. On the other hand, we have used the $Fe^+(cp)$ moiety to yield diaryl ethers cleanly, and in good yield.[62,63] In a recent communication by Pearson and Gelormini,[64] the advantages of using the cyclopentadienyliron moiety in the synthesis of triaryl diether monomers is clearly demonstrated.

Interest in the preparation of organometallic polymers is due to their potential uses in material science, with considerable

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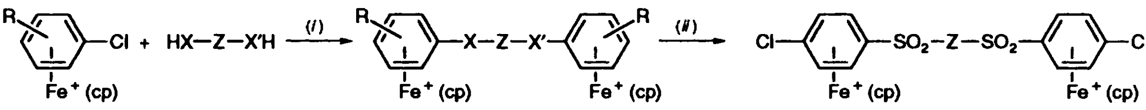


	R	X	X'	Z
1	2-Cl	O	O	1,4-C_6H_4
2	3-Cl	O	S	1,4-C_6H_4
3	4-Cl	O	O	4,4'-$C_6H_4C_6H_4$
		S	S	$(CH_2)_2$
		S	S	$(CH_2)_4$
		S	S	$(CH_2)_6$
		S	S	$(CH_2)_8$
		O	O	1,5-$C_{10}H_6$
		O	O	4,4'-$C_6H_4(CO)C_6H_4$

	R	X	X'	Z
4	2-Cl	O	O	1,4-C_6H_4
5	3-Cl	O	O	1,4-C_6H_4
6	4-Cl	O	O	1,4-C_6H_4
7	2-Cl	O	S	1,4-C_6H_4
8	3-Cl	O	S	1,4-C_6H_4
9	4-Cl	O	O	4,4'-$C_6H_4C_6H_4$
10	4-Cl	S	S	$(CH_2)_2$
11	4-Cl	S	S	$(CH_2)_4$
12	4-Cl	S	S	$(CH_2)_6$
13	4-Cl	S	S	$(CH_2)_8$
14	4-Cl	O	O	1,5-$C_{10}H_6$
15	4-Cl	O	O	4,4'-$C_6H_4(CO)C_6H_4$

	Z
19	$(CH_2)_2$
20	$(CH_2)_4$
21	$(CH_2)_6$
22	$(CH_2)_8$

Scheme 1 (*i*) Dimethylformamide (dmf), K_2CO_3; (*ii*) 3-chloroperbenzoic acid, dmf, CH_2Cl_2 (for complexes **10–13**)

attention being given to their electrical and thermal properties. An important class of organometallic polymers is the pendant type, where the metal moieties are pendant to the backbone of the polymer. To date, there have been a limited number of reports dealing with these types of materials.[65–67] The $Ru^+(C_5Me_5)$ moiety has recently been used in the preparation of poly(phenylenedithioxy) and poly(phenylenedioxy) derivatives.[68] It was found that π-complexation to the polymer backbone enhanced the solubility of these polymers over the analogous organic systems.

This article reports a unique and versatile synthetic method for the preparation of poly(cyclopentadienyliron) cations of polyaromatic ethers and thioethers. This methodology allows for the tailored design of a large number of oligomeric systems containing a variety of functional groups (sulfide, sulfone and carbonyl).

Results and Discussion

Over the last few years we have been interested in the synthesis, characterization and functionalization of a series of bis(cyclopentadienyliron) arene complexes which possess heteroatomic linkages due to their potential use as building blocks in polymer chemistry.[69–71] We have also demonstrated that our methodology is a viable route to the preparation of a number of aromatic ethers, amines, and sulfides which cannot be easily prepared by traditional ligand-exchange reactions.[69–72] The introduction of electron-withdrawing bridges such as keto and sulfonyl groups into the diiron system could be achieved using two different routes. The first involves the use of a dinucleophile containing a keto group, in the nucleophilic aromatic substitution reactions with chloroarene complexes. The second involves the oxidation of the sulfide bridges of the bis(cyclopentadienyliron) arene complexes using 3-chloroperbenzoic acid. Scheme 1 summarizes a number of bimetallic complexes that we have prepared to be used in this study as building blocks.

Due to our interest in determining the molecular structures of these types of diiron complexes, we have attempted to crystallize some of these materials. Three complexes, the hexafluorophosphate salts of *ortho* and *meta* isomers of phenylenedioxybis[(η^6-benzene)(η^5-cyclopentadienyl)iron] dications (**16**, **17**) as well as the *ortho* isomer of phenylenedithioxybis[(η^6-benzene)(η^5-cyclopentadienyl)iron] dication (**18**) yielded crystals of reasonable quality for analysis. The ORTEP drawings of the cationic portions of these complexes are shown in Fig. 1. Unfortunately, these complexes exhibit little measurable scatter beyond 2θ = 40°, which is presumably

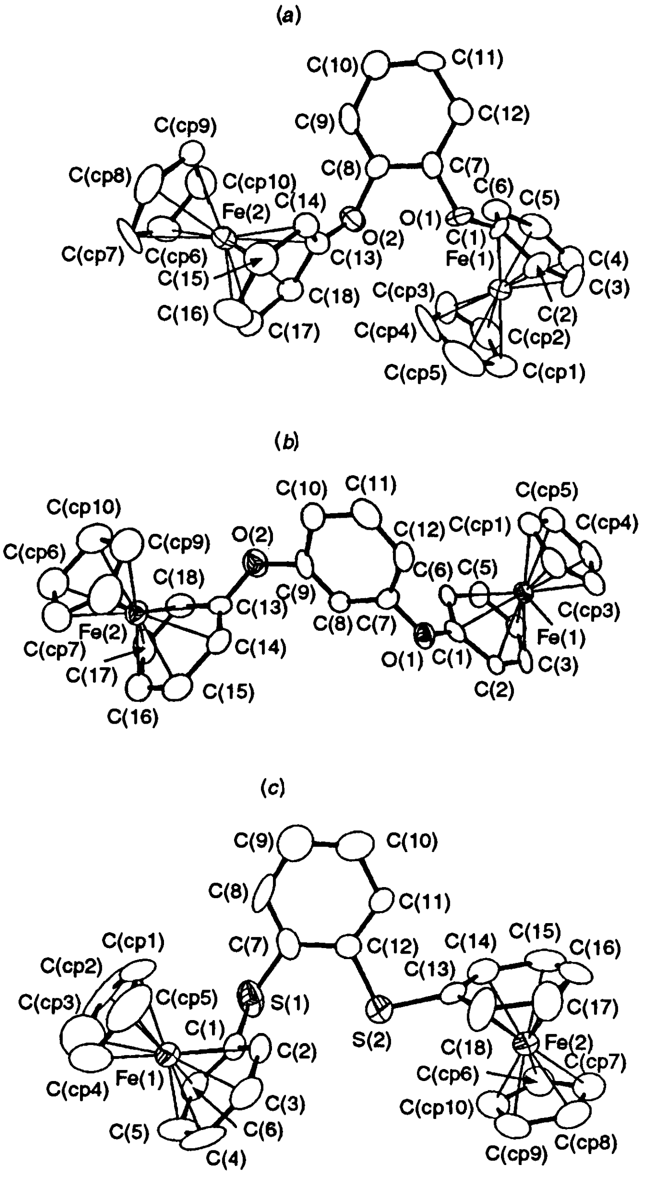


Fig. 1 The ORTEP drawings for the cationic portions of **16** (*a*), **17** (*b*) and **18** (*c*)

Table 1 Crystal data and summary of intensity data collection and structure refinement

Complex	**16**	**17**	**18**
Formula	$C_{28}H_{24}F_{12}Fe_2O_2P_2 \cdot CH_2Cl_2$	$C_{28}H_{24}F_{12}Fe_2O_2P_2$	$C_{28}H_{24}F_{12}Fe_2P_2S_2$
Formula weight	879.0	794.1	826.2
Crystal dimensions/mm	0.30 × 0.40 × 0.50	0.30 × 0.40 × 0.50	0.10 × 0.20 × 0.20
Crystal colour	Pale yellow	Yellow	Yellow
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1/n$	$P\bar{1}$
T/°C	17	17	22
a/Å	11.576(3)	13.653(3)	10.698(5)
b/Å	15.014(2)	8.013(1)	11.618(2)
c/Å	19.660(4)	27.794(6)	14.926(7)
α/°	—	—	110.669(2)
β/°	104.210(3)	103.450(3)	99.040(5)
γ/°	—	—	107.30(4)
U/Å^3	3312.3(1)	2957.3(1)	1584.4(1)
Z	4	4	2
D_c/g cm^{-3}	1.76	1.78	1.73
F(000)	1760	1592	828
μ/cm^{-1}	10.6	11.9	12.3
Transmission range	^{a}	0.55, 0.99	^{a}
Solvent	CH_2Cl_2	—	—
Decay of standards (%)	−40	±1	±1
$2\theta_{max}$/°	40	45	45
No. of data collected	3194	3962	4339
No. of independent data	3086	3867	4145
No. of observed data [$I_{obs} \geq 3\sigma(I)$], N_o	1793	2244	1653
No. of parameters refined, N_v	442	415	410
R^b	0.063	0.070	0.069
R'^b	0.053	0.062	0.060
Goodness of fit, S^c	2.67	3.91	2.30
Final shift/error residual	0.001	0.001	0.002

^{a} No correction was made for absorption. ^{b} $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R' = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{\frac{1}{2}}$. ^{c} $S = [\sum w(|F_o| - |F_c|)^2/(N_o - N_v)]^{\frac{1}{2}}$.

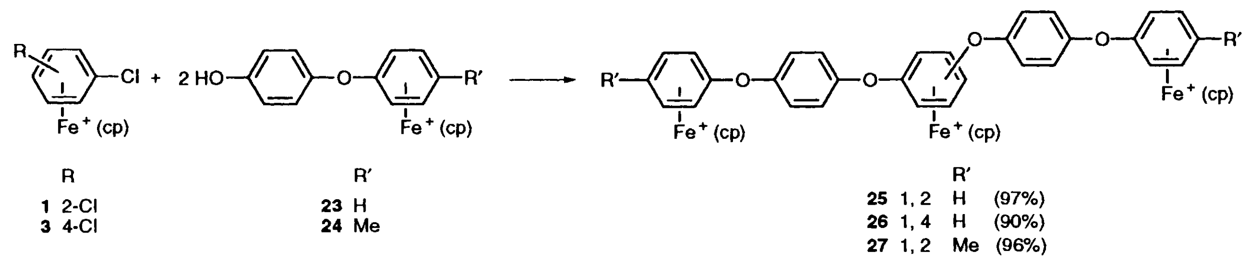
a consequence of high thermal motion in the hexafluorophosphate anions and the cyclopentadienyl rings.[73–77] The limited number of observed data reduces the accuracy of the interatomic distance and angles but does not affect our ability to interpret the overall conformation and crystal packing. The Fe ··· Fe distances are 7.25, 9.81 and 8.61 Å for **16**, **17** and **18** respectively, the differences possibly being rationalized by the type of substitution on the uncomplexed arene ring. Data collection and cell parameters are given in Table 1, and atomic coordinates in Tables 2–4. The bond lengths and angles of these complexes are within the range previously reported for arene cyclopentadienyliron complexes (Tables 5–7).[73–77]

In order to control the design of the polyaromatic ether complexes, it was first essential to study fully the synthesis, characterization, and application of the monomeric and dimeric complexes.[69–72,78–80] As can be seen from Scheme 1, a number of dinucleophiles could be reacted with a disubstituted chloroarene complex (**1**–**3**) under very mild reaction conditions to yield the bimetallic complexes, **4**–**15**. It should be pointed out that complexes **13**–**15**, **21** and **22** have not been reported previously; their spectroscopic data are given in the Experimental section. These bimetallic complexes have terminal chlorine atoms and hence they could be used as building blocks in the synthesis of the polymeric species.

The successful preparation of a wide range of bis[Fe$^+$(cp)] arene complexes prompted us to develop novel synthetic routes to poly[Fe$^+$(cp)] arene complexes. In a recent communication,[81] we briefly outlined the preparation of a few polyiron complexes which contained from three to six metal moieties. Here, we report the results of our first detailed investigation on the synthesis of polymetallic ethers with pendant Fe$^+$(cp) moieties. Following the synthesis of the diiron systems, we focused our strategy on building the oligomeric materials which were also used as building blocks in the synthesis of the polymeric materials. The tris[Fe$^+$(cp)] complexes are generally prepared by the reaction of two different monometallic complexes as shown in Schemes 2 and 3. It should be stated that there are two factors which control the design of the trimetallic complexes. The first factor is whether a mono- (**23** or **24**) or dihydroxyaromatic (**28**) nucleophile is used, as this will control the type of terminal groups. The second factor is the molar ratio of the disubstituted chloroarene complex (**1**–**3**, **29**). Reactions of chloroarene complexes (**1** or **3**) with monohydroxy complexes (**23** or **24**) lead to the formation of tris[Fe$^+$(cp)] arene complexes (**25**–**27**) in good yield as described in Scheme 2. On the other hand, the trimetallic complexes (**27**, **30** and **31**) could successfully be synthesized from the reaction of the dihydroxy complex (**28**) with chloroarene complexes (**2**, **3** or **29**) in a molar ratio of 1 : 2 (Scheme 3). It is important that complex **27** may be prepared in both ways, in comparative yields. Although a larger pool of trimetallic complexes could have been prepared, these few examples illustrate the versatility of our methodology.

The controlled design in building larger polymetallic systems is also coupled with the possibility of selectively introducing certain bridges, and terminal functionalities, allowing for the preparation of complexes which are both symmetric and unsymmetric in nature. Schemes 4–6 outline the synthesis of a number of tetra[Fe$^+$(cp)] complexes which have some of these characteristics. The tetrametallic complexes (**32**–**42**) were synthesized, which all have terminal ends (Scheme 4), that is, those complexes which may not undergo further nucleophilic substitution reactions. It was observed that isomeric complexes **32**–**34** gave similar NMR spectra for the terminal complexed arenes, and cyclopentadienyl ligands. On the other hand, there was an obvious difference in the inner complexed aromatic region, as was anticipated.

In this series of complexes it was found that certain trends



Scheme 2

Table 2 Non-hydrogen atomic parameters for complex **16** with estimated standard deviations (e.s.d.s) in parentheses

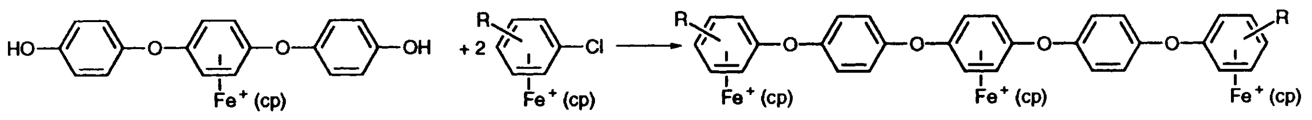
Atom	*x*	*y*	*z*
Fe(1)	0.415 89(16)	0.593 99(14)	0.152 69(11)
Fe(2)	−0.037 60(15)	0.259 01(13)	0.148 07(10)
O(1)	0.375 9(9)	0.436 0(7)	0.251 0(5)
O(2)	0.133 7(8)	0.425 3(7)	0.197 8(6)
C(1)	0.431 7(13)	0.514 8(13)	0.243 4(7)
C(2)	0.531 0(17)	0.505 6(14)	0.218 6(8)
C(3)	0.589 5(18)	0.583 7(22)	0.204 2(12)
C(4)	0.551 3(24)	0.668 2(18)	0.216 6(13)
C(5)	0.449 6(21)	0.676 6(11)	0.240 2(9)
C(6)	0.383 1(13)	0.598 4(13)	0.252 1(8)
C(7)	0.301 6(14)	0.438 2(8)	0.296 6(9)
C(8)	0.180 4(16)	0.428 5(9)	0.270 3(9)
C(9)	0.103 5(12)	0.430 1(10)	0.313 6(11)
C(10)	0.149 0(17)	0.442 7(10)	0.386 3(10)
C(11)	0.270 5(18)	0.450 9(11)	0.413 6(8)
C(12)	0.347 2(12)	0.451 0(9)	0.369 7(10)
C(13)	0.110 5(12)	0.346 4(11)	0.167 6(10)
C(14)	0.142 4(10)	0.265 3(11)	0.200 8(7)
C(15)	0.113 3(13)	0.183 4(10)	0.162 6(11)
C(16)	0.058 1(14)	0.186 0(12)	0.090 9(10)
C(17)	0.024 1(12)	0.271 1(13)	0.060 4(8)
C(18)	0.051 9(13)	0.349 8(10)	0.097 1(10)
C(cp1)	0.428 5(17)	0.612 5(20)	0.051 4(8)
C(cp2)	0.356 0(24)	0.675 2(11)	0.069 0(11)
C(cp3)	0.265 7(21)	0.637 0(24)	0.089 0(13)
C(cp4)	0.268(3)	0.547(3)	0.080 3(14)
C(cp5)	0.372(3)	0.531 5(14)	0.060 3(12)
C(cp6)	−0.211 5(17)	0.289 9(20)	0.119 8(13)
C(cp7)	−0.200 2(21)	0.199 6(25)	0.118 9(17)
C(cp8)	−0.142 2(17)	0.181 8(13)	0.190 4(15)
C(cp9)	−0.123 8(12)	0.258 3(16)	0.227 3(8)
C(cp10)	−0.165 1(14)	0.329 0(12)	0.183 5(14)
P(1)	0.231 7(4)	0.927 4(3)	0.107 77(25)
F(1)	0.184 8(9)	0.964 6(6)	0.170 8(5)
F(2)	0.329 0(8)	0.872 6(5)	0.161 0(5)
F(3)	0.147 2(9)	0.846 2(6)	0.103 1(5)
F(4)	0.136 4(9)	0.983 2(7)	0.055 6(5)
F(5)	0.276 6(9)	0.888 5(6)	0.046 1(5)
F(6)	0.317 1(9)	1.006 1(7)	0.115 0(6)
P(2)	0.863 4(9)	0.614 4(3)	0.104 4(3)
F(7)	0.802 6(12)	0.647 8(8)	0.033 3(7)
F(8)	0.931 4(12)	0.554 1(9)	0.066 9(7)
F(9)	0.912 3(15)	0.573 5(10)	0.175 8(6)
F(10)	0.956 9(12)	0.683 5(10)	0.113 9(7)
F(11)	0.794 3(11)	0.675 1(7)	0.141 3(7)
F(12)	0.769 5(14)	0.543 8(9)	0.096 1(7)
Cl(1)	0.500 5(4)	0.163 9(3)	0.042 2(3)
Cl(2)	0.399 1(5)	0.295 3(3)	0.116 4(3)
C(19)	0.371 5(12)	0.203 4(10)	0.060 6(9)

could be noted. In the mixed-system complexes **37**–**39**, it was observed that the increase in the chain length of the aliphatic bridge afforded an increase in the complex yield. The synthesis of complex **40** is an example of how a diiron sulfone may be used to prepare effectively a tetrairon system with a sulfone bridge present. Also, in accordance with our previous investigations of the mixed bimetallic systems, the ^{1}H NMR of complex **35** showed the presence of seven different cp

Table 3 Non-hydrogen atomic parameters for **17**, with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Fe(1)	0.191 55(11)	0.857 08(21)	0.094 89(6)
Fe(2)	−0.325 31(12)	0.068 91(22)	0.145 23(6)
O(1)	0.051 0(5)	0.530 6(8)	0.072 0(3)
O(2)	−0.174 6(5)	0.376 0(10)	0.173 1(3)
C(1)	0.064 7(7)	0.696 7(12)	0.068 68(4)
C(2)	0.100 0(7)	0.761 2(16)	0.028 6(4)
C(3)	0.117 9(8)	0.927 9(15)	0.024 1(4)
C(4)	0.097 7(8)	1.044 5(15)	0.058 3(4)
C(5)	0.063 6(8)	0.988 1(14)	0.100 6(4)
C(6)	0.047 6(7)	0.806 3(13)	0.105 8(4)
C(7)	0.031 9(8)	0.462 2(13)	0.114 3(3)
C(8)	−0.064 3(7)	0.455 9(14)	0.120 1(4)
C(9)	−0.077 1(7)	0.381 4(14)	0.161 9(4)
C(10)	−0.001 7(9)	0.321 6(14)	0.200 0(4)
C(11)	0.097 9(8)	0.335 1(15)	0.191 6(4)
C(12)	0.112 5(8)	0.407 4(14)	0.149 7(4)
C(13)	−0.251 9(8)	0.298 9(13)	0.138 6(3)
C(14)	−0.236 5(8)	0.188 4(14)	0.104 3(4)
C(15)	−0.324 9(9)	0.113 1(17)	0.071 6(4)
C(16)	−0.417 4(9)	0.134 5(17)	0.077 9(4)
C(17)	−0.430 3(8)	0.254 9(17)	0.113 1(5)
C(18)	−0.350 4(8)	0.327 6(15)	0.146 5(4)
C(cp1)	0.281 0(8)	0.767 5(16)	0.157 8(4)
C(cp2)	0.311 9(8)	0.696 1(15)	0.118 1(4)
C(cp3)	0.338 5(7)	0.844 5(18)	0.091 4(4)
C(cp4)	0.322 7(9)	0.987 5(15)	0.117 8(5)
C(cp5)	0.289 9(8)	0.932 9(15)	0.159 5(4)
C(cp6)	−0.400 9(9)	−0.070 7(16)	0.185 6(4)
C(cp7)	−0.365 4(10)	−0.170 9(16)	0.153 4(5)
C(cp8)	−0.259 2(10)	−0.156 1(16)	0.163 9(5)
C(cp9)	−0.234 8(9)	−0.045 6(18)	0.203 6(5)
C(cp10)	−0.318 6(9)	0.002 0(16)	0.217 5(4)
P(1)	−0.302 2(3)	−0.353 3(5)	0.003 30(12)
F(1)	−0.349 5(11)	−0.354 1(16)	0.044 7(4)
F(2)	−0.391 7(7)	−0.433 8(14)	−0.031 7(4)
F(3)	−0.251 3(9)	−0.352 4(12)	−0.040 1(4)
F(4)	−0.214 1(7)	−0.261 4(14)	0.036 5(4)
F(5)	−0.340 7(8)	−0.175 7(10)	−0.012 7(3)
F(6)	−0.259 3(7)	−0.528 9(10)	0.016 8(3)
P(2)	0.428 26(23)	0.356 6(4)	0.237 35(11)
F(7)	0.506 4(6)	0.229 9(12)	0.228 8(4)
F(8)	0.489 8(6)	0.498 2(10)	0.218 21(25)
F(9)	0.348 8(5)	0.488 0(10)	0.244 7(3)
F(10)	0.366 9(6)	0.217 1(9)	0.256 7(3)
F(11)	0.366 3(5)	0.332 0(10)	0.182 96(25)
F(12)	0.488 9(5)	0.392 1(11)	0.291 38(24)

resonances which may be attributed to the diastereomeric nature of the complex.[70] Fig. 2 shows a ^{1}H NMR spectral comparison of the cp region for both the di- and tetra-iron complexes. As we described earlier,[70] the bridging ligands created in the reaction involving the *ortho*-substituent starting-material complex (**7**) are prochiral when considered apart from the Fe$^+$(cp) moieties. Upon complexation of an iron moiety this complex becomes chiral in nature. We have also assigned these complexes as (*R*,*R*) or (*S*,*S*) (enantiomeric pair) of one diastereoisomer and (*R*,*S*) or (*S*,*R*) (enantiomeric pair) for the



28

R
2 3-Cl
3 4-Cl
29 4-Me

R
27 4-Me (96%)
30 3-Cl (93%)
31 4-Cl (92%)

Scheme 3

Table 4 Non-hydrogen atomic parameters for **18** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Fe(1)	0.341 45(22)	0.661 91(19)	0.368 06(15)
Fe(2)	0.138 94(22)	−0.017 48(19)	−0.190 14(15)
S(1)	0.083 7(4)	0.513 0(4)	0.134 7(3)
S(2)	0.115 1(5)	0.275 2(4)	−0.028 9(3)
P(1)	0.860 0(5)	0.685 0(4)	0.416 5(3)
P(2)	0.416 3(5)	0.132 9(4)	0.205 6(3)
F(1)	0.742 3(10)	0.679 4(12)	0.337 3(8)
F(2)	0.951 5(12)	0.704 8(13)	0.350 0(9)
F(3)	0.825 3(16)	0.543 3(10)	0.368 9(11)
F(4)	0.978 0(12)	0.689 3(13)	0.490 7(8)
F(5)	0.768 2(14)	0.664 5(15)	0.480 0(10)
F(6)	0.897 7(18)	0.831 4(11)	0.463 3(9)
F(7)	0.377 7(12)	0.198 5(10)	0.298 7(7)
F(8)	0.350 0(13)	0.199 3(11)	0.154 6(8)
F(9)	0.456 0(11)	0.065 8(10)	0.109 5(7)
F(10)	0.275 4(12)	0.020 5(10)	0.159 0(10)
F(11)	0.555 3(11)	0.237 3(11)	0.246 8(10)
F(12)	0.466 8(13)	0.053 0(11)	0.252 2(8)
C(cp1)	0.421 6(17)	0.830 7(13)	0.352 7(11)
C(cp2)	0.305 1(17)	0.833 8(13)	0.387 8(17)
C(cp3)	0.356 1(21)	0.827 4(20)	0.466 7(16)
C(cp4)	0.472(3)	0.816 0(16)	0.497 7(11)
C(cp5)	0.512 5(14)	0.819 6(13)	0.416 2(14)
C(cp6)	−0.038 0(16)	−0.178 9(15)	−0.241 1(12)
C(cp7)	0.065 2(18)	−0.222 0(12)	−0.263 6(11)
C(cp8)	0.163 8(17)	−0.173 7(15)	−0.171 9(13)
C(cp9)	0.116 4(17)	−0.108 2(15)	−0.097 4(11)
C(cp10)	−0.009 8(16)	−0.112 0(15)	−0.139 6(12)
C(1)	0.194 1(14)	0.513 7(12)	0.233 5(10)
C(2)	0.319 5(14)	0.507 9(12)	0.235 6(9)
C(3)	0.405 5(16)	0.504 5(13)	0.316 8(12)
C(4)	0.351 4(17)	0.504 7(14)	0.399 0(12)
C(5)	0.224 0(17)	0.514 1(15)	0.396 2(12)
C(6)	0.146 9(13)	0.517 9(11)	0.316 9(11)
C(7)	0.188 1(14)	0.548 2(13)	0.059 2(9)
C(8)	0.245 7(16)	0.675 4(12)	0.063 2(10)
C(9)	0.317 1(17)	0.698 2(15)	−0.000 9(11)
C(10)	0.326 2(16)	0.594 0(14)	−0.074 5(11)
C(11)	0.270 5(16)	0.467 1(12)	−0.081 7(10)
C(12)	0.198 8(14)	0.441 3(12)	−0.017 5(10)
C(13)	0.167 1(14)	0.183 3(12)	−0.128 1(10)
C(14)	0.084 4(18)	0.121 1(13)	−0.225 2(11)
C(15)	0.131 5(22)	0.045 6(15)	−0.302 5(11)
C(16)	0.261 6(19)	0.040 4(14)	−0.270 9(12)
C(17)	0.333 9(17)	0.091 3(15)	−0.175 5(13)
C(18)	0.293 8(14)	0.171 1(13)	−0.100 8(12)

second isomer, as shown in Fig. 2(*a*). Using the same analogy we were able to assign the tetrairon complex (**35**) shown in Fig. 2(*b*). The flexibility of our method is evident from the incorporation of 1,4-phenylenedioxy, 4-phenoxythio, or 1,5-naphthyldioxy units into the backbone of the polyaromatic ethers to yield complexes **43**–**45** in almost quantitative yield as shown in Schemes 5 and 6.

Following our successful investigations into the preparation of a wide variety of di-, tri- and tetra-iron complexes, our next goal was to build larger polymetallic materials with these complexes used as building blocks. There are many routes which may lead to the formation of the polymetallic complexes. In this study we have investigated various routes allowing for the synthesis of these materials. One important route is the functionalization of the existing (di-, tri- and tetra-iron) arene complexes containing terminal chloro groups with dihydroxybenzene allowing for the formation of the analogous complexes with terminal hydroxy groups. As an example complexes **6**, **31** or **43** were treated with 1,4-dihydroxybenzene in a 1 : 5 molar ratio, in *N*,*N'*-dimethylformamide to produce complexes **46**–**48** as shown in Scheme 7. It was found that the solubility of such complexes (**46**–**48**) decreased when compared to the starting complexes (**6**, **31** and **43**). However, the preparation of these complexes is rather important as they may now serve as dinucleophiles for further reactions which allows for building larger systems in even fewer steps (see below). It is also very important that these reactions were conducted using very low starting complex concentrations (100–250 mg complex per 10 cm^3 dmf) to prevent polymerization.[65,68]

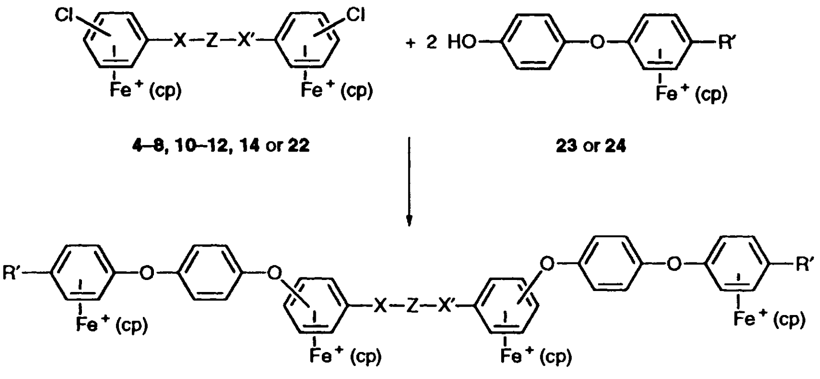
The type of system which we wish to prepare may contain either an odd or even number of Fe^+(cp) moieties. Schemes 8–10 show some methods for preparing the odd-numbered systems. Scheme 8 outlines the reaction between the trimetallic complex with terminal hydroxy groups (**47**) and a chlorobenzene complex (**3**, **29** or **49**) with one of three different substituents. The use of a 1 : 2 molar ratio allowed for the preparation of the pentametallic complexes in very high yields (86–89%). Complex **51** was then further treated with either 1,4-dihydroxybenzene or complex **28** to produce the penta- and hepta-metallic complexes with terminal hydroxy groups. Complex **29** was then treated with these products in a 2 : 1 molar ratio to yield the analogous complexes with terminal methyl groups (Scheme 9). To demonstrate the efficiency, flexibility, and accuracy of our method in preparing and characterizing these types of complexes different routes have been investigated which yield the same products. As an example, complex **52** may be prepared from complex **28** and complex **57** in a 1 : 2 molar ratio as described in Scheme 10.

The characterization of these polymetallic complexes was based on the proton and carbon NMR, as well as elemental analyses data, which are included in the Experimental section. The NMR spectra of various series of complexes such as the capped methyl system show a certain trend. Fig. 3 shows the proton NMR spectra of complexes **27**, **52**, **55** and **56** (the capped methyl series). As shown in these spectra, the change in the relative intensity and integration of the cp peaks to the methyl group increases. It is also very important to note the change in the relative intensity of the inner cp compared to the outer cp peaks as the systems become larger. This trend has been noticed in other series such as terminal hydroxyl systems, as well as in unsubstituted systems.

The synthesis of larger oligomeric materials containing an even number of cyclopentadienyliron moieties could also be achieved following the above described synthetic strategy but with different starting complexes. Schemes 11–14 outline representative examples of such materials containing six cyclopentadienyliron moieties. In this study, we have clearly

Table 5 Interatomic distances (Å) and angles (°) for **16**

Fe(1)–C(1)	2.114(15)	Fe(2)–C(13)	2.117(15)	O(1)–C(7)	1.387(20)	C(8)–C(9)	1.38(3)
Fe(1)–C(2)	2.089(15)	Fe(2)–C(14)	2.089(11)	O(2)–C(8)	1.395(21)	C(9)–C(10)	1.41(3)
Fe(1)–C(3)	2.022(20)	Fe(2)–C(15)	2.044(14)	O(2)–C(13)	1.323(20)	C(10)–C(11)	1.38(3)
Fe(1)–C(4)	2.076(22)	Fe(2)–C(16)	2.074(15)	C(1)–C(2)	1.36(3)	C(11)–C(12)	1.38(3)
Fe(1)–C(5)	2.079(16)	Fe(2)–C(17)	2.030(14)	C(1)–C(6)	1.40(3)	C(13)–C(14)	1.388(23)
Fe(1)–C(6)	2.082(15)	Fe(2)–C(18)	2.108(13)	C(2)–C(3)	1.42(4)	C(13)–C(18)	1.39(3)
Fe(1)–C(cp1)	2.051(16)	Fe(2)–C(cp6)	2.007(20)	C(3)–C(4)	1.38(4)	C(14)–C(15)	1.437(24)
Fe(1)–C(cp2)	2.029(18)	Fe(2)–C(cp7)	2.034(20)	C(4)–C(5)	1.37(4)	C(15)–C(16)	1.40(3)
Fe(1)–C(cp3)	1.985(22)	Fe(2)–C(cp8)	2.000(16)	C(5)–C(6)	1.45(3)	C(16)–C(17)	1.42(3)
Fe(1)–C(cp4)	2.062(22)	Fe(2)–C(cp9)	2.045(14)	C(7)–C(8)	1.379(24)	C(17)–C(18)	1.38(3)
Fe(1)–C(cp5)	1.995(20)	Fe(2)–C(cp10)	2.067(15)	P(1)–F(1)	1.573(10)	P(2)–F(7)	1.490(12)
C(cp1)–C(cp2)	1.36(4)	C(cp6)–C(cp7)	1.36(5)	P(1)–F(2)	1.569(9)	P(2)–F(8)	1.506(12)
C(cp1)–C(cp5)	1.41(4)	C(cp6)–C(cp10)	1.37(4)	P(1)–F(3)	1.551(10)	P(2)–F(9)	1.509(12)
C(cp2)–C(cp3)	1.33(4)	C(cp7)–C(cp8)	1.43(5)	P(1)–F(4)	1.554(10)	P(2)–F(10)	1.479(11)
C(cp3)–C(cp4)	1.36(5)	C(cp8)–C(cp9)	1.35(3)	P(1)–F(5)	1.546(10)	P(2)–F(11)	1.511(11)
C(cp4)–C(cp5)	1.37(6)	C(cp9)–C(cp10)	1.38(3)	P(1)–F(6)	1.525(10)	P(2)–F(12)	1.498(12)
O(1)–C(1)	1.374(21)	C(7)–C(12)	1.42(3)	C(11)–C(19)	1.726(15)	C(12)–C(19)	1.742(17)
C(1)–O(1)–C(7)	115.6(11)	O(2)–C(8)–C(9)	119.1(15)	F(1)–P(1)–F(2)	89.5(6)	F(7)–P(2)–F(8)	85.8(8)
C(8)–O(2)–C(13)	118.3(12)	C(7)–C(8)–C(9)	121.3(16)	F(1)–P(1)–F(3)	89.5(6)	F(7)–P(2)–F(9)	173.2(9)
O(1)–C(1)–C(2)	114.4(17)	C(8)–C(9)–C(10)	119.5(14)	F(1)–P(1)–F(4)	90.2(6)	F(7)–P(2)–F(10)	92.5(8)
O(1)–C(1)–C(6)	123.0(14)	C(9)–C(10)–C(11)	119.8(14)	F(1)–P(1)–F(5)	178.6(6)	F(7)–P(2)–F(11)	93.6(8)
C(2)–C(1)–C(6)	122.2(17)	C(10)–C(11)–C(12)	120.5(14)	F(1)–P(1)–F(6)	89.5(6)	F(7)–P(2)–F(12)	88.5(8)
C(1)–C(2)–C(3)	118.4(18)	C(7)–C(12)–C(11)	119.7(13)	F(2)–P(1)–F(3)	88.1(6)	F(8)–P(2)–F(9)	95.1(8)
C(2)–C(3)–C(4)	122.3(20)	O(2)–C(13)–C(14)	125.0(16)	F(2)–P(1)–F(4)	179.0(6)	F(8)–P(2)–F(10)	91.6(8)
C(3)–C(4)–C(5)	118.8(21)	O(2)–C(13)–C(18)	114.3(14)	F(2)–P(1)–F(5)	90.0(5)	F(8)–P(2)–F(11)	179.4(8)
C(4)–C(5)–C(6)	120.8(18)	C(14)–C(13)–C(18)	120.7(15)	F(2)–P(1)–F(6)	90.0(6)	F(8)–P(2)–F(12)	88.5(8)
C(1)–C(6)–C(5)	117.3(15)	C(13)–C(14)–C(15)	120.2(13)	F(3)–P(1)–F(4)	92.9(6)	F(9)–P(2)–F(10)	94.2(9)
O(1)–C(7)–C(8)	119.3(15)	C(14)–C(15)–C(16)	119.6(13)	F(3)–P(1)–F(5)	89.1(6)	F(9)–P(2)–F(11)	85.5(8)
O(1)–C(7)–C(12)	121.6(13)	C(15)–C(16)–C(17)	117.4(14)	F(3)–P(1)–F(6)	177.9(6)	F(9)–P(2)–F(12)	84.8(9)
C(8)–C(7)–C(12)	119.1(15)	C(16)–C(17)–C(18)	122.8(14)	F(4)–P(1)–F(5)	90.4(6)	F(10)–P(2)–F(11)	88.5(7)
O(2)–C(8)–C(7)	119.4(15)	C(13)–C(18)–C(17)	119.0(13)	F(4)–P(1)–F(6)	89.0(6)	F(10)–P(2)–F(12)	179.0(9)
C(cp2)–C(cp1)–C(cp5)	103.2(19)	C(cp7)–C(cp6)–C(cp10)	114.8(23)	F(5)–P(1)–F(6)	91.8(6)	F(11)–P(2)–F(12)	91.4(7)
C(cp1)–C(cp2)–C(cp3)	110.7(19)	C(cp6)–C(cp7)–C(cp8)	101.4(19)			Cl(1)–C(19)–Cl(2)	111.7(8)
C(cp2)–C(cp3)–C(cp4)	110(3)	C(cp7)–C(cp8)–C(cp9)	110.1(20)				
C(cp3)–C(cp4)–C(cp5)	104.6(23)	C(cp8)–C(cp9)–C(cp10)	109.7(17)				
C(cp1)–C(cp5)–C(cp4)	110.6(22)	C(cp6)–C(cp10)–C(cp9)	103.9(17)				

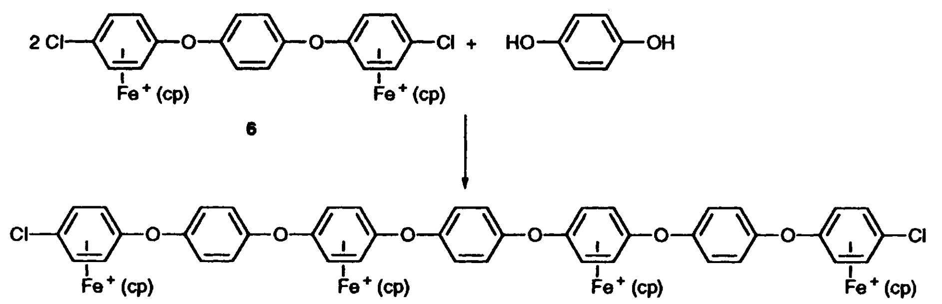


	X	X'	Z	R'	
32	O	O	1,4-C_6H_4	H	(95%)
33	O	O	1,4-C_6H_4	H	(93%)
34	O	O	1,4-C_6H_4	H	(90%)
35	O	S	1,4-C_6H_4	H	(86%)
36	O	S	1,4-C_6H_4	H	(87%)
37	S	S	$(CH_2)_2$	H	(57%)
38	S	S	$(CH_2)_4$	H	(83%)
39	S	S	$(CH_2)_6$	H	(86%)
40	SO_2	SO_2	$(CH_2)_8$	Me	(70%)
41	O	O	1,5-$C_{10}H_6$	H	(88%)
42	O	O	1,4-C_6H_4	Me	(92%)

Scheme 4 In complexes **32** and **35** the $Fe^+(cp)C_6H_4R'OC_6H_4O$– groups are attached at the *ortho* positions, in complex **33** at the *meta* positions and in all other complexes at the *para* positions

Table 6 Interatomic distances (Å) and angles (°) for **17**

Fe(1)–C(1)	2.143(9)	Fe(2)–C(13)	2.126(11)	O(1)–C(1)	1.350(12)	C(7)–C(12)	1.367(14)
Fe(1)–C(2)	2.116(10)	Fe(2)–C(14)	2.079(10)	O(1)–C(7)	1.376(12)	C(8)–C(9)	1.352(15)
Fe(1)–C(3)	2.069(11)	Fe(2)–C(15)	2.078(11)	O(2)–C(9)	1.436(12)	C(9)–C(10)	1.379(16)
Fe(1)–C(4)	2.079(11)	Fe(2)–C(16)	2.066(12)	O(2)–C(13)	1.393(12)	C(10)–C(11)	1.437(16)
Fe(1)–C(5)	2.076(11)	Fe(2)–C(17)	2.117(12)	C(1)–C(2)	1.415(15)	C(11)–C(12)	1.355(16)
Fe(1)–C(6)	2.096(10)	Fe(2)–C(18)	2.103(12)	C(1)–C(6)	1.411(14)	C(13)–C(14)	1.353(14)
Fe(1)–C(cp1)	2.018(11)	Fe(2)–C(cp6)	2.028(12)	C(2)–C(3)	1.369(17)	C(13)–C(18)	1.431(15)
Fe(1)–C(cp2)	2.070(11)	Fe(2)–C(cp7)	2.025(13)	C(3)–C(4)	1.405(17)	C(14)–C(15)	1.462(16)
Fe(1)–C(cp3)	2.034(10)	Fe(2)–C(cp8)	2.029(13)	C(4)–C(5)	1.434(16)	C(15)–C(16)	1.326(17)
Fe(1)–C(cp4)	2.043(11)	Fe(2)–C(cp9)	2.017(12)	C(5)–C(6)	1.485(15)	C(16)–C(17)	1.413(20)
Fe(1)–C(cp5)	2.067(11)	Fe(2)–C(cp10)	2.061(12)	C(7)–C(8)	1.362(14)	C(17)–C(18)	1.387(17)
C(cp1)–C(cp2)	1.392(17)	C(cp6)–C(cp7)	1.373(19)	P(1)–F(1)	1.445(9)	P(2)–F(7)	1.531(8)
C(cp1)–C(cp5)	1.331(17)	C(cp6)–C(cp10)	1.387(17)	P(1)–F(2)	1.517(9)	P(2)–F(8)	1.576(8)
C(cp2)–C(cp3)	1.491(18)	C(cp7)–C(cp8)	1.416(19)	P(1)–F(3)	1.525(9)	P(2)–F(9)	1.558(8)
C(cp3)–C(cp4)	1.405(19)	C(cp8)–C(cp9)	1.393(20)	P(1)–F(4)	1.525(9)	P(2)–F(10)	1.566(8)
C(cp4)–C(cp5)	1.405(17)	C(cp9)–C(cp10)	1.345(17)	P(1)–F(5)	1.546(9)	P(2)–F(11)	1.563(7)
				P(1)–F(6)	1.537(9)	P(2)–F(12)	1.563(7)
C(1)–O(1)–C(7)	120.4(8)	O(2)–C(9)–C(8)	120.7(9)	C(cp3)–C(cp4)–C(cp5)	107.1(11)	C(cp8)–C(cp9)–C(cp10)	110.2(11)
C(9)–O(2)–C(13)	117.2(8)	O(2)–C(9)–C(10)	112.8(9)	C(cp1)–C(cp5)–C(cp4)	109.0(11)	C(cp6)–C(cp10)–C(cp9)	108.3(11)
O(1)–C(1)–C(2)	119.4(9)	C(8)–C(9)–C(10)	126.2(9)	F(1)–P(1)–F(2)	93.8(7)	F(7)–P(2)–F(8)	88.8(5)
O(1)–C(1)–C(6)	121.1(9)	C(9)–C(10)–C(11)	114.5(9)	F(1)–P(1)–F(3)	179.4(8)	F(7)–P(2)–F(9)	178.4(5)
C(2)–C(1)–C(6)	119.5(10)	C(10)–C(11)–C(12)	120.4(10)	F(1)–P(1)–F(4)	87.5(7)	F(7)–P(2)–F(10)	91.6(5)
C(1)–C(2)–C(3)	121.9(10)	C(7)–C(12)–C(11)	120.0(10)	F(1)–P(1)–F(5)	92.8(7)	F(7)–P(2)–F(11)	90.3(5)
C(2)–C(3)–C(4)	121.4(10)	O(2)–C(13)–C(14)	123.9(9)	F(1)–P(1)–F(6)	90.9(7)	F(7)–P(2)–F(12)	92.2(5)
C(3)–C(4)–C(5)	119.8(10)	O(2)–C(13)–C(18)	114.3(9)	F(2)–P(1)–F(3)	86.7(7)	F(8)–P(2)–F(9)	90.0(5)
C(4)–C(5)–C(6)	118.1(10)	C(14)–C(13)–C(18)	121.3(10)	F(2)–P(1)–F(4)	176.1(7)	F(8)–P(2)–F(10)	179.5(5)
C(1)–C(6)–C(5)	119.2(9)	C(13)–C(14)–C(15)	117.8(10)	F(2)–P(1)–F(5)	92.1(6)	F(8)–P(2)–F(11)	88.6(4)
O(1)–C(7)–C(8)	119.7(9)	C(14)–C(15)–C(16)	122.6(11)	F(2)–P(1)–F(6)	88.4(6)	F(8)–P(2)–F(12)	89.3(4)
O(1)–C(7)–C(12)	117.6(9)	C(15)–C(16)–C(17)	117.1(11)	F(3)–P(1)–F(4)	92.0(7)	F(9)–P(2)–F(10)	89.6(4)
C(8)–C(7)–C(12)	122.7(9)	C(16)–C(17)–C(18)	123.1(11)	F(3)–P(1)–F(5)	87.4(6)	F(9)–P(2)–F(11)	88.6(4)
C(7)–C(8)–C(9)	116.0(9)	C(13)–C(18)–C(17)	116.8(10)	F(3)–P(1)–F(6)	88.8(6)	F(9)–P(2)–F(12)	88.9(5)
C(cp2)–C(cp1)–C(cp5)	113.2(11)	C(cp7)–C(cp6)–C(cp10)	107.9(11)	F(4)–P(1)–F(5)	84.1(6)	F(10)–P(2)–F(11)	91.8(4)
C(cp1)–C(cp2)–C(cp3)	102.8(10)	C(cp6)–C(cp7)–C(cp8)	108.4(11)	F(4)–P(1)–F(6)	95.3(6)	F(10)–P(2)–F(12)	90.3(4)
C(cp2)–C(cp3)–C(cp4)	107.7(10)	C(cp7)–C(cp8)–C(cp9)	105.1(10)	F(5)–P(1)–F(6)	176.2(6)	F(11)–P(2)–F(12)	176.7(5)



6

43
96%

Scheme 5

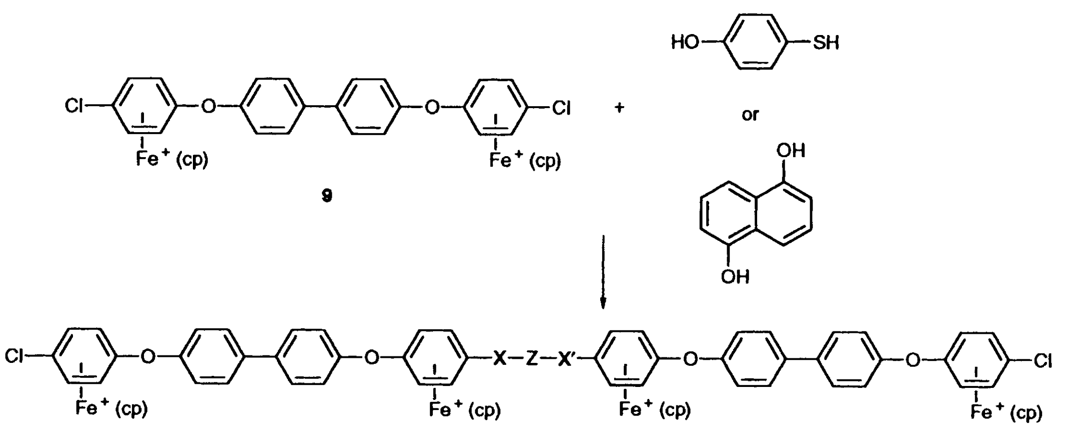
demonstrated the generality of our technique which allows for the synthesis of hexairon complexes with a number of starting mono-, tri- and tetra-iron complexes. The first example (Scheme 11) shows the preparation of a hexairon complex which was prepared in very high yield by the reaction of the monohydroxy complex (**23**) with the tetrairon complex **43** in a 2:1 molar ratio. Similar reactions between 1,4-dihydroxybenzene and **30** or **31** (Scheme 12), **48** and **29** (Scheme 13) or **43** and **28** (Scheme 14) all in 1:2 molar ratios produced the hexairon systems with terminal chloro, methyl and hydroxyl groups, respectively. Once again it was possible to prepare some of these systems in more than one fashion. Two examples are the reaction of **43** with **23**, and **48** with **49**, in a 1:2 molar ratio, to yield complex **58**. Comparison of the NMR spectra for both examples proved to be identical lending further proof of our ability to determine the molecular structure of this class of compounds. It also demonstrates that the size and nature of the type of systems desired can be controlled. Likewise, the preparation of octametallic species was achieved using similar methods as shown in Schemes 15 and 16.

One of the most important and critical questions to be addressed is how these systems can be extended based on the knowledge and the technology that we have developed. Schemes 17 and 18 show two examples of how the number of repeating units could be designed and controlled, yielding polyaromatic ethers with thirteen, seventeen and thirty-five Fe^+ (cp) moieties. An important observation in these reactions was that the yields were above 80% in all cases. In addition, the solubility of these systems was found to be good in solvents such as dimethyl sulfoxide (dmso), and dimethylformamide (100 mg per cm^3). These materials were fully characterized using both spectroscopic and analytical techniques, and the data are summarized in the Experimental section.

The functionalization of these oligomeric and polymeric systems is of importance due to the possible changes in the physical properties of these materials.[7,69–72] We have used

Table 7 Interatomic distances (Å) and angles (°) for **18**

Fe(1)–C(1)	2.105(13)	Fe(2)–C(13)	2.087(12)	S(1)–C(1)	1.735(13)	C(7)–C(12)	1.410(18)
Fe(1)–C(2)	2.068(12)	Fe(2)–C(14)	2.065(14)	S(1)–C(7)	1.770(14)	C(8)–C(9)	1.363(24)
Fe(1)–C(3)	2.079(14)	Fe(2)–C(15)	2.053(14)	S(2)–C(12)	1.803(13)	C(9)–C(10)	1.359(23)
Fe(1)–C(4)	2.063(13)	Fe(2)–C(16)	2.042(14)	S(2)–C(13)	1.772(13)	C(10)–C(11)	1.373(18)
Fe(1)–C(5)	2.024(15)	Fe(2)–C(17)	2.022(17)	C(1)–C(2)	1.360(19)	C(11)–C(12)	1.376(19)
Fe(1)–C(6)	2.060(12)	Fe(2)–C(18)	2.099(13)	C(1)–C(6)	1.405(20)	C(13)–C(14)	1.372(20)
Fe(1)–C(cp1)	2.003(12)	Fe(2)–C(cp6)	2.027(16)	C(2)–C(3)	1.422(20)	C(13)–C(18)	1.416(19)
Fe(1)–C(cp2)	2.075(13)	Fe(2)–C(cp7)	2.060(13)	C(3)–C(4)	1.436(25)	C(14)–C(15)	1.443(24)
Fe(1)–C(cp3)	1.907(20)	Fe(2)–C(cp8)	2.014(14)	C(4)–C(5)	1.395(24)	C(15)–C(16)	1.42(3)
Fe(1)–C(cp4)	2.030(15)	Fe(2)–C(cp9)	2.017(14)	C(5)–C(6)	1.356(20)	C(16)–C(17)	1.328(25)
Fe(1)–C(cp5)	1.971(14)	Fe(2)–C(cp10)	2.056(14)	C(7)–C(8)	1.397(19)	C(17)–C(18)	1.394(21)
C(cp1)–C(cp2)	1.43(3)	C(cp6)–C(cp7)	1.382(23)	P(1)–F(1)	1.554(10)	P(2)–F(7)	1.517(9)
C(cp1)–C(cp5)	1.315(22)	C(cp6)–C(cp10)	1.370(23)	P(1)–F(2)	1.526(11)	P(2)–F(8)	1.500(10)
C(cp2)–C(cp3)	1.26(3)	C(cp7)–C(cp8)	1.398(24)	P(1)–F(3)	1.442(11)	P(2)–F(9)	1.564(10)
C(cp3)–C(cp4)	1.32(3)	C(cp8)–C(cp9)	1.372(22)	P(1)–F(4)	1.518(11)	P(2)–F(10)	1.523(12)
C(cp4)–C(cp5)	1.36(3)	C(cp9)–C(cp10)	1.379(22)	P(1)–F(5)	1.494(11)	P(2)–F(11)	1.474(11)
				P(1)–F(6)	1.486(12)	P(2)–F(12)	1.507(10)
C(1)–S(1)–C(7)	104.0(6)	C(8)–C(9)–C(10)	119.5(13)	C(cp3)–C(cp4)–C(cp5)	93.5(14)	C(cp8)–C(cp9)–C(cp10)	109.2(14)
C(12)–S(2)–C(13)	100.5(6)	C(9)–C(10)–C(11)	120.7(14)	C(cp1)–C(cp5)–C(cp4)	112.5(17)	C(cp6)–C(cp10)–C(cp9)	106.4(13)
S(1)–C(1)–C(2)	125.5(10)	C(10)–C(11)–C(12)	120.9(13)	F(1)–P(1)–F(2)	87.8(6)	F(7)–P(2)–F(8)	89.7(6)
S(1)–C(1)–C(6)	116.3(10)	S(2)–C(12)–C(7)	118.4(10)	F(1)–P(1)–F(3)	93.1(8)	F(7)–P(2)–F(9)	179.7(6)
C(2)–C(1)–C(6)	118.2(12)	S(2)–C(12)–C(11)	122.5(10)	F(1)–P(1)–F(4)	177.7(7)	F(7)–P(2)–F(10)	91.2(7)
C(1)–C(2)–C(3)	123.9(13)	C(7)–C(12)–C(11)	119.1(12)	F(1)–P(1)–F(5)	91.2(7)	F(7)–P(2)–F(11)	91.8(7)
C(2)–C(3)–C(4)	116.0(13)	S(2)–C(13)–C(14)	121.3(11)	F(1)–P(1)–F(6)	86.6(7)	F(7)–P(2)–F(12)	90.2(6)
C(3)–C(4)–C(5)	118.9(12)	S(2)–C(13)–C(18)	116.4(11)	F(2)–P(1)–F(3)	90.0(8)	F(8)–P(2)–F(9)	89.9(6)
C(4)–C(5)–C(6)	122.3(15)	C(14)–C(13)–C(18)	122.2(13)	F(2)–P(1)–F(4)	90.0(7)	F(8)–P(2)–F(10)	83.9(7)
C(1)–C(6)–C(5)	120.5(13)	C(13)–C(14)–C(15)	118.6(15)	F(2)–P(1)–F(5)	178.9(8)	F(8)–P(2)–F(11)	97.0(8)
S(1)–C(7)–C(8)	122.7(10)	C(14)–C(15)–C(16)	116.5(14)	F(2)–P(1)–F(6)	88.4(8)	F(8)–P(2)–F(12)	173.3(8)
S(1)–C(7)–C(12)	118.8(10)	C(15)–C(16)–C(17)	123.6(15)	F(3)–P(1)–F(4)	86.2(8)	F(9)–P(2)–F(10)	88.9(7)
C(8)–C(7)–C(12)	117.9(12)	C(16)–C(17)–C(18)	120.1(16)	F(3)–P(1)–F(5)	89.7(9)	F(9)–P(2)–F(11)	88.2(7)
C(7)–C(8)–C(9)	121.7(12)	C(13)–C(18)–C(17)	118.4(14)	F(3)–P(1)–F(6)	178.4(9)	F(9)–P(2)–F(12)	90.2(6)
C(cp2)–C(cp1)–C(cp5)	110.5(16)	C(cp7)–C(cp6)–C(cp10)	110.5(14)	F(4)–P(1)–F(5)	91.0(7)	F(10)–P(2)–F(11)	177.0(7)
C(cp1)–C(cp2)–C(cp3)	92.7(15)	C(cp6)–C(cp7)–C(cp8)	105.7(13)	F(4)–P(1)–F(6)	94.1(8)	F(10)–P(2)–F(12)	89.4(8)
C(cp2)–C(cp3)–C(cp4)	130.8(22)	C(cp7)–C(cp8)–C(cp9)	108.1(14)	F(5)–P(1)–F(6)	91.9(9)	F(11)–P(2)–F(12)	89.7(8)



	X	X′	Z	
44	O	S	1,4-C_6H_4	(97%)
45	O	O	1,5-$C_{10}H_6$	(96%)

Scheme 6

naphthol effectively to cap the ends of some of the systems containing chlorine groups *via* nucleophilic aromatic substitution reactions as described in Scheme 19. The oxidation of the sulfide compounds using 3-chloroperbenzoic acid led to the formation of their corresponding sulfones. This once again demonstrates the generality of our methodology since oxidation of the sulfide could take place in the synthesis of the diiron complexes (the buliding blocks for these systems) or at a later stage after the synthesis of the polymeric materials. In Scheme 20, the oxidation of compounds **37** or **39** led to the formation of **72** or **73**. These compounds also could have been prepared from the reaction of **19** or **21** with **23**.

Conclusion

This is the first study where the number of Fe^+(cp) moieties pendant to the backbone of the polyaromatic materials could be controlled. We have also demonstrated the possibility of preparing cationic Fe^+(cp) arene complexes where the number of the metallic moieties varies from two to thirty-five.

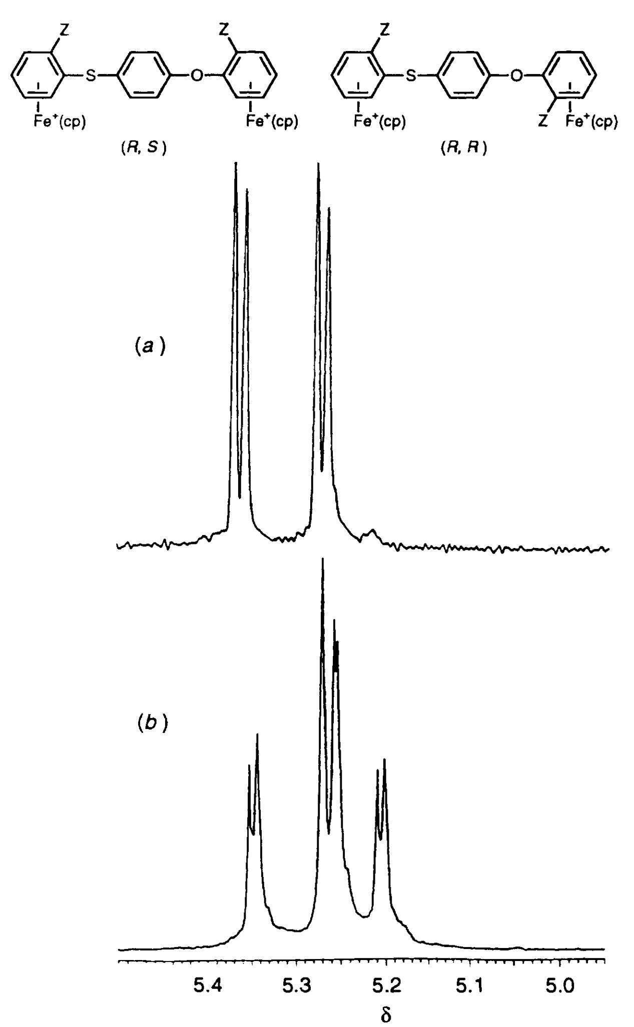
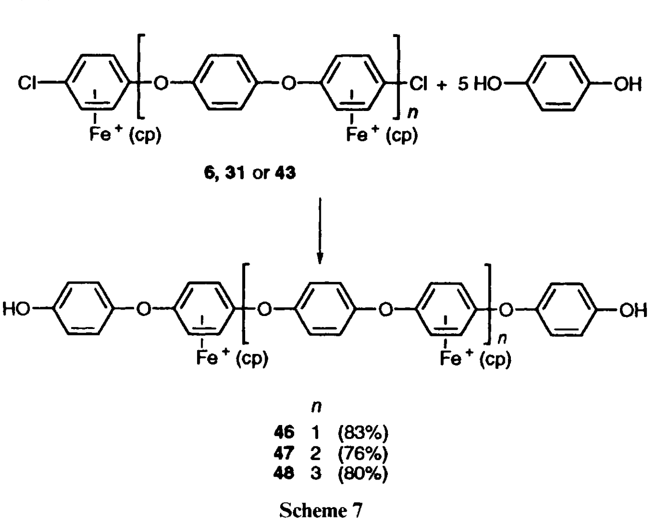


Fig. 2 (*a*) ^{1}H NMR (200 MHz, CD_3COCD_3) of the cp region of complex 7; Z = Cl and (*b*) 35; Z = (η^6-C_6H_5)(*p*-OC_6H_4O)(η^5-C_5H_5)Fe^+



Scheme 7

The efficiency of our methodological approach enabled both the size and nature of the backbone linkage of these polymetallic materials to be controlled. The ease with which these polymetallic systems may be functionalized has distinct advantages over previously reported methods. Other methods which utilize metal moieties often suffer from the high cost of Ru^+(cp), toxicity, and the difficulty in preparing some of the dichloroarene complexes.[44,60] Our approach involves both the preparation of odd- and even-numbered metal-moiety systems, which are built in successive reactions utilizing the very mild reaction conditions outlined. Once again the iron system has proved to be successful in providing the most general, least expensive, and least toxic route to the synthesis of this class of compounds.

We are now investigating the preparation of polymetallic ethers and thioethers as well as co-polymers with larger molecular weights, together with the synthesis and characterization of a number of poly-(ether ketones), -(ether sulfones), -(ether sulfides), -(sulfide sulfones), and -amines. Electrochemical studies of these systems are also currently underway.

Experimental

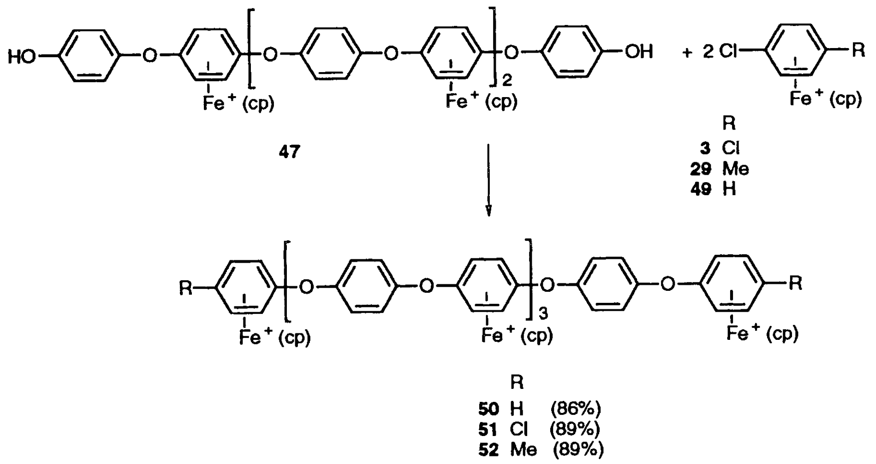
General Methods.—Proton and ^{13}C NMR spectra were recorded at 200 and 50 MHz, respectively, on a Gemini 200 NMR spectrometer, with chemical shifts calculated from the solvent signals; coupling constants were calculated in Hz. Infrared spectra were recorded on a Perkin-Elmer Model 781 spectrophotometer. Elemental analyses were performed at the University of Saskatchewan and Guelph Chemical Laboratories Ltd.

Starting Materials.—The starting complexes **1–3**, **29** and **49** were prepared according to previously reported ligand exchange reactions.[82,83] The bimetallic complexes **4–18** were also prepared according to previous methods.[69–72] Anhydrous aluminium chloride, aluminum powder, ferrocene, ammonium hexafluorophosphate, 3-chloroperbenzoic acid, chloroarenes, and the sulfur- and oxygen-containing nucleophiles are commercially available and were used without further purification. All solvents (reagent grade) were used without purification, with the exception of tetrahydrofuran (thf), which was distilled over sodium metal under nitrogen.

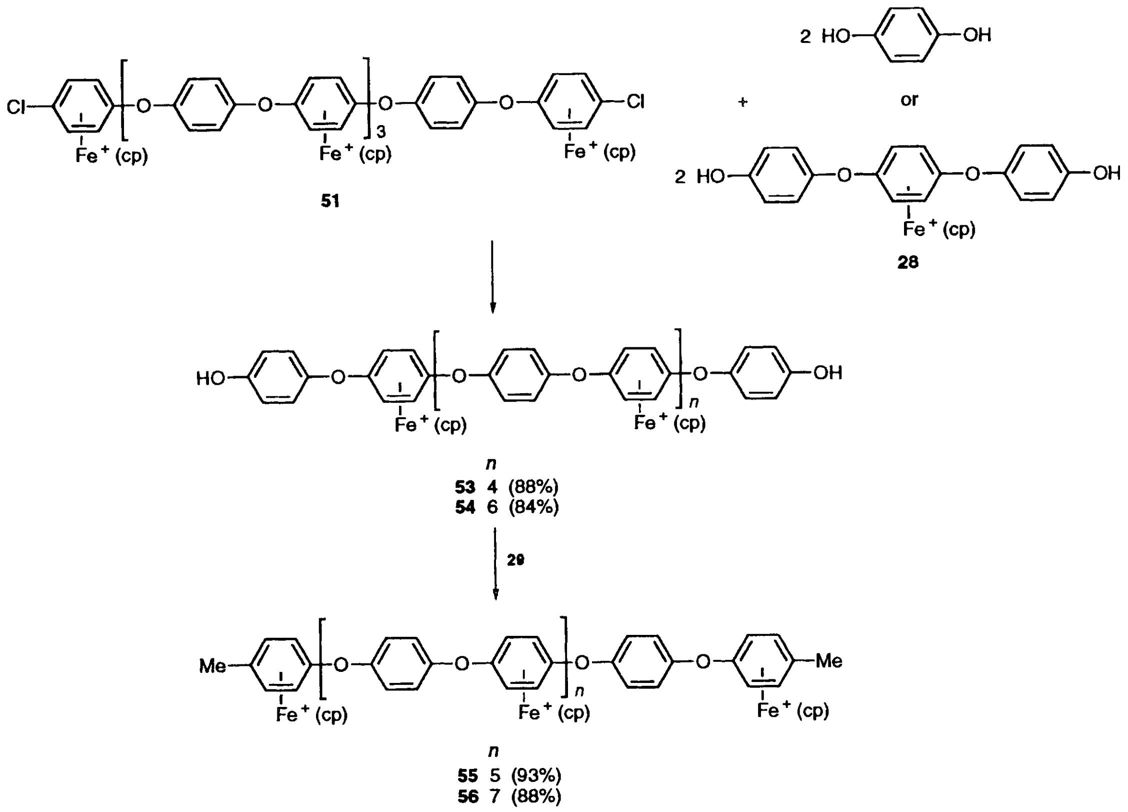
Nucleophilic Substitution Reactions.—Complexes **13–15** were prepared according to our previously reported methods.[69–72] Typically, the appropriate (η^6-arene)(η^5-cyclopentadienyl)iron hexafluorophosphate complex (1.0 mmol) was combined with the dinucleophile (0.5 mmol) in a 50 cm^3 round-bottom flask containing K_2CO_3 (2.5 mmol, 0.345 g) and dmf (10 cm^3). The resulting green–gold solution was stirred under a nitrogen atmosphere for 16 h at room temperature, while it changed to yellow–brown. A standard work-up procedure was followed, in which the reaction mixture was filtered through a sintered glass crucible into a 10% (v/v) HCl solution, causing the formation of a granular precipitate. Acetone washings were added to the filtrate, causing dissolution of the product. This solution was then concentrated by evaporation of the acetone under reduced pressure, and the desired diiron complex precipitated as a yellow granular solid upon the addition of a concentrated aqueous solution of NH_4PF_6. At this point, the product was recovered by filtration and washed with several portions of cold distilled water. After drying for several hours under vacuum, the product was washed with small amounts of diethyl ether and further dried. The resulting products (yellow powders) did not require additional purification.

Complex **13** (Found: C, 38.6; H, 3.70. $C_{30}H_{34}Cl_2F_{12}Fe_2P_2S_2$ requires C, 38.7; H, 3.68%). δ_H[$(CD_3)_2CO$]: 1.29–1.44 (8 H, m, δ, γ-CH_2), 1.65–1.80 (4 H, m, β-CH_2), 3.26 (4 H, t, *J* = 7.4, α-CH_2), 5.27 (10 H, s, cp), 6.61 (4 H, d, *J* = 6.8, complexed aryl H), 6.83 (4 H, d, *J* = 7.0 Hz, complexed aryl H). δ_C-[$(CD_3)_2CO$]: 29.09 (2 C, δ-CH_2), 29.50 (2 C, γ-CH_2), 32.54 (2 C, β-CH_2), 38.95 (2 C, α-CH_2), 81.25 (10 C, cp), 84.64 (4 C, complexed aryl C), 88.44 (4 C, complexed aryl C), 105.97 (2 C, complexed aryl C^q), 108.60 (2 C, complexed aryl C^q).

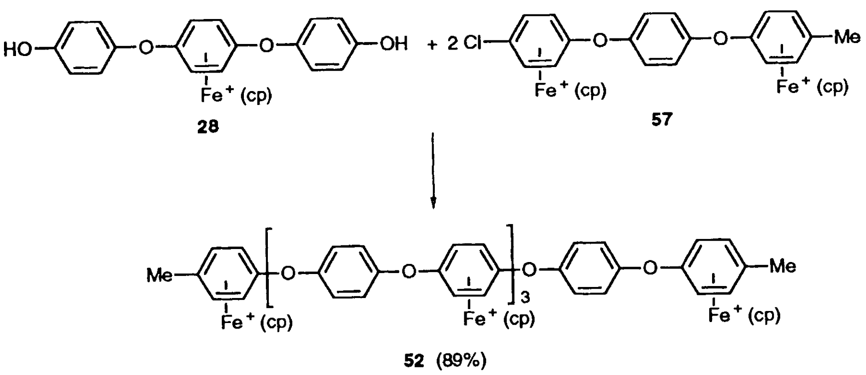
Complex **14** (Found: C, 42.2; H, 2.70. $C_{32}H_{24}Cl_2F_{12}Fe_2O_2P_2$ requires C, 42.1; H, 2.65%). δ_H([$^2H_6$]dmso): 5.32 (10 H, s, cp), 6.55 (4 H, d, *J* 6.7, complexed aryl H), 6.85 (4 H, d, *J* 6.8,



Scheme 8



Scheme 9



Scheme 10

complexed aryl H), 7.59 (2 H, d, *J* 7.3, uncomplexed aryl H), 7.70 (2 H, t, *J* 7.8, uncomplexed aryl H), 7.97 (2 H, d, *J* 8.4, uncomplexed aryl H). δ_C([$^2H_6$]dmso): 76.95 (4 C, complexed aryl C), 79.54 (10 C, cp), 86.75 (4 C, aryl C), 103.87 (2 C, complexed aryl quaternary C, C^q), 117.46 (2 C, uncomplexed aryl C^q), 119.25 (2 C, uncomplexed aryl C), 127.23 (2 C, complexed aryl C^q), 127.56 (2 C, uncomplexed aryl C^q), 131.90 (2 C, uncomplexed aryl C^q), 149.45 (2 C, uncomplexed aryl C^q).

Complex **15** (Found: C, 43.6; H, 2.80. $C_{35}H_{26}Cl_2F_{12}Fe_2O_3P_2$ requires C, 43.5; H, 2.70%). δ_H([$^2H_6$]dmso): 5.30 (10 H, s, cp), 6.52 (1 H, s, complexed aryl H), 6.59 (3 H, d, *J* 6.2, complexed aryl H), 6.85 (2 H, d, *J* 6.5, complexed aryl H), 7.48 (4 H, d, *J* 8.1, uncomplexed aryl H), 7.92 (4 H, d, *J* 8.4, uncomplexed aryl H). δ_C([$^2H_6$]dmso): 77.23 (4 C, complexed aryl C), 79.28 (10 C, cp), 86.62 (4 C, complexed aryl C), 103.78 (2 C, complexed aryl C^q), 119.93 (4 C, uncomplexed aryl C), 130.47 (2 C, complexed aryl C^q), 132.17 (4 C, uncomplexed aryl C), 134.18 (2 C, uncomplexed aryl C^q), 156.53 (2 C, uncomplexed aryl C^q), 193.08 (CO).

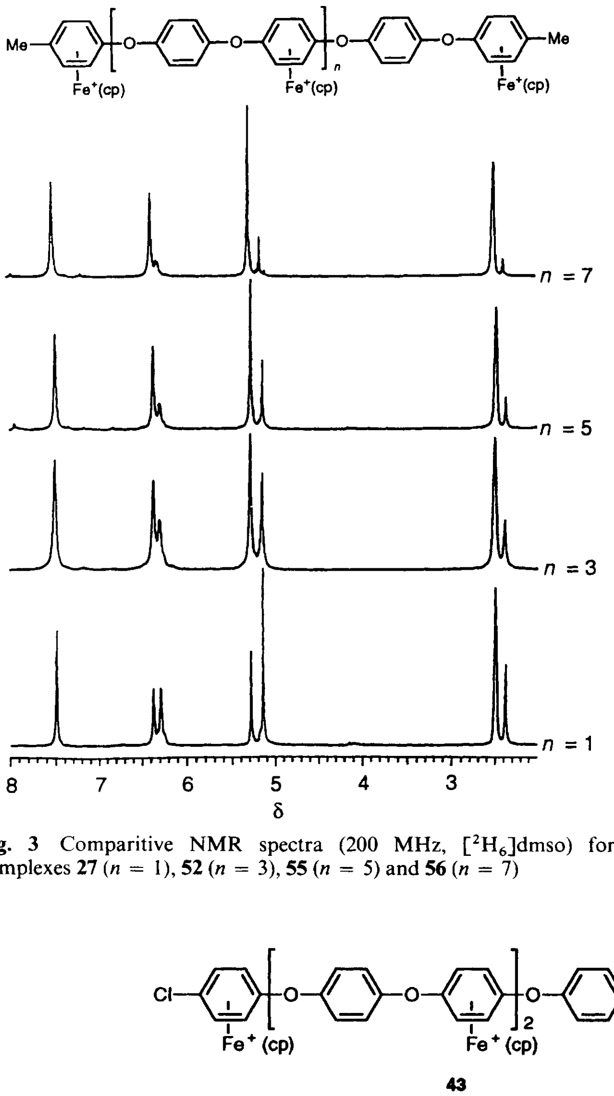


Fig. 3 Comparitive NMR spectra (200 MHz, [$^2H_6$]dmso) for complexes **27** (*n* = 1), **52** (*n* = 3), **55** (*n* = 5) and **56** (*n* = 7)

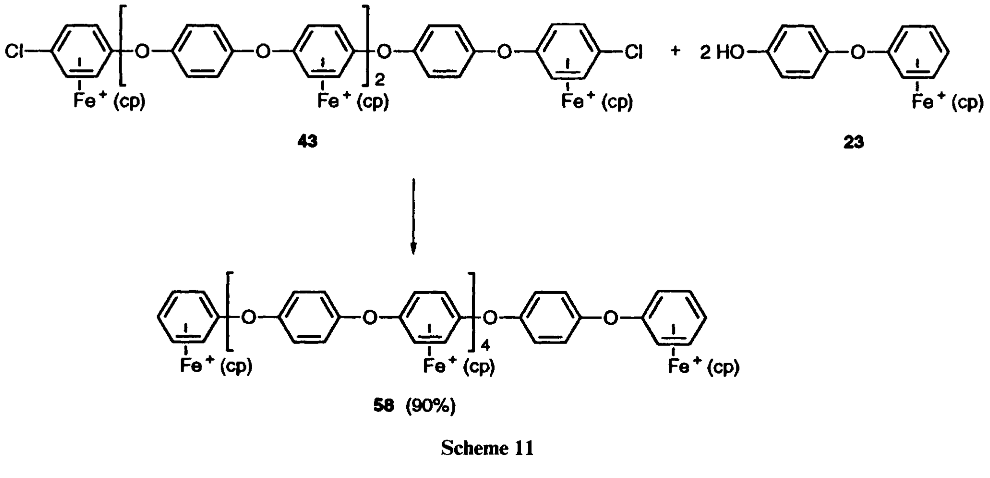
Synthesis of the Polymetallic Complexes **25–27**, **30–45**, **50–56** *and* **58–67**.—These complexes were prepared by utilizing either a 1 : 2 or 2 : 1 molar ratio of starting complex to nucleophile, an excess of base (K_2CO_3), and dmf as solvent. After stirring magnetically under a nitrogen atmosphere for 16 h, the desired polymetallic complexes were isolated in the same manner as complexes **4–15**.

Complex **25** (Found: C, 43.6; H, 3.10. $C_{45}H_{37}F_{18}Fe_3O_4P_3$ requires C, 43.4; H, 3.00%). δ_H[$(CD_3)_2CO$]: 5.26 (10 H, s, cp), 5.31 (5 H, s, cp), 6.19–6.21 (2 H, m, complexed aryl H), 6.31–6.46 (2 H, m, complexed aryl H), 6.44 (8 H, br s, complexed aryl H), 6.53–6.55 (2 H, m, complexed aryl H), 7.58 (4 H, d, *J* 9.2, uncomplexed aryl H), 7.65 (4 H, d, *J* 9.4 Hz, uncomplexed aryl H). δ_C[$(CD_3)_2CO$]: 77.68 (4 C, complexed aryl C), 78.14 (10 C, cp), 78.60 (2 C, complexed aryl C), 78.95 (10 C, cp), 84.28 (2 C, complexed aryl C), 85.89 (2 C, complexed aryl C), 87.85 (4 C, complexed aryl C), 123.46 (4 C, uncomplexed aryl C), 124.34 (4 C, uncomplexed aryl C), 124.49 (2 C, complexed aryl C^q), 134.68 (2 C, uncomplexed aryl C^q), 151.53 (2 C, uncomplexed aryl C^q), 153.00 (2 C, uncomplexed aryl C^q).

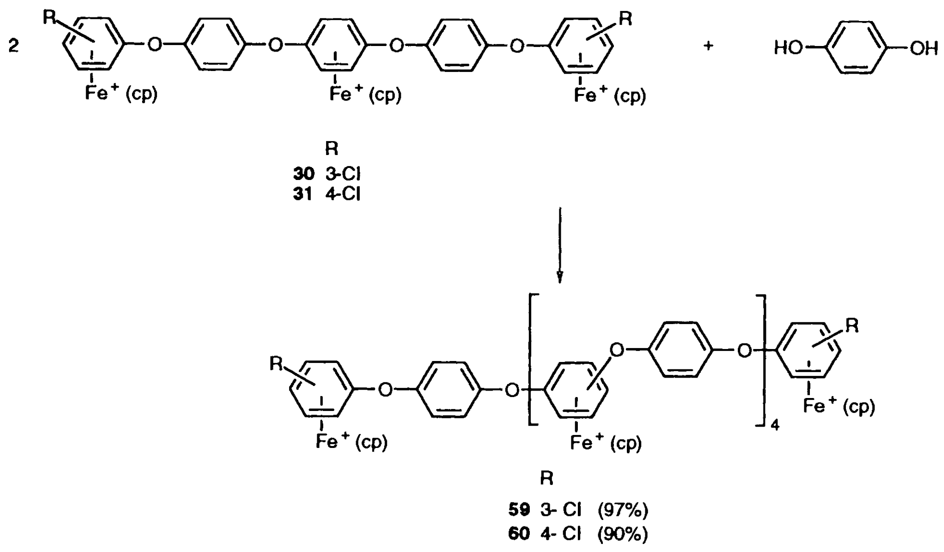
Complex **26** (Found: C, 43.3; H, 2.95. $C_{45}H_{37}F_{18}Fe_3O_4P_3$ requires C, 43.4; H, 3.00%). δ_H[$(CD_3)_2CO$]: 5.26 (10 H, s, cp), 5.35 (5 H, s, cp), 6.35–6.46 (14 H, m, complexed aryl H), 7.60 (8 H, s, uncomplexed aryl H). δ_C[$(CD_3)_2CO$]: 75.43 (2 C, complexed aryl C), 77.44 (2 C, complexed aryl C), 78.09 (10 C, cp), 78.97 (5 C, cp), 85.84 (2 C, complexed aryl C), 87.79 (8 C, complexed aryl C), 124.46 (4 C, uncomplexed aryl C), 124.49 (4 C, uncomplexed aryl C), 132.32 (2 C, complexed aryl C^q), 134.76 (2 C, complexed aryl C^q), 151.75 (2 C, uncomplexed aryl C^q), 152.21 (2 C, uncomplexed aryl C^q).

Complex **27** (Found: C, 44.5; H, 3.15. $C_{47}H_{41}F_{18}Fe_3O_4P_3$ requires C, 44.4; H, 3.25%). δ_H([$^2H_6$]dmso): 2.38 (6 H, s, Me), 5.14 (10 H, s, cp), 5.28 (5 H, s, cp), 6.28 (8 H, br s, complexed aryl H), 6.37 (4 H, br s, complexed aryl C), 7.49 (8 H, s, uncomplexed aryl H). δ_C[$(CD_3)_2CO$]: 19.92 (2 C, Me), 75.45 (4 C, complexed aryl C), 76.74 (4 C, complexed aryl C), 78.51 (5 C, cp), 78.96 (10 C, cp), 87.80 (4 C, complexed aryl C), 101.54 (2 C, complexed aryl C^q), 124.33 (4 C, uncomplexed aryl C), 124.43 (4 C, uncomplexed aryl C), 132.24 (2 C, complexed aryl C^q), 133.67 (2 C, complexed aryl C^q), 151.92 (2 C, uncomplexed aryl C^q), 152.08 (2 C, uncomplexed aryl C^q).

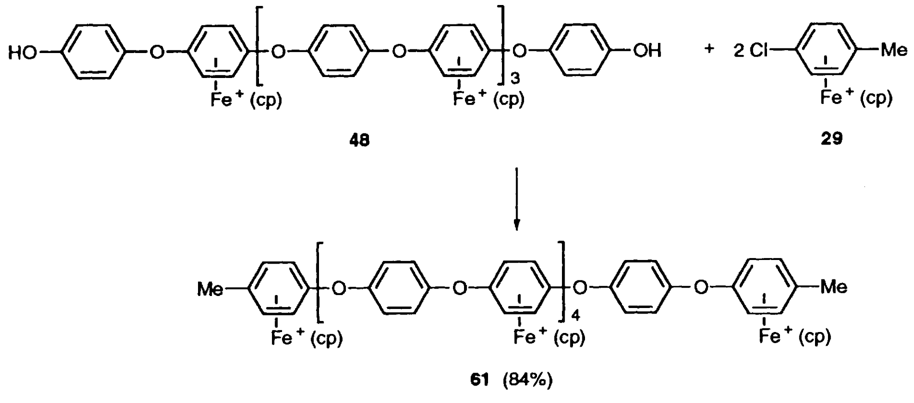
Complex **30** (Found: C, 41.35; H, 2.65. $C_{45}H_{35}Cl_2F_{18}Fe_3O_4P_3$ requires C, 41.2; H, 2.70%). δ_H[$(CD_3)_2CO$]: 5.34 (5 H, s, cp), 5.37 (10 H, s, cp), 6.34 (2 H, d, *J* 6.8, complexed aryl H), 6.39 (4 H, br s, complexed aryl H), 6.52 (2 H, t, *J* 6.6, complexed aryl H), 6.70 (2 H, d, *J* 6.0, complexed aryl H), 6.98 (2 H, br s, complexed aryl H), 7.56 (4 H, d, *J* 9.3,



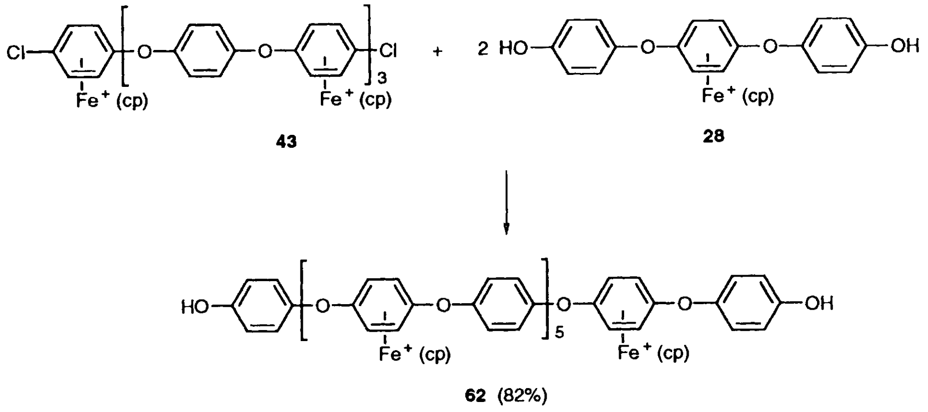
Scheme 11



Scheme 12



Scheme 13



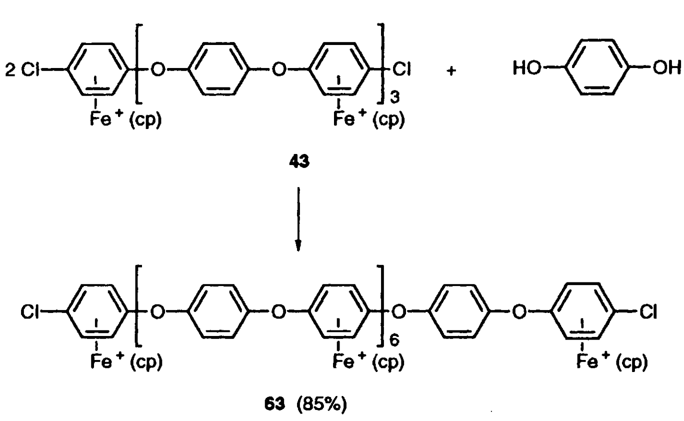
Scheme 14

uncomplexed aryl H), 7.63 (4 H, d, *J* 9.1 Hz, uncomplexed aryl H). δ_C[$(CD_3)_2CO$]: 75.67 (4 C complexed aryl C), 76.10 (2 C, complexed aryl C), 78.95 (5 C, cp), 80.37 (10 C, cp), 86.34 (2 C, complexed aryl C), 86.76 (4 C, complexed aryl C), 107.19 (2 C, complexed aryl C^q), 124.17 (4 C, uncomplexed aryl C), 124.24 (4 C, uncomplexed aryl C), 131.96 (2 C, complexed aryl C^q), 134.33 (2 C, complexed aryl C^q), 151.52 (2 C, uncomplexed aryl C^q), 152.45 (2 C, uncomplexed aryl C^q).

Complex **31** (Found: C, 41.3; H, 2.70. $C_{45}H_{35}Cl_2F_{18}Fe_3O_4P_3$ requires C, 41.2; H, 2.70%). δ_H[$(CD_3)_2CO$]: 5.34 (5 H, s, cp), 5.39 (10 H, s, cp), 6.38 (4 H, s, complexed aryl H), 6.52 (4 H, d, *J* 6.6, complexed aryl H), 6.78 (4 H, d, *J* 6.6 Hz, complexed aryl H), 7.60 (br s, 8 H, uncomplexed aryl C). δ_C[$(CD_3)_2CO$]: 75.45 (4 C, complexed aryl C), 76.95 (5 C, cp), 79.01 (4 C, complexed aryl C), 80.55 (10 C, cp), 87.83 (4 C, complexed aryl C), 105.00 (2 C, complexed aryl C^q), 124.50 (4 C, uncomplexed aryl C), 124.54 (4 C, uncomplexed aryl C), 132.25 (2 C, complexed aryl C^q), 134.12 (2 C, complexed aryl C^q), 151.66 (2 C, uncomplexed aryl C^q), 152.37 (2 C, uncomplexed aryl C^q).

Complex **32** (Found: C, 43.8; H, 2.90. $C_{62}H_{50}F_{24}Fe_4O_6P_4$ requires C, 43.95; H, 2.95%). δ_H[$(CD_3)_2CO$]: 5.26 (10 H, s, cp), 5.30 (10 H, s, cp), 6.20 (2 H, s, complexed aryl H), 6.31 (2 H, s, complexed aryl H), 6.45 (10 H, br s, complexed aryl H), 6.53 (4 H, br s, complexed aryl H), 7.60–7.67 (12 H, m, uncomplexed aryl H). δ_C([$^2H_6$]dmso): 76.65 (4 C, complexed aryl C), 76.95 (10 C, cp), 77.83 (10 C, cp), 79.06 (2 C, complexed aryl C), 83.35 (2 C, complexed aryl C), 84.91 (2 C, complexed aryl C), 86.70 (4 C, complexed aryl C), 122.05 (8 C, uncomplexed aryl C), 122.75 (2 C, complexed aryl C^q), 123.08 (4 C, uncomplexed aryl C), 132.70 (2 C, complexed aryl C^q), 150.22 (2 C, complexed aryl C^q), 151.35 (2 C, uncomplexed aryl C^q), 151.69 (4 C, uncomplexed aryl C^q).

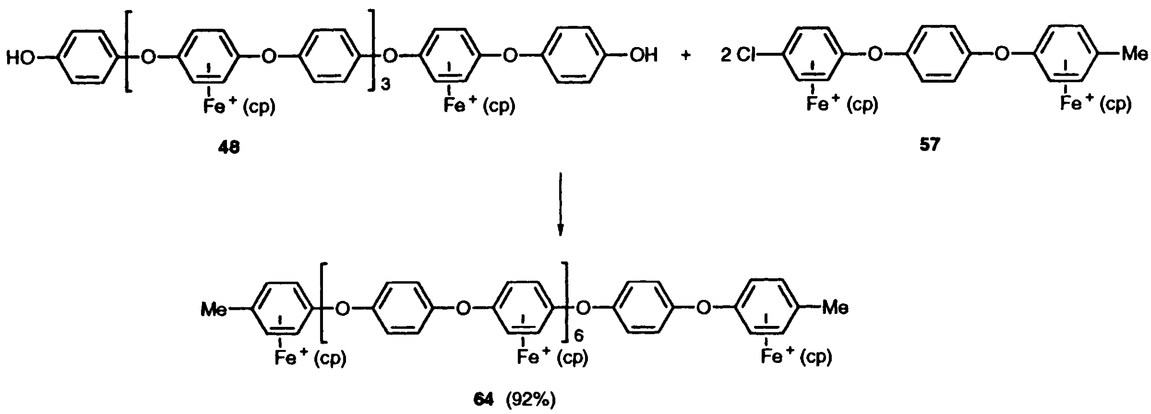
Complex **33** (Found: C, 44.0; H, 3.00. $C_{62}H_{50}F_{24}Fe_4O_6P_4$ requires C, 43.95; H, 3.00%). δ_H[$(CD_3)_2CO$]: 5.26 (10 H, s, cp), 5.31 (10 H, s, cp), 6.28–6.35 (8 H, m, complexed aryl H), 6.45 (8 H, br s, complexed aryl H), 6.66 (2 H, s, complexed aryl H), 7.59 (12 H, br s, uncomplexed aryl C). δ_C[$(CD_3)_2CO$]: 68.92 (2 C, complexed aryl C), 74.32 (2 C, complexed aryl C), 74.45 (2 C, complexed aryl C), 77.61 (2 C, complexed aryl C), 78.06 (10 C, cp), 78.68 (10 C, cp), 85.77 (4 C, complexed aryl C), 87.71 (4 C, complexed aryl C), 124.00 (4 C, uncomplexed aryl C), 124.07 (4 C, uncomplexed aryl C), 124.27 (4 C, uncomplexed aryl C), 133.85 (2 C, complexed aryl C^q), 133.93 (2 C, complexed aryl C^q), 134.43 (2 C, complexed aryl C^q), 151.73 (2 C, uncomplexed aryl C^q), 152.04 (2 C, uncomplexed aryl C^q), 152.09 (2 C, uncomplexed aryl C^q).



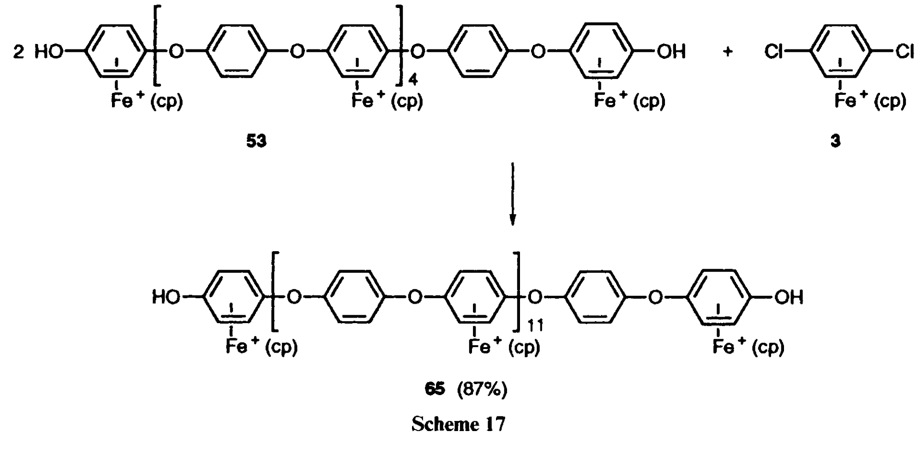
Scheme 15

Complex **34** (Found: C, 43.8; H, 2.80. $C_{62}H_{50}F_{24}Fe_4O_6P_4$ requires C, 43.95; H, 2.95%). δ_H[$(CD_3)_2CO$]: 5.26 (10 H, s, cp), 5.35 (10 H, s, cp), 6.37 (br s, 10 H, complexed aryl H), 6.43 (8 H, br s, complexed aryl H), 7.59 (12 H, s, uncomplexed aryl H). δ_C[$(CD_3)_2CO$]: 75.37 (2 C, complexed aryl C), 75.56 (4 C, complexed aryl C), 77.50 (4 C, complexed aryl C), 78.08 (10 C, cp), 78.98 (10 C, cp), 85.83 (4 C, complexed aryl C), 87.79 (4 C, complexed aryl C), 124.26 (4 C, uncomplexed aryl C), 124.46 (4 C, uncomplexed aryl C), 124.50 (4 C, uncomplexed aryl C), 132.16 (2 C, complexed aryl C^q), 132.32 (2 C, complexed aryl C^q), 134.69 (2 C, complexed aryl C^q), 151.70 (2 C, uncomplexed aryl C^q), 152.12 (2 C, uncomplexed aryl C^q), 152.25 (2 C, uncomplexed aryl C^q).

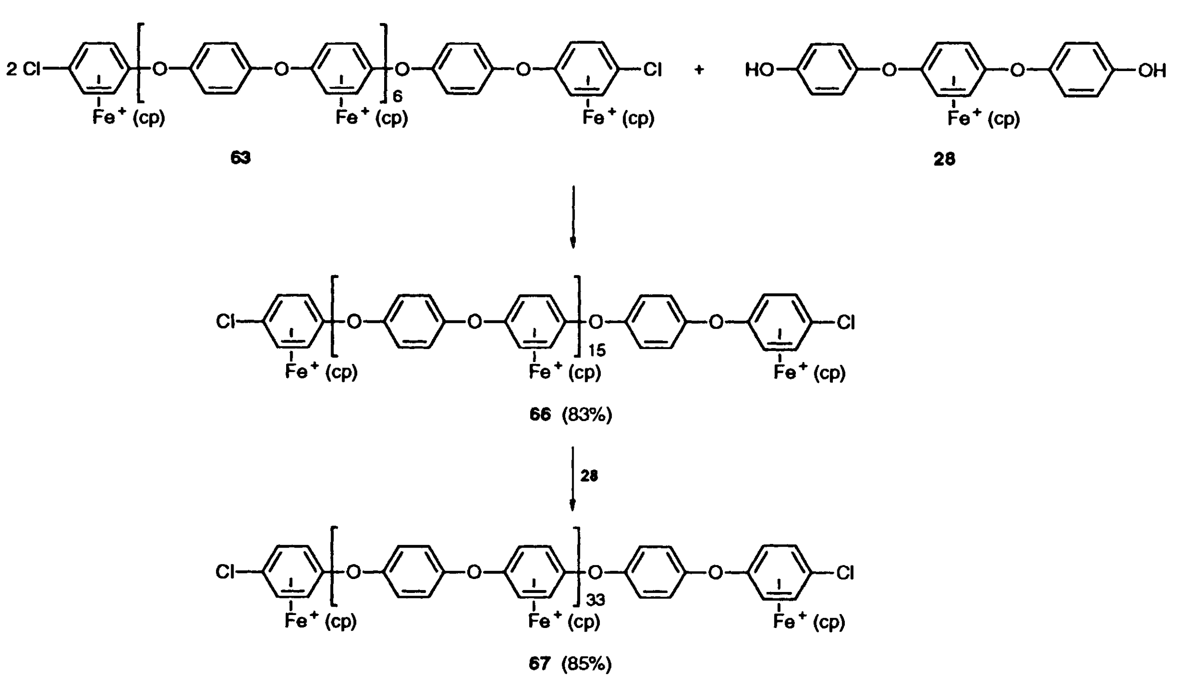
Complex **35** (Found: C, 43.6; H, 3.00. $C_{62}H_{50}F_{24}Fe_4O_5P_4S$ requires C, 43.5; H, 2.95%). δ_H[$(CD_3)_2CO$]: 5.20, 5.21 (5 H, 2 s, cp), 5.26 (5 H, s, cp), 5.27 (5 H, s, cp), 5.34, 5.35 (5 H, s, cp), 6.13–6.34 (8 H, m, complexed aryl H), 6.46 (8 H, t, *J* 3.8, complexed aryl C), 6.56 (1 H, d, *J* 6.1, complexed aryl H), 6.70–6.73 (1 H, m, complexed aryl H), 7.56–7.69 (10 H, m, uncomplexed aryl H), 8.00 (2 H, d, *J* 8.4 Hz, uncomplexed aryl H). δ_C[$(CD_3)_2CO$]: 76.93 (1 C, complexed aryl C), 77.32 (1 C, complexed aryl C), 77.56 (4 C, complexed aryl C), 78.03 (10 C, cp), 78.27 (1 C, complexed aryl C), 79.13 (5 C, cp), 79.38 (5 C, cp), 80.59 (1 C, complexed aryl C), 84.49 (1 C, complexed aryl C), 84.87 (1 C, complexed aryl C), 84.98 (1 C, complexed aryl C), 85.16 (1 C, complexed aryl C), 85.77 (2 C, complexed aryl C), 87.73 (4 C, complexed aryl C), 121.84 (1 C, uncomplexed aryl C), 123.58 (2 C, uncomplexed aryl C), 123.98



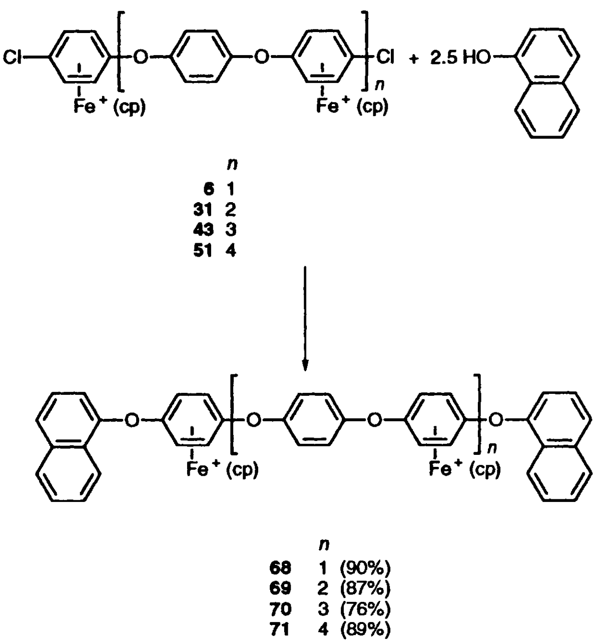
Scheme 16



Scheme 17



Scheme 18



Scheme 19

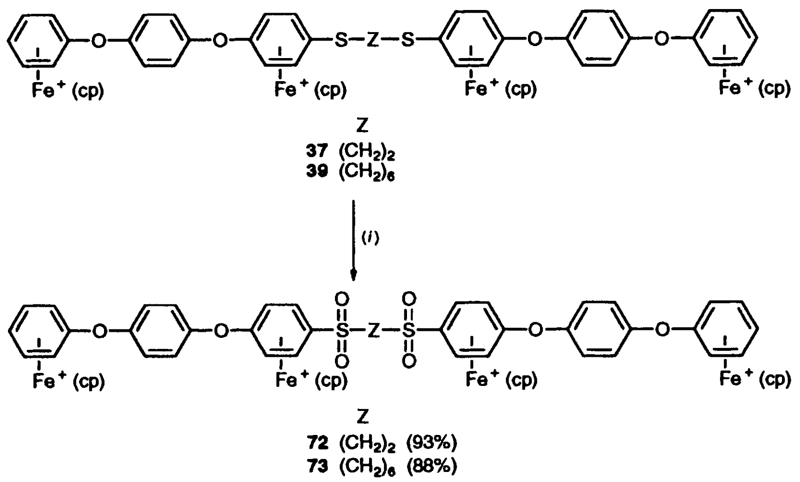
(2 C, uncomplexed aryl C), 124.29 (2 C, uncomplexed aryl C), 124.38 (2 C, uncomplexed aryl C), 126.01 (2 C, complexed aryl C^q), 129.08 (2 C, complexed aryl C^q), 134.55 (2 C, complexed aryl C^q), 144.38 (2 C, complexed aryl C^q), 151.41, 151.64, 152.02, 152.34, 157.97 (6 C, uncomplexed aryl C^q).

Complex **36** (Found: C, 43.7; H, 2.90. $C_{62}H_{50}F_{24}Fe_4O_5P_4S$ requires C, 43.5; H, 2.95%). $\delta_H[(CD_3)_2CO]$: 5.24 (10 H, s, cp), 5.27 (5 H, s, cp), 5.35 (5 H, s, cp), 6.32 (2 H, br s, complexed aryl H), 6.44 (16 H, br s, complexed aryl H), 7.59 (10 H, br s, uncomplexed aryl H), 7.94 (2 H, br s, uncomplexed aryl H). $\delta_C[(CD_3)_2CO]$: 75.79 (2 C, complexed aryl C), 76.59 (2 C, complexed aryl C), 76.81 (2 C, complexed aryl C), 77.49 (4 C, complexed aryl C), 78.11 (10 C, cp), 79.23 (5 C, cp), 79.80 (5 C, cp), 83.75 (2 C, complexed aryl C), 85.79 (2 C, complexed aryl C), 87.77 (4 C, complexed aryl C), 107.73 (1 C, complexed aryl C^q), 123.37 (1 C, uncomplexed aryl C), 124.25 (2 C, uncomplexed aryl C), 124.44 (4 C, uncomplexed aryl C), 124.53 (4 C, uncomplexed aryl C), 126.10 (1 C, complexed aryl C^q), 130.80 (1 C, complexed aryl C^q), 132.26 (1 C, uncomplexed aryl C^q), 133.43 (1 C, complexed aryl C^q), 134.54 (2 C, complexed aryl C^q), 139.14 (1 C, uncomplexed aryl C), 151.57, 151.65, 152.10, 156.80 (5 C, uncomplexed aryl C).

Complex **37** (Found: C, 41.4; H, 3.00. $C_{58}H_{50}F_{24}Fe_4O_4P_4S_2$ requires C, 41.5; H, 3.00%). $\delta_H[(CD_3)_2CO]$: 3.61 (4 H, s, CH_2), 5.25 (20 H, br s, cp), 6.31–6.54 (18 H, m, complexed aryl H), 7.57 (8 H, br s, uncomplexed aryl H). $\delta_C[(CD_3)_2CO]$: 33.46 (2 C, CH_2), 76.88 (4 C, complexed aryl C), 77.45 (4 C, complexed aryl C), 78.02 (10 C, cp), 79.68 (10 C, cp), 85.71 (2 C, complexed aryl C), 86.19 (4 C, complexed aryl C), 87.67 (4 C, complexed aryl C), 103.88 (2 C, complexed aryl C^q), 124.24 (4 C, uncomplexed aryl C), 124.37 (4 C, uncomplexed aryl C), 133.46 (2 C, complexed aryl C^q), 134.47 (2 C, complexed aryl C^q), 151.61 (2 C, uncomplexed aryl C^q), 151.68 (2 C, uncomplexed aryl C^q).

Complex **38** (Found: C, 42.4; H, 3.20. $C_{60}H_{54}F_{24}Fe_4O_5P_4S$ requires C, 42.2; H, 3.20%). $\delta_H[(CD_3)_2CO]$: 2.01–2.03 (4 H, m, β-CH_2), 3.61 (4 H, m, α-CH_2), 5.23 (10 H, s, cp), 5.26 (10 H, s, cp), 6.44–6.48 (18 H, m, complexed aryl H), 7.58 (8 H, br s, uncomplexed aryl H). $\delta_C[(CD_3)_2CO]$: 29.02 (2 C, β-CH_2), 32.34 (2 C, α-CH_2), 76.49 (4 C, complexed aryl C), 77.40 (4 C, complexed aryl C), 77.98 (10 C, cp), 79.56 (10 C, cp), 84.02 (4 C, complexed aryl C), 85.67 (2 C, complexed aryl C), 87.63 (4 C, complexed aryl C), 106.63 (2 C, complexed aryl C^q), 124.22 (4 C, uncomplexed aryl C), 124.33 (4 C, uncomplexed aryl C), 133.04 (2 C, complexed aryl C^q), 134.47 (2 C, complexed aryl C^q), 151.57 (2 C, uncomplexed aryl C^q), 151.73 (2 C, uncomplexed aryl C^q).

Complex **39** (Found: C, 43.1; H, 3.30. $C_{62}H_{58}F_{24}Fe_4O_4P_4S_2$ requires C, 42.9; H, 3.35%). $\delta_H[(CD_3)_2CO]$: 1.59 (4 H, m, γ-CH_2), 1.81 (4 H, m, β-CH_2), 3.25 (4 H, t, *J* 7.3 Hz, α-CH_2), 5.22 (10 H, s, cp), 5.26 (10 H, s, cp), 6.31–6.52 (18 H, m, complexed aryl H), 7.58 (8 H, br s, uncomplexed aryl H). $\delta_C[(CD_3)_2CO]$: 28.78 (2 C, γ-CH_2), 29.04 (2 C, β-CH_2), 32.95 (2 C, α-CH_2), 76.61 (4 C, complexed aryl C), 77.58 (10 C, cp), 78.11 (4 C, complexed aryl C), 79.66 (10 C, cp), 83.95 (4 C, complexed aryl C), 85.85 (2 C, complexed aryl C), 87.81 (4 C, complexed aryl



Scheme 20 (i) 3-chloroperbenzoic acid, CH$_2$Cl$_2$, dmf

C), 107.34 (2 C, complexed aryl C^q), 124.34 (4 C, uncomplexed aryl C), 124.46 (4 C, uncomplexed aryl C), 133.18 (2 C, complexed aryl C^q), 134.69 (2 C, complexed aryl C^q), 151.79 (2 C, uncomplexed aryl C^q), 151.95 (2 C, uncomplexed aryl C^q).

Complex **40** (Found: C, 42.9; H, 3.70. $C_{66}H_{64}F_{24}Fe_4O_8P_4S_2$ requires C, 42.7; H, 3.60%). $\delta_H[(CD_3)_2CO]$: 1.28–1.39 (4 H, m, δ-CH$_2$), 1.40–1.44 (4 H, m, γ-CH$_2$), 1.72–1.74 (4 H, m, β-CH$_2$), 2.52 (6 H, s, Me), 3.52 (4 H, t, *J* 7.8, α-CH$_2$), 5.22 (10 H, s, cp), 5.43 (10 H, s, cp), 6.33 (2 H, d, *J* 6.8 Hz, complexed aryl H), 6.42 (2 H, d, *J* 6.9, complexed aryl H), 6.69 (2 H, d, *J* 6.8, complexed aryl H), 6.92 (2 H, d, *J* 6.7 Hz, complexed aryl H), 7.60 (8 H, br s, uncomplexed aryl H). $\delta_C[(CD_3)_2CO]$: 19.88 (2 C, Me), 23.13 (2 C, δ-CH$_2$), 29.40 (2 C, γ-CH$_2$), 30.18 (2 C, β-CH$_2$), 55.94 (2 C, α-CH$_2$), 76.95 (4 C, complexed aryl C), 77.16 (4 C, complexed aryl C), 78.55 (10 C, cp), 80.32 (10 C, cp), 87.82 (2 C, complexed aryl C), 88.30 (4 C, complexed aryl C), 101.02 (2 C, complexed aryl C^q), 101.58 (2 C, complexed aryl C^q), 124.41 (4 C, uncomplexed aryl C), 124.49 (4 C, uncomplexed aryl C), 133.52 (2 C, complexed aryl C^q), 136.62 (2 C, complexed aryl C^q), 151.31 (2 C, uncomplexed aryl C^q), 152.37 (2 C, uncomplexed aryl C^q).

Complex **41** (Found: C, 45.2; H, 2.95. $C_{76}H_{51}F_{24}Fe_4O_6P_4$ requires C, 45.4; H, 3.00%). $\delta_H([^2H_6]dmso)$: 5.19 (10 H, s, cp), 5.33 (10 H, s, cp), 6.21 (2 H, br s, complexed aryl H), 6.36 (8 H, br s, complexed aryl H), 6.44 (8 H, br s, complexed aryl H), 7.53 (10 H, br s, uncomplexed aryl H), 7.68 (2 H, t, *J* 4.0, uncomplexed aryl H), 8.04 (2 H, d, *J* 7.5 Hz, uncomplexed aryl H). $\delta_C([^2H_6]dmso)$: 74.80 (2 C, complexed aryl C), 75.72 (2 C, complexed aryl C), 76.37 (2 C, complexed aryl C), 76.66 (10 C, cp), 77.90 (10 C, cp), 84.62 (2 C, complexed aryl C), 86.40 (2 C, complexed aryl C), 116.34 (2 C, naphthyl C), 118.63 (2 C, naphthyl C), 122.56 (4 C, uncomplexed aryl C), 122.58 (4 C, uncomplexed aryl C), 127.14 (2 C, naphthyl C), 126.90 (2 C, complexed aryl C^q), 129.57 (2 C, complexed aryl C^q), 130.17 (2 C, complexed aryl C^q), 132.44 (2 C, naphthyl C^q), 149.95 (2 C, naphthyl C^q), 150.18 (2 C, uncomplexed aryl C^q), 150.80 (2 C, uncomplexed aryl C^q).

Complex **42** (Found: C, 44.7; H, 3.20. $C_{64}H_{54}F_{24}Fe_4O_6P_4$ requires C, 44.6; H, 3.15%). $\delta_H[(CD_3)_2CO]$: 2.51 (6 H, s, Me), 5.22 (10 H, s, cp), 5.34 (10 H, s, cp), 6.35 (16 H, br s, complexed aryl H), 7.57 (12 H, m, uncomplexed aryl H). $\delta_C[(CD_3)_2CO]$: 19.91 (2 C, Me), 75.40 (4 C, complexed aryl C), 75.59 (4 C, complexed aryl C), 76.79 (4 C, complexed aryl C), 78.53 (10 C, cp), 78.99 (10 C, cp), 87.79 (4 C, complexed aryl C), 101.53 (2 C, complexed aryl C^q), 124.38 (4 C, uncomplexed aryl C), 124.39 (4 C, uncomplexed aryl C), 124.46 (4 C, uncomplexed aryl C), 132.12 (2 C, complexed aryl C^q), 132.29 (4 C, complexed aryl C^q), 133.61 (2 C, uncomplexed aryl C^q), 151.88 (2 C, uncomplexed aryl C^q), 152.15 (2 C, uncomplexed aryl C^q).

Complex **43** (Found: C, 42.4; H, 2.90. $C_{62}H_{48}Cl_2F_{24}Fe_4O_6P_4$ requires C, 42.2; H, 2.75%). $\delta_H[(CD_3)_2CO]$: 5.35 (10 H, s, cp), 5.39 (10 H, s, cp), 6.38 (8 H, br s, complexed aryl H), 6.57 (4 H, d, *J* 6.8, complexed aryl H), 6.78 (4 H, d, *J* 6.2 Hz, complexed aryl H), 7.60 (12 H, s, uncomplexed aryl H). $\delta_C[(CD_3)_2CO]$: 75.61 (4 C, complexed aryl C), 77.25 (8 C, complexed aryl C), 79.14 (10 C, cp), 80.63 (10 C, cp), 87.92 (4 C, complexed aryl C), 105.06 (2 C, complexed aryl C^q), 107.96 (2 C, complexed aryl C^q), 124.48 (4 C, uncomplexed aryl C), 124.49 (4 C, uncomplexed aryl C), 124.53 (4 C, uncomplexed aryl C), 132.14 (2 C, complexed aryl C^q), 151.68 (2 C, uncomplexed aryl C^q), 151.95 (2 C, uncomplexed aryl C^q).

Complex **44** (Found: C, 46.1; H, 3.00. $C_{84}H_{56}Cl_2F_{24}Fe_4O_5P_4S$ requires C, 45.4; H, 3.00%). $\delta_H([^2H_6]dmso)$: 5.22 (5 H, s, cp), 5.28 (5 H, s, cp), 5.29 (10 H, s, cp), 6.31–6.40 (8 H, m, complexed aryl H), 6.47 (4 H, d, *J* 6.9, complexed aryl H), 6.82 (4 H, d, *J* 6.9 Hz, complexed aryl H), 7.43–7.48 (10 H, m, uncomplexed aryl H), 7.80–7.89 (10 H, m, uncomplexed aryl H). $\delta_C[(CD_3)_2CO]$: 75.26 (2 C, complexed aryl C), 76.29 (4 C, complexed aryl C), 77.88 (4 C, complexed aryl C), 78.03 (5 C, cp), 78.59 (5 C, cp), 79.24 (10 C, cp), 84.57 (2 C, complexed aryl C), 86.66 (4 C, complexed aryl C), 103.56, 104.03 (3 C, complexed aryl C^q), 120.80 (2 C, uncomplexed aryl C), 121.11 (2 C, uncomplexed aryl C), 121.61 (1 C, complexed aryl C), 123.00, 126.06, 129.30 (3 C, complexed aryl C^q), 128.92 (4 C, uncomplexed aryl C^q), 131.51, 137.11 (5 C, uncomplexed aryl C^q), 136.69 (1 C, uncomplexed aryl C), 137.11, 152.61, 153.10 (5 C, uncomplexed aryl C^q).

Complex **45** (Found: C, 47.8; H, 3.00. $C_{88}H_{58}Cl_2F_{24}Fe_4O_6P_4$ requires C, 47.7; H, 2.95%). $\delta_H([^2H_6]dmso)$: 5.30 (10 H, s, cp), 5.31 (10 H, s, cp), 6.33–6.49 (12 H, m, complexed aryl H), 6.81 (4 H, d, *J* 6.3, complexed aryl H), 7.38–7.55 (10 H, m, uncomplexed aryl H), 7.72 (2 H, t, *J* 8.1, uncomplexed aryl H), 7.88 (8 H, d, *J* 8.4, uncomplexed aryl H), 8.05 (2 H, d, *J* 8.5 Hz, uncomplexed aryl H). $\delta_C([^2H_6]dmso)$: 75.05 (4 C, complexed aryl C), 76.87 (2 C, complexed aryl C), 76.11 (2 C, complexed aryl C), 77.71 (4 C, complexed aryl C), 77.92 (10 C, cp), 79.06 (10 C, cp), 86.48 (4 C, complexed aryl C), 103.37 (2 C, complexed aryl C^q), 116.28 (2 C, naphthyl C), 118.58 (2 C, naphthyl C), 120.69 (2 C, uncomplexed aryl C), 120.94 (2 C, uncomplexed aryl C), 126.88 (2 C, complexed aryl C^q), 127.15 (2 C, naphthyl C), 128.68 (4 C, uncomplexed aryl C), 129.94, 131.63 (4 C, complexed aryl C^q), 129.46, 136.59, 136.65, 149.99, 152.38, 152.92, 152.99 (12 C, uncomplexed aryl C^q).

Complex **50** (Found: C, 44.4; H, 2.80. $C_{79}H_{63}F_{30}Fe_5O_8P_5$ requires C, 44.25; H, 2.95%). $\delta_H[(CD_3)_2CO]$: 5.26 (10 H, s, cp), 5.34 (15 H, s, cp), 6.37 (12 H, br s, complexed aryl H), 6.43 (8 H, br s, complexed aryl H), 7.59 (16 H, s, uncomplexed aryl H). δ_C[(CD$_3$)$_2$CO]: 75.50 (12 C, complexed aryl C), 77.54 (4 C, complexed aryl C), 78.14 (15 C, cp), 79.04 (10 C, cp), 85.88 (2 C, complexed aryl C), 87.84 (4 C, complexed aryl C), 124.47 (8 C, uncomplexed aryl C), 124.58 (8 C, uncomplexed aryl C), 132.25, 134.74 (8 C, complexed aryl C$^\mathrm{q}$), 151.76 (4 C, uncomplexed aryl C$^\mathrm{q}$), 152.26 (4 C, uncomplexed aryl C$^\mathrm{q}$).

Complex **51** (Found: C, 43.0; H, 2.75. $\mathrm{C_{79}H_{61}Cl_2F_{30}Fe_5O_8P_5}$ requires C, 42.9; H, 2.80%). δ_H([^{2}H$_6$]dmso): 5.29 (25 H, br s, cp), 6.36 (16 H, br s, complexed aryl H), 6.46 (4 H, br s, complexed aryl H), 7.51 (16 H, br s, uncomplexed aryl H). δ_C([^{2}H$_6$]dmso): 74.98 (12 C, complexed aryl C), 76.22 (4 C, complexed aryl C), 77.98 (15 C, cp), 79.36 (10 C, cp), 86.71 (4 C, complexed aryl C), 103.73 (2 C, complexed aryl C$^\mathrm{q}$), 122.80 (12 C, uncomplexed aryl C), 122.85 (4 C, uncomplexed aryl C), 130.22 (6 C, complexed aryl C$^\mathrm{q}$), 132.08 (2 C, complexed aryl C$^\mathrm{q}$), 150.46 (2 C, uncomplexed aryl C$^\mathrm{q}$), 151.01 (4 C, uncomplexed aryl C$^\mathrm{q}$), 151.32 (2 C, uncomplexed aryl C$^\mathrm{q}$).

Complex **52** (Found: C, 44.9; H, 3.15. $\mathrm{C_{81}H_{67}F_{30}Fe_5O_8P_5}$ requires C, 44.8; H, 3.10%). δ_H([^{2}H$_6$]dmso): 2.39 (6 H, s, Me), 5.15 (10 H, s, cp), 5.28 (15 H, s, cp), 6.30 (8 H, s, complexed aryl H), 6.37 (12 H, s, complexed aryl H), 7.50 (16 H, s, uncomplexed aryl H). δ_C([^{2}H$_6$]dmso): 19.13 (2 C, Me), 74.85 (12 C, complexed aryl C), 75.85 (4 C, complexed aryl C), 77.27 (10 C, cp), 77.82 (15 C, cp), 86.53 (4 C, complexed aryl C), 100.26 (2 C, complexed aryl C$^\mathrm{q}$), 122.64 (12 C, uncomplexed aryl C), 122.85 (4 C, uncomplexed aryl C), 130.05 (6 C, complexed aryl C$^\mathrm{q}$), 131.42 (2 C, complexed aryl C$^\mathrm{q}$), 150.56 (2 C, uncomplexed aryl C$^\mathrm{q}$), 150.86 (6 C, uncomplexed aryl C$^\mathrm{q}$).

Complex **53** (Found: C, 46.4; H, 3.00. $\mathrm{C_{91}H_{71}F_{30}Fe_5O_{12}P_5}$ requires C, 46.3; H, 3.05%). δ_H([^{2}H$_6$]dmso): 5.22 (5 H, s, cp), 5.28 (20 H, br s, cp), 6.10–6.22 (4 H, m, complexed aryl H), 6.36 (16 H, br s, complexed aryl H), 6.90 (4 H, d, *J* 8.7, uncomplexed aryl H), 7.15 (4 H, d, *J* 8.3 Hz, uncomplexed aryl H), 7.50 (16 H, br s, uncomplexed aryl H), 9.74 (2 H, s, OH). δ_C([^{2}H$_6$]dmso): 73.02 (4 C, complexed aryl C), 74.36 (16 C, complexed aryl C), 77.28 (10 C, cp), 77.38 (15 C, cp), 116.25 (4 C, uncomplexed aryl C), 121.49 (4 C, uncomplexed aryl C), 122.25 (16 C, uncomplexed aryl C), 129.69 (2 C, complexed aryl C$^\mathrm{q}$), 130.15 (6 C, complexed aryl C$^\mathrm{q}$), 132.01 (2 C, complexed aryl C$^\mathrm{q}$), 144.66 (2 C, uncomplexed aryl C$^\mathrm{q}$), 150.90 (8 C, uncomplexed aryl C$^\mathrm{q}$), 155.64 (2 C, uncomplexed aryl C$^\mathrm{q}$).

Complex **54** (Found: C, 46.1; H, 3.10. $\mathrm{C_{135}H_{97}F_{42}Fe_7O_{16}P_7}$ requires C, 46.0; H, 3.00%). δ_H([^{2}H$_6$]dmso): 5.22 (10 H, s, cp), 5.28 (25 H, br s, cp), 6.17 (4 H, d, *J* 6.7, complexed aryl H), 6.36 (24 H, br s, complexed aryl H), 6.90 (4 H, d, *J* 8.4, uncomplexed aryl H), 7.15 (4 H, d, *J* 7.6 Hz, uncomplexed aryl H), 7.50 (24 H, br s, uncomplexed aryl H), 9.74 (2 H, s, OH). δ_C([^{2}H$_6$]dmso): 73.49 (4 C, complexed aryl C), 74.80 (24 C, complexed aryl C), 77.56 (10 C, cp), 77.84 (25 C, cp), 116.71 (4 C, uncomplexed aryl C), 121.95 (4 C, uncomplexed aryl C), 122.71 (24 C, uncomplexed aryl C), 129.66 (2 C, complexed aryl C$^\mathrm{q}$), 130.13 (10 C, complexed aryl C$^\mathrm{q}$), 131.50 (2 C, complexed aryl C$^\mathrm{q}$), 144.63 (2 C, uncomplexed aryl C$^\mathrm{q}$), 150.87 (12 C, uncomplexed aryl C$^\mathrm{q}$), 155.60 (2 C, uncomplexed aryl C$^\mathrm{q}$).

Complex **55** (Found: C, 45.1; H, 3.10. $\mathrm{C_{115}H_{93}F_{42}Fe_7O_{12}P_7}$ requires C, 44.95; H, 3.05%). δ_H([^{2}H$_6$]dmso): 2.38 (6 H, s, Me), 5.14 (10 H, s, cp), 5.28 (25 H, s, cp), 6.29 (8 H, m, complexed aryl H), 6.36 (20 H, br s, complexed aryl H), 7.50 (28 H, br s, uncomplexed aryl H). δ_C([^{2}H$_6$]dmso): 19.30 (2 C, Me), 74.97 (20 C, complexed aryl C), 76.00 (4 C, complexed aryl C), 77.44 (10 C, cp), 77.98 (25 C, cp), 86.69 (4 C, complexed aryl C), 100.41 (2 C, complexed aryl C$^\mathrm{q}$), 122.83 (20 C, uncomplexed aryl C), 123.04 (4 C, uncomplexed aryl C), 130.24 (10 C, complexed aryl C$^\mathrm{q}$), 131.62 (2 C, complexed aryl C$^\mathrm{q}$), 150.71 (2 C, uncomplexed aryl C$^\mathrm{q}$), 151.00 (10 C, uncomplexed aryl C$^\mathrm{q}$).

Complex **56** (Found: C, 45.3; H, 3.10. $\mathrm{C_{149}H_{119}F_{54}Fe_9O_{16}P_9}$ requires C, 45.05; H, 3.00%). δ_H([^{2}H$_6$]dmso): 2.38 (6 H, s, Me), 5.14 (10 H, s, cp), 5.28 (35 H, s, cp), 6.28 (8 H, m, complexed aryl H), 6.36 (28 H, br s, complexed aryl H), 7.50 (32 H, br s, uncomplexed aryl H). δ_C([^{2}H$_6$]dmso): 19.27 (2 C, Me), 74.97 (28 C, complexed aryl C), 75.99 (4 C, complexed aryl C), 77.40 (10 C, cp), 77.94 (35 C, cp), 86.66 (4 C, complexed aryl C), 100.38 (2 C, complexed aryl C$^\mathrm{q}$), 122.77 (28 C, uncomplexed aryl C), 122.81 (4 C, uncomplexed aryl C), 130.16 (14 C, uncomplexed aryl C$^\mathrm{q}$), 131.53 (2 C, complexed aryl C$^\mathrm{q}$), 150.69 (2 C, uncomplexed aryl C$^\mathrm{q}$), 150.96 (14 C, uncomplexed aryl C$^\mathrm{q}$).

Complex **58** (Found: C, 44.6; H, 2.85. $\mathrm{C_{96}H_{76}F_{36}Fe_6O_{10}P_6}$ requires C, 44.4; H, 2.95%). δ_H([^{2}H$_6$]dmso): 5.18 (10 H, s, cp), 5.28 (20 H, s, cp), 6.20 (2 H, br s, complexed aryl H), 6.36 (24 H, br s, complexed aryl H), 7.51 (20 H, br s, uncomplexed aryl H). δ_C([^{2}H$_6$]dmso): 74.93 (16 C, complexed aryl C), 76.52 (4 C, complexed aryl C), 76.93 (10 C, cp), 77.94 (20 C, cp), 84.91 (2 C, complexed aryl C), 86.67 (4 C, complexed aryl C), 122.79 (16 C, uncomplexed aryl C), 123.19 (4 C, uncomplexed aryl C), 130.22 (8 C, complexed aryl C$^\mathrm{q}$), 132.69 (2 C, complexed aryl C$^\mathrm{q}$), 150.44 (2 C, uncomplexed aryl C$^\mathrm{q}$), 150.98 (6 C, uncomplexed aryl C$^\mathrm{q}$), 151.10 (2 C, uncomplexed aryl C$^\mathrm{q}$).

Complex **59** (Found: C, 43.2; H, 2.80. $\mathrm{C_{96}H_{74}Cl_2F_{36}Fe_6O_{10}P_6}$ requires C, 43.3; H, 2.80%). δ_H([^{2}H$_6$]dmso): 5.30 (10 H, s, cp), 5.33 (10 H, s, cp), 5.36 (10 H, s, cp), 6.17 (4 H, d, *J* 7.1 Hz, complexed aryl H), 6.24–6.39 (16 H, m, complexed aryl H), 6.65 (4 H, br s, complexed aryl H), 7.58 (20 H, br s, uncomplexed aryl H). δ_C([^{2}H$_6$]dmso): 68.87 (2 C, complexed aryl C), 74.11 (2 C, complexed aryl C), 74.46 (2 C, complexed aryl C), 75.68 (4 C, complexed aryl C), 76.16 (2 C, complexed aryl C), 78.67 (10 C, cp), 78.70 (10 C, cp), 78.97 (10 C, cp), 80.40 (4 C, complexed aryl C), 84.89 (2 C, complexed aryl C), 86.39 (2 C, complexed aryl C), 86.81 (2 C, complexed aryl C), 107.23 (2 C, complexed aryl C$^\mathrm{q}$), 124.03 (8 C, uncomplexed aryl C), 124.19 (8 C, uncomplexed aryl C), 124.28 (4 C, uncomplexed aryl C), 132.02 (2 C, complexed aryl C$^\mathrm{q}$), 133.89 (2 C, complexed aryl C$^\mathrm{q}$), 134.04 (2 C, complexed aryl C$^\mathrm{q}$), 134.38 (2 C, complexed aryl C$^\mathrm{q}$), 151.58 (2 C, uncomplexed aryl C$^\mathrm{q}$), 151.95 (2 C, uncomplexed aryl C$^\mathrm{q}$), 152.11 (2 C, uncomplexed aryl C$^\mathrm{q}$), 152.26 (2 C, uncomplexed aryl C$^\mathrm{q}$), 152.49 (2 C, uncomplexed aryl C$^\mathrm{q}$).

Complex **60** (Found: C, 43.35; H, 2.90. $\mathrm{C_{96}H_{74}Cl_2F_{36}Fe_6O_{10}P_6}$ requires C, 43.3; H, 2.80%). δ_H([^{2}H$_6$]dmso): 5.28 (30 H, br s, cp), 6.09 (4 H, s, complexed aryl H), 6.35 (12 H, br s, complexed aryl H), 6.46 (4 H, s, complexed aryl H), 6.80 (4 H, s, complexed aryl H), 7.50 (24 H, br s, uncomplexed aryl H). δ_C([^{2}H$_6$]dmso): 73.58 (4 C, complexed aryl C), 74.97 (12 C, complexed aryl C), 76.22 (4 C, complexed aryl C), 77.95 (20 C, cp), 79.33 (10 C, cp), 103.71 (2 C, complexed aryl C$^\mathrm{q}$), 122.77 (12 C, uncomplexed aryl C), 123.05 (4 C, uncomplexed aryl C), 124.44 (4 C, uncomplexed aryl C), 130.18 (6 C, complexed aryl C$^\mathrm{q}$), 130.38 (2 C, complexed aryl C$^\mathrm{q}$), 132.08 (2 C, complexed aryl C$^\mathrm{q}$), 150.45 (2 C, uncomplexed aryl C$^\mathrm{q}$), 150.98 (6 C, uncomplexed aryl C$^\mathrm{q}$), 151.43 (2 C, uncomplexed aryl C$^\mathrm{q}$).

Complex **61** (Found: C, 45.0; H, 3.10. $\mathrm{C_{96}H_{80}F_{36}Fe_6O_{10}P_6}$ requires C, 44.9; H, 3.05%). δ_H([^{2}H$_6$]dmso): 2.38 (6 H, s, Me), 5.15 (10 H, s, cp), 5.28 (20 H, br s, cp), 6.36 (24 H, br s, complexed aryl H), 7.49 (20 H, br s, uncomplexed aryl H). δ_C([^{2}H$_6$]dmso): 19.24 (2 C, Me), 74.96 (16 C, complexed aryl C), 75.04 (4 C, complexed aryl C), 77.38 (10 C, cp), 77.92 (20 C, cp), 86.63 (4 C, complexed aryl C), 100.36 (2 C, complexed aryl C$^\mathrm{q}$), 122.73 (16 C, uncomplexed aryl C), 122.95 (4 C, uncomplexed aryl C), 130.13 (8 C, complexed aryl C$^\mathrm{q}$), 131.50 (2 C, complexed aryl C$^\mathrm{q}$), 150.68 (2 C, uncomplexed aryl C$^\mathrm{q}$), 150.96 (8 C, uncomplexed aryl C$^\mathrm{q}$).

Complex **62** (Found: C, 46.3; H, 2.85. $\mathrm{C_{108}H_{84}F_{36}Fe_6O_{14}P_6}$ requires C, 46.15; H, 3.00%). δ_H([^{2}H$_6$]dmso): 5.15 (10 H, s, cp), 5.38 (20 H, br s, cp), 6.13 (4 H, d, *J* 9.2, complexed aryl H), 6.28 (4 H, d, *J* 9.5, complexed aryl H), 6.36 (16 H, br s, complexed aryl H), 6.88 (4 H, d, *J* 9.0, uncomplexed aryl H), 7.13 (4 H, d, *J* 8.8 Hz, uncomplexed aryl H), 7.50 (20 H, br s, uncomplexed aryl H), 9.69 (2 H, s, OH). δ_C([^{2}H$_6$]dmso): 72.74 (4 C, complexed aryl C), 74.18 (20 C, complexed aryl C), 76.60 (10 C, cp), 77.18 (20 C, cp), 115.98 (4 C, uncomplexed aryl C), 121.24

(4 C, uncomplexed aryl C), 122.02 (20 C, uncomplexed aryl C), 129.43 (8 C, complexed aryl C^q), 130.37 (2 C, complexed aryl C^q), 131.26 (2 C, complexed aryl C^q), 144.03 (2 C, uncomplexed aryl C^q), 150.21 (10 C, uncomplexed aryl C^q), 154.86 (2 C, uncomplexed aryl C^q).

Complex **63** (Found: C, 43.7; H, 2.75. $C_{130}H_{100}Cl_2F_{48}Fe_8O_{14}P_8$ requires C, 43.8; H, 2.85%). δ_H([$^2H_6$]dmso): 5.28 (40 H, br s, cp), 6.37 (16 H, br s, complexed aryl H), 6.47 (8 H, d, *J* 5.9, complexed aryl H), 6.83 (8 H, d, *J* 6.1 Hz, complexed aryl H), 7.50 (28 H, br s, uncomplexed aryl H). δ_C([$^2H_6$]dmso): 72.19 (24 C, complexed aryl C), 73.43 (4 C, complexed aryl C), 75.08 (30 C, cp), 76.57 (10 C, cp), 83.91 (4 C, complexed aryl C), 100.92 (2 C, complexed aryl C^q), 119.86 (4 C, uncomplexed aryl C), 120.00 (24 C, uncomplexed aryl C), 127.75 (10 C, complexed aryl C^q), 129.39 (2 C, complexed aryl C^q), 130.53 (2 C, complexed aryl C^q), 147.66 (2 C, uncomplexed aryl C^q), 148.20 (10 C, uncomplexed aryl C^q), 148.52 (2 C, uncomplexed aryl C^q).

Complex **64** (Found: C, 45.2; H, 3.00. $C_{132}H_{106}F_{48}Fe_8O_{14}P_8$ requires C, 45.0; H, 3.05%). δ_H([$^2H_6$]dmso): 2.38 (6 H, s, Me), 5.15 (10 H, s, cp), 5.28 (30 H, s, cp), 6.29 (8 H, m, complexed aryl H), 6.36 (24 H, br s, complexed aryl H), 7.50 (28 H, br s, uncomplexed aryl H). δ_C([$^2H_6$]dmso): 19.58 (2 C, Me), 75.28 (24 C, complexed aryl C), 76.41 (4 C, complexed aryl C), 77.72 (10 C, cp), 78.28 (30 C, cp), 86.99 (4 C, complexed aryl C), 100.71 (2 C, complexed aryl C^q), 123.29 (24 C, uncomplexed aryl C), 124.72 (4 C, uncomplexed aryl C), 130.48 (12 C, complexed aryl C^q), 132.40 (2 C, complexed aryl C^q), 150.77 (2 C, uncomplexed aryl C^q), 151.29 (14 C, uncomplexed aryl C^q).

Complex **65** (Found: C, 44.9; H, 3.00. $C_{215}H_{165}F_{78}Fe_{13}O_{26}P_{13}$ requires C, 44.7; H, 2.90%). δ_H([$^2H_6$]dmso): 5.22 (10 H, s, cp), 5.27 (55 H, s, cp), 6.36 (52 H, br s, complexed aryl H), 6.90 (4 H, br s, uncomplexed aryl H), 7.17 (4 H, br s, uncomplexed aryl H), 7.49 (48 H, br s, uncomplexed aryl H). δ_C([$^2H_6$]dmso): 73.47 (4 C, complexed aryl C), 74.85 (136 C, complexed aryl C), 77.69 (10 C, cp), 77.81 (55 C, cp), 119.60 (4 C, uncomplexed aryl C), 120.55 (4 C, uncomplexed aryl C), 122.60 (48 C, uncomplexed aryl C), 130.00 (22 C, complexed aryl C^q), 130.53 (4 C, complexed aryl C^q), 131.73 (4 C, complexed aryl C^q), 144.52 (2 C, uncomplexed aryl C^q), 150.84 (24 C, uncomplexed aryl C^q), 154.87 (2 C, uncomplexed aryl C^q).

Complex **66** (Found: C, 44.8; H, 2.95. $C_{283}H_{217}F_{102}Fe_{17}O_{32}P_{17}$ requires C, 44.6; H, 2.85%). δ_H([$^2H_6$]dmso): 5.28 (85 H, br s, cp), 6.36 (52 H, br s, complexed aryl H), 6.82 (4 H, br s, complexed aryl H), 7.17 (4 H, br s, complexed aryl H), 7.50 (64 H, br s, uncomplexed aryl H). δ_C([$^2H_6$]dmso): 74.87 (60 C, complexed aryl C), 76.12 (4 C, complexed aryl C), 77.84 (75 C, cp), 79.22 (10 C, cp), 86.59 (4 C, complexed aryl C), 103.60 (2 C, complexed aryl C^q), 122.64 (60 C, uncomplexed aryl C), 122.95 (4 C, uncomplexed aryl C), 130.05 (30 C, complexed aryl C^q), 130.65 (2 C, complexed aryl C^q), 131.91 (2 C, complexed aryl C^q), 150.34 (2 C, uncomplexed aryl C^q), 150.86 (28 C, uncomplexed aryl C^q), 151.17 (2 C, uncomplexed aryl C^q).

Complex **67** (Found: C, 45.3; H, 3.00. $C_{589}H_{451}F_{210}Fe_{35}O_{68}P_{35}$ requires C, 45.0; H, 2.90%). δ_H([$^2H_6$]dmso): 5.28 (175 H, br s, cp), 6.36 (132 H, br s, complexed aryl H), 6.82 (4 H, m, complexed aryl H), 7.17 (4 H, m, complexed aryl H), 7.50 (136 H, br s, uncomplexed aryl H). δ_C([$^2H_6$]dmso): 74.82 (132 C, complexed aryl C), 76.08 (4 C, complexed aryl C), 77.79 (165 C, cp), 79.18 (10 C, cp), 86.56 (4 C, complexed aryl C), 103.56 (2 C, complexed aryl C^q), 122.26 (4 C, uncomplexed aryl C), 122.59 (132 C, uncomplexed aryl C), 130.00 (66 C, complexed aryl C^q), 130.59 (2 C, complexed aryl C^q), 131.84 (2 C, complexed aryl C^q), 150.37 (2 C, uncomplexed aryl C^q), 150.81 (64 C, uncomplexed aryl C^q), 151.90 (2 C, uncomplexed aryl C^q).

Synthesis of Complexes **28** *and* **46–48**.—To 0.5 mmol of a complex with two terminal chlorine atoms were added 1,4-dihydroxybenzene (0.275 g, 2.5 mmol), K_2CO_3 (0.345 g, 2.5 mmol) and dmf (10 cm^3). The red solution was magnetically stirred under a nitrogen atmosphere for 12 h. The complexes were isolated in a similar manner to complexes **4–15**.

Complex **28** (Found: C, 49.1; H, 3.30. $C_{23}H_{19}F_6FeO_4P$ requires C, 49.3; H, 3.40%). δ_H([$^2H_6$]dmso): 5.14 (5 H, s, cp), 6.10 (4 H, s, complexed aryl H), 6.90 (4 H, d, *J* 8.4, uncomplexed aryl H), 7.12 (4 H, d, *J* 8.4 Hz, uncomplexed aryl H), 9.88 (2 H, s, OH). δ_C([$^2H_6$]dmso): 73.58 (4 C, complexed aryl C), 77.46 (5 C, cp), 116.88 (4 C, uncomplexed aryl C), 122.08 (4 C, uncomplexed aryl C), 131.23 (2 C, complexed aryl C^q), 144.84 (2 C, uncomplexed aryl C^q), 155.78 (2 C, uncomplexed aryl C^q).

Complex **46** (Found: C, 47.6; H, 3.20. $C_{40}H_{32}F_{12}Fe_2O_6P_2$ requires C, 47.55; H, 3.20%). δ_H([$^2H_6$]dmso): 5.22 (10 H, s, cp), 6.16 (4 H, d, *J* 8.8, complexed aryl H), 6.30 (4 H, d, *J* 7.0, complexed aryl H), 6.90 (4 H, d, *J* 8.8, uncomplexed aryl H), 7.14 (4 H, d, *J* 8.8 Hz, uncomplexed aryl H), 7.45 (4 H, s, uncomplexed aryl H), 9.77 (2 H, s, OH). δ_C([$^2H_6$]dmso): 73.59 (4 C, complexed aryl C), 74.93 (4 C, complexed aryl C), 77.69 (10 C, cp), 116.83 (4 C, uncomplexed aryl C), 122.04 (4 C, uncomplexed aryl C), 122.76 (4 C, uncomplexed aryl C), 129.82 (2 C, complexed aryl C^q), 131.60 (2 C, complexed aryl C^q), 144.71 (2 C, uncomplexed aryl C^q), 151.01 (2 C, uncomplexed aryl C^q), 155.76 (2 C, uncomplexed aryl C^q).

Complex **47** (Found: C, 46.8; H, 3.15. $C_{57}H_{45}F_{18}Fe_3O_8P_3$ requires C, 46.9; H, 3.10%). δ_H([$^2H_6$]dmso): 5.30 (10 H, s, cp), 5.32 (5 H, s, cp), 6.25 (4 H, br s, complexed aryl H), 6.35 (8 H, br s, complexed aryl H), 6.99 (4 H, d, *J* 8.8, uncomplexed aryl H), 7.19 (4 H, d, *J* 8.8 Hz, uncomplexed aryl H), 7.56 (8 H, s, uncomplexed aryl H), 9.73 (2 H, s, OH). δ_C([$^2H_6$]dmso): 74.29 (4 C, complexed aryl C), 75.40 (5 C, cp), 78.34 (10 C, cp), 78.37 (8 C, complexed aryl C), 117.42 (4 C, uncomplexed aryl C), 122.48 (4 C, uncomplexed aryl C), 123.57 (8 C, uncomplexed aryl C), 131.34 (2 C, complexed aryl C^q), 132.53 (2 C, complexed aryl C^q), 145.53 (2 C, uncomplexed aryl C^q), 151.68 (2 C, uncomplexed aryl C^q), 151.85 (2 C, uncomplexed aryl C^q), 156.71 (2 C, uncomplexed aryl C^q).

Complex **48** (Found: C, 46.6; H, 3.10. $C_{74}H_{58}F_{24}Fe_4O_{10}P_4$ requires C, 46.5; H, 3.05%). δ_H([$^2H_6$]dmso): 5.20 (10 H, s, cp), 5.25 (10 H, s, cp), 6.15 (4 H, br s, complexed aryl H), 6.33 (16 H, br s, complexed aryl H), 6.90 (4 H, m, uncomplexed aryl H), 7.12 (4 H, m, uncomplexed aryl H), 7.46 (12 H, br s, uncomplexed aryl H), 9.71 (2 H, s, OH). δ_C([$^2H_6$]dmso): 73.61 (4 C, complexed aryl C), 74.94 (12 C, complexed aryl C), 77.69 (10 C, cp), 77.96 (10 C, cp), 116.81 (4 C, uncomplexed aryl C), 122.07 (4 C, uncomplexed aryl C), 122.78 (12 C, uncomplexed aryl C), 129.79 (2 C, complexed aryl C^q), 130.25 (4 C, complexed aryl C), 131.61 (2 C, complexed aryl C^q), 144.75 (2 C, uncomplexed aryl C^q), 150.98 (6 C, uncomplexed aryl C^q), 155.72 (2 C, uncomplexed aryl C^q).

Synthesis of Complexes **68–71**.—To 0.5 mmol of **6**, **31**, **43** or **51** were added naphthol (0.180 g, 1.25 mmol), K_2CO_3 (0.345 g, 2.5 mmol) and dmf (10 cm^3). The red solution was magnetically stirred under a nitrogen atmosphere for 8 h, whereupon the capped naphthyloxy products were isolated in the usual fashion.

Complex **68** (Found: C, 53.35; H, 3.40. $C_{48}H_{36}F_{12}Fe_2O_4P_2$ requires C, 53.5; H, 3.35%). δ_H([$^2H_6$]dmso): 5.37 (10 H, s, cp), 6.36 (8 H, s, complexed aryl H), 7.41–7.49 (6 H, m, uncomplexed aryl H), 7.58–7.66 (6 H, m, uncomplexed aryl H), 7.93–8.11 (6 H, m, uncomplexed aryl H). δ_C([$^2H_6$]dmso): 75.08 (4 C, complexed aryl C), 75.47 (4 C, complexed aryl C), 78.18 (10 C, cp), 116.08, 120.93 (4 C, uncomplexed aryl C), 122.96 (4 C, uncomplexed aryl C), 125.50 (2 C, complexed aryl C^q), 126.18, 126.20, 126.30, 127.38, 127.45 (10 C, uncomplexed aryl C), 130.35 (2 C, complexed aryl C^q), 130.57, 134.85, 149.56, 151.08 (8 C, uncomplexed aryl C^q).

Complex **69** (Found: C, 50.9; H, 3.10. $C_{65}H_{49}F_{18}Fe_3O_6P_3$ requires C, 51.1; H, 3.25%). δ_H([$^2H_6$]dmso): 5.27 (15 H, br s, cp), 6.36 (12 H, br s, complexed aryl H), 7.49 (10 H, br s, uncomplexed aryl H), 7.63 (6 H, br s, uncomplexed aryl H), 7.91–8.09 (6 H, m, uncomplexed aryl H). δ_C[$(CD_3)_2CO$]: 75.45

(4 C, complexed aryl C), 75.68 (4 C, complexed aryl C), 76.49 (4 C, complexed aryl C), 78.99 (5 C, cp), 79.20 (10 C, cp), 116.08, 121.73 (4 C, uncomplexed aryl C), 124.37, 124.44 (8 C, uncomplexed aryl C), 126.68 (2 C, complexed aryl C^q), 126.81, 126.99, 127.95, 128.09, 129.17 (10 C, uncomplexed aryl C), 131.83 (2 C, uncomplexed aryl C^q), 132.23 (4 C, complexed aryl C^q), 136.06, 150.71, 152.09 (8 C, uncomplexed aryl C^q).

Complex **70** (Found: C, 49.6; H, 3.00. $C_{82}H_{62}F_{24}Fe_4O_8P_4$ requires C, 49.8; H, 3.15%). δ_H([$^2H_6$]dmso): 5.28 (20 H, s, cp), 6.37 (16 H, br s, complexed aryl H), 7.46–7.50 (14 H, m, uncomplexed aryl H), 7.55–7.67 (6 H, m, uncomplexed aryl H), 7.93–8.10 (6 H, m, uncomplexed aryl H). δ_C([$^2H_6$]dmso): 75.47 (12 C, complexed aryl C), 76.15 (4 C, complexed aryl C), 78.69 (10 C, cp), 78.84 (10 C, cp), 116.51, 121.49 (4 C, uncomplexed aryl C), 123.74 (12 C, uncomplexed aryl C), 126.33 (2 C, complexed aryl C^q), 126.64, 126.71, 127.73, 127.84, 128.94 (10 C, uncomplexed aryl C), 131.44 (6 C, complexed aryl C^q), 131.62, 135.68, 150.34 (6 C, uncomplexed aryl C^q), 151.83 (6 C, uncomplexed aryl C^q).

Complex **71** (Found: C, 48.8; H, 3.00. $C_{99}H_{73}F_{30}Fe_5O_{10}P_5$ requires C, 49.0; H, 3.10%). δ_H([$^2H_6$]dmso): 5.27 (25 H, br s, cp), 6.35 (20 H, br s, complexed aryl H), 7.50 (18 H, br s, uncomplexed aryl H), 7.60–7.66 (6 H, m, uncomplexed aryl H), 7.93–8.09 (6 H, m, uncomplexed aryl H). δ_C([$^2H_6$]dmso): 74.97 (16 C, complexed aryl C), 75.43 (4 C, complexed aryl C), 77.98 (15 C, cp), 78.10 (10 C, cp), 115.92, 120.85 (4 C, uncomplexed aryl C), 122.82 (16 C, uncomplexed aryl C), 125.39 (2 C, complexed aryl C^q), 126.05, 126.18, 127.26, 127.33, 128.35 (10 C, uncomplexed aryl C), 130.23 (10 C, complexed aryl C^q), 130.44, 134.75, 149.50 (6 C, uncomplexed aryl C^q), 151.01 (8 C, uncomplexed aryl C^q).

Synthesis of Complexes **21**, **22**, **72** *and* **73**.—The oxidation of complexes **12**, **13**, **37** or **39** using 3-chloroperbenzoic acid to give **21**, **22**, **72** or **73** were conducted following our previously described methodology.[70]

Complex **21** (Found: C, 35.0; H, 3.10. $C_{28}H_{30}Cl_2F_{12}Fe_2O_4P_2S_2$ requires C, 34.8; H, 3.15%). δ_H[$(CD_3)_2CO$]: 1.44–1.45 (4 H, m, γ-CH_2), 1.73–1.82 (4 H, m, β-CH_2), 3.53 (4 H, t, J = 7.9, α-CH_2), 5.52 (10 H, s, cp), 7.11 (4 H, d, J = 7.0, complexed aryl H), 7.13 (4 H, d, J = 7.0 Hz, complexed aryl H). δ_C[$(CD_3)_2CO$]: 22.65 (2 C, γ-CH_2), 27.72 (2 C, β-CH_2), 55.52 (2 C, α-CH_2), 82.23 (10 C, cp), 89.26 (4 C, complexed aryl C), 89.57 (4 C, complexed aryl C), 103.14 (2 C, complexed aryl C^q), 110.09 (2 C, complexed aryl C^q).

Complex **22** (Found: C, 35.9; H, 3.25. $C_{30}H_{34}Cl_2F_{12}Fe_2O_4P_2S_2$ requires C, 36.20; H, 3.45%). δ_H[$(CD_3)_2CO$]: 1.29–1.39 (8 H, m, δ, γ-CH_2), 1.72–1.81 (4 H, m, β-CH_2), 3.54 (4 H, t, J = 7.0 Hz, α-CH_2), 5.52 (10 H, s, cp), 7.11 (8 H, br s, complexed aryl H). δ_C[$(CD_3)_2CO$]: 22.98 (2 C, γ-CH_2), 28.63 (2 C, γ-CH_2), 30.18 (2 C, β-CH_2), 55.79 (2 C, α-CH_2), 82.27 (10 C, cp), 89.32 (4 C, complexed aryl C), 89.64 (4 C, complexed aryl C), 103.24 (2 C, complexed aryl C^q), 110.08 (2 C, complexed aryl C^q).

Complex **72** (Found: C, 40.1; H, 3.05. $C_{58}H_{50}F_{24}Fe_4O_8P_2S_2$ requires C, 40.0; H, 2.90%). δ_H([$^2H_6$]dmso): 4.11 (4 H, s, CH_2), 5.25 (10 H, s, cp), 5.44 (10 H, s, cp), 6.33 (2 H, s, complexed aryl H), 6.45 (8 H, s, complexed aryl H), 6.69 (2 H, d, J 5.3, complexed aryl H), 6.94 (2 H, d, J 5.4 Hz, complexed aryl H), 7.60 (8 H, s, uncomplexed aryl H). δ_C([$^2H_6$]dmso): 49.41 (2 C, CH_2), 77.21 (4 C, complexed aryl C), 77.58 (4 C, complexed aryl C), 78.10 (10 C, cp), 80.48 (10 C, cp), 85.82 (2 C, complexed aryl C), 87.77 (4 C, complexed aryl C), 88.65 (4 C, complexed aryl C), 99.58 (2 C, complexed aryl C^q), 124.40 (4 C, uncomplexed aryl C), 124.64 (4 C, uncomplexed aryl C), 134.53 (2 C, complexed aryl C^q), 136.87 (2 C, complexed aryl C^q), 151.30 (2 C, uncomplexed aryl C^q), 152.11 (2 C, uncomplexed aryl C^q).

Complex **73** (Found: C, 41.3; H, 3.30. $C_{62}H_{58}F_{24}Fe_4O_8P_2S_2$ requires C, 41.4; H, 3.25%). δ_H([$^2H_6$]dmso): 1.48 (4 H, m, γ-CH_2), 1.78 (4 H, m, β-CH_2), 3.51 (4 H, t, J 7.2, α-CH_2), 5.26 (10 H, s, cp), 5.43 (10 H, s, cp), 6.31–6.36 (2 H, m, complexed aryl H), 6.41 (8 H, br s, complexed aryl H), 6.68 (2 H, d, J 6.5, complexed aryl H), 6.90 (2 H, d, J 6.5 Hz, complexed aryl H), 7.62 (8 H, s, uncomplexed aryl H). δ_C([$^2H_6$]dmso): 22.80 (2 C, γ-CH_2), 27.72 (2 C, β-CH_2), 55.72 (2 C, α-CH_2), 77.10 (4 C, complexed aryl C), 77.55 (4 C, complexed aryl C), 78.07 (10 C, cp), 80.23 (10 C, cp), 85.79 (2 C, complexed aryl C), 87.73 (4 C, complexed aryl C), 88.18 (4 C, complexed aryl C), 100.79 (2 C, complexed aryl C^q), 124.40 (4 C, uncomplexed aryl C), 124.58 (4 C, uncomplexed aryl C), 134.51 (2 C, complexed aryl C^q), 136.59 (2 C, complexed aryl C^q), 151.34 (2 C, uncomplexed aryl C^q), 152.05 (2 C, uncomplexed aryl C^q).

X-Ray Crystallography.—Single crystals were mounted in thin-walled glass capillaries and placed on an Enraf-Nonius CAD-4 diffractometer. Unit-cell dimensions were determined *via* least-squares refinement of the setting angles of 24 high-angle reflections and intensity data were collected using ω–2θ scan mode. Data were corrected for Lorentz, polarization and absorption (where directed by crystal shape or absorption coefficient) effects but not for extinction. In several compounds, poor scattering, which we attribute to disorder and/or high thermal motion in solvent or spacer molecules, precluded collection of data to a 2θ limit of 50°. However, this in no way prejudices our assignment of space group or interpretation of the crystal packing.

Pertinent data collection and structure refinement parameters for complexes **16**–**18** are presented in Table 1. The structures were solved using direct methods and all non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were located *via* Fourier-difference map inspection or calculated, given isotropic thermal parameters based upon the atom to which they are bonded, and fixed during least-squares refinement. Weights based upon counting statistics were used with the weight modifier, k, in $kF_o{}^2$ being determined *via* evaluation of the variation in standard reflections during the course of data collection. Values of R and R' were given by $\Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ and $[\Sigma w(|F_o| - |F_c|^2)/\Sigma w|F_o{}^2|]^{\frac{1}{2}}$. All crystallographic calculations were effected using the PC version of the NRCVAX suite of programs and 80486-based IBM-compatible computers. Crystallographic figures were drawn using ORTEP.[84]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates and thermal parameters.

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