Nucleophilic addition to di- and poly-iron arene complex cations

Alaa S. Abd-El-Aziz, Debbie A. Armstrong, Shelly Bernardin, and Harold M. Hutton

Abstract: Hydride and cyanide addition to a series of di- and polycyclopentadienyliron arene complex cations with etheric bridges is described. Reaction of the di-iron complexes with sodium borohydride resulted in the formation of a number of adducts. *p*-Methyl- and *o,o*-dimethylphenoxybenzene cyclopentadienyliron complexes were used as models in this study to allow for the characterization of the analagous di-iron complexes. The use of HH COSY and CH COSY NMR techniques enabled us to identify the isomeric nature of these adducts. The hydride addition results indicated that the etheric substituent had the predominant effect over the methyl group, leading to a higher addition ratio to the *meta*-, followed by the *ortho*-, then the *para*-positions. It was also clear that in the di-iron system, the hydride addition to each complexed arene ring took place independently. The addition of the cyanide anion to di- and poly-iron arene systems was more selective than that of the hydride anion. Reaction of sodium cyanide with *p*-methyl- or *o*-methyl-substituted arene complexes led to the formation of one adduct, with the cyanide being added to the *meta* position to the etheric bridges. However, cyanide addition to the di-iron complex, with a methyl substituent attached at the *meta* position of each complexed arene, led to the formation of a mixture of adducts. Cyanide addition to the poly-iron system with *p*-substituted arenes proved to be very selective, allowing for the formation of one adduct. Oxidative demetallation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) produced the uncomplexed polyaromatic ethers with cyano groups in a very good yield.

Key words: cyclopentadienyliron, arene, nucleophilic addition, hydride, cyanide.

Résumé : On décrit l'addition des ions hydrure et cyanure à une série de complexes cationiques di- et polycyclopentadiénylfer–arène avec ponts éthers. La réaction des complexes bi-fer avec le borohydrure de sodium conduit à la formation d'un certain nombre d'adduits. Dans cette étude, on a utilisé les *p*-méthyl- et *o,o*-diméthylphénoxybenzène cyclopentadiénylfer comme modèles permettant de caractériser les complexes di-fer analogues. L'utilisation des techniques de RMN HH COSY et CH COSY ont permis d'identifier la nature des produits isomères de ces adduits. Les résultats obtenus pour l'addition d'hydrure ont indiqué que le substituant éther a un effet plus important que celle du méthyle; ceci conduit à un rapport d'addition plus élevé pour la position *méta*, suivie alors par les positions *ortho* et *para*. Il est également clair que, dans le système bi-fer, l'addition d'hydrure à chacun des noyaux arènes se fait d'une façon indépendante. L'addition de l'anion cyanure aux systèmes di- et poly-fer–arène est plus sélective que celle de l'anion hydrure. La réaction du cyanure de sodium avec les complexes arènes *p*-méthyl- ou *o*-méthyl-substitués conduit à la formation d'un adduit dans lequel le cyanure s'ajoute en position *méta* par rapport au pont éther. Toutefois, l'addition du cyanure au complexe di-fer portant un substituant méthyle en position *méta* de chaque arène complexé conduit à la formation d'un mélange d'adduits. L'addition de cyanure au système poly-fer avec des arènes *p*-substitués s'avère sélective et conduit à la formation d'un seul adduit. La démétallation oxydante de la 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) conduit, avec de très bons rendements, à des éthers polyaromatiques non complexés portant des groupes cyano.

Mots clés : cyclopentadiénylfer, arène, addition nucléophile, hydrure, cyanure.

[Traduit par la rédaction]

Introduction

Addition of carbanions, hydrides, phosphorus and nitrogen anions to organometallic complexes has led to novel routes to the functionalization of aromatic compounds (1–15). It is well known that the complexation of a metal moiety, such as $(CO)_3Cr$, $(CO)_3Mn^+$, $(C_6H_6)Fe^{2+}$, or $CpFe^+$ to an aromatic system activates the arene ring towards nucleophilic addition reactions (4-26). In a review by Davies et al., a set of rules was presented to predict the site of nucleophilic addition to organo-transition metal cations containing unsaturated hydrocarbon ligands (1). Other reports have indicated that addition occurs on the *exo* face of the arene ligand, as confirmed by NMR and X-ray crystallographic studies (27, 28).

Due to the ease of complexation of the $(CO)_3Cr$ moiety with aromatic systems, the vast majority of research in this field has involved the use of these types of complexes (8). Addition of

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A.S. Abd-El-Aziz,[1] D.A. Armstrong, S. Bernardin, and H.M. Hutton. Department of Chemistry, University of Winnipeg, Winnipeg, MB, R3B 2E9, Canada.

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[1] Author to whom correspondence may be addressed. Telephone: (204) 786-9335. Fax: (204) 786-1824. E-mail: abdelaziz@uwinnipeg.ca

nucleophiles to (arene)$Cr(CO)_3$ has led to the formation of anionic $[(CO)_3Cr(cyclohexadienyl)]$ intermediates. These adducts are air sensitive and usually undergo oxidative demetallation without isolation, allowing for the functionalization of the arene compounds (2). A novel characteristic of the cyclohexadienyl intermediates is that they may react with electrophilic reagents, enhancing the flexibility of this methodology.

Tremendous effort has been directed toward the use of cationic metal moieties such as $(CO)_3Mn^+$, $CpFe^+$, or $(C_6H_6)Fe^{2+}$ for the activation of arenes, allowing for the formation of neutral functionalized cyclohexadienyl complexes. The use of $(CO)_3Mn^+$ species as an activating group has led to the synthesis of a number of potentially biologically active chiral compounds (16, 17), as well as the functionalization of heterocyclic and cyclohexadiene compounds (15, 18, 19). Addition reactions of a variety of nucleophiles (H^-, CN^-, $CH_3COCH_2^-$, CH_3^-, Cl_3C^-) to cyclopentadienyliron arene cations have also been investigated (27–43). Sutherland et al. examined the hydride addition reactions of various substituted $[(C_6H_5X)FeCp]^+$ systems (37). This study demonstrated that strongly electron-donating substitutents direct hydride addition to the *meta* and *para* positions of the substituent, while the strongly electron-withdrawing substituent directs to the *ortho* position. These results are consistent with those predicted from molecular orbital calculations (32–36). Steric effects from the methyl groups *ortho* to the electron-withdrawing substituent of arene complexes have been reported with hydride addition (41). When *ortho* positions were hindered, addition in the *meta* and *para* positions increased. However, cyanide addition did not display the same sensitivity to steric factors; addition in this case occurred in the *ortho* position only. It was proposed that steric, electronic, and free valency effects all play a role in nucleophilic addition reactions (32, 37).

We have developed an efficient synthetic route to di- and polycyclopentadienyliron arene cations (44–48). The need to devise simple methods for functionalization of these types of complexes led us to the study of nucleophilic substitution and addition reactions. Our recent investigation of the functionalization of polyaromatic arene complexes via nucleophilic substitution has been successful (44–46). In this article we report hydride and cyanide addition to a number of methyl-substituted mono-, di-, and polycyclopentadienyliron complexes.

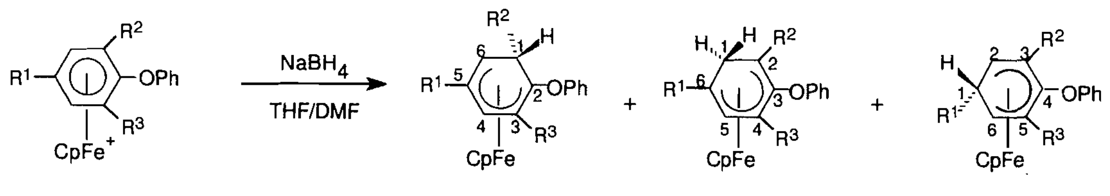
Results and discussion

Hydride addition

Hydride addition to bis(cyclopentadienyliron) arene di-cations resulted in the formation of a number of isomers. Due to the complexity of the NMR spectra of these adducts, the mono-iron systems were used as models for this investigation. While hydride addition to $CpFe^+$ complexes of monosubstituted arenes has been carefully examined (37), hydride addition to disubstituted arene complexes has not been reported. Reactions of (η^6-isomeric phenoxytoluene-η^5-cyclopentadienyliron) cations with an excess of sodium borohydride gave rise to a mixture of adducts, as illustrated in Scheme 1. The ^1H and ^{13}C NMR spectra were complicated by the number of isomers present; thus it was necessary to characterize the products using HH COSY and CH COSY techniques. For proton assignment, the chemical shifts of the individual isomers were determined from the connectivities in the HH COSY spectrum. Once this information was obtained, ^{13}C chemical shifts were then assigned using CH COSY.

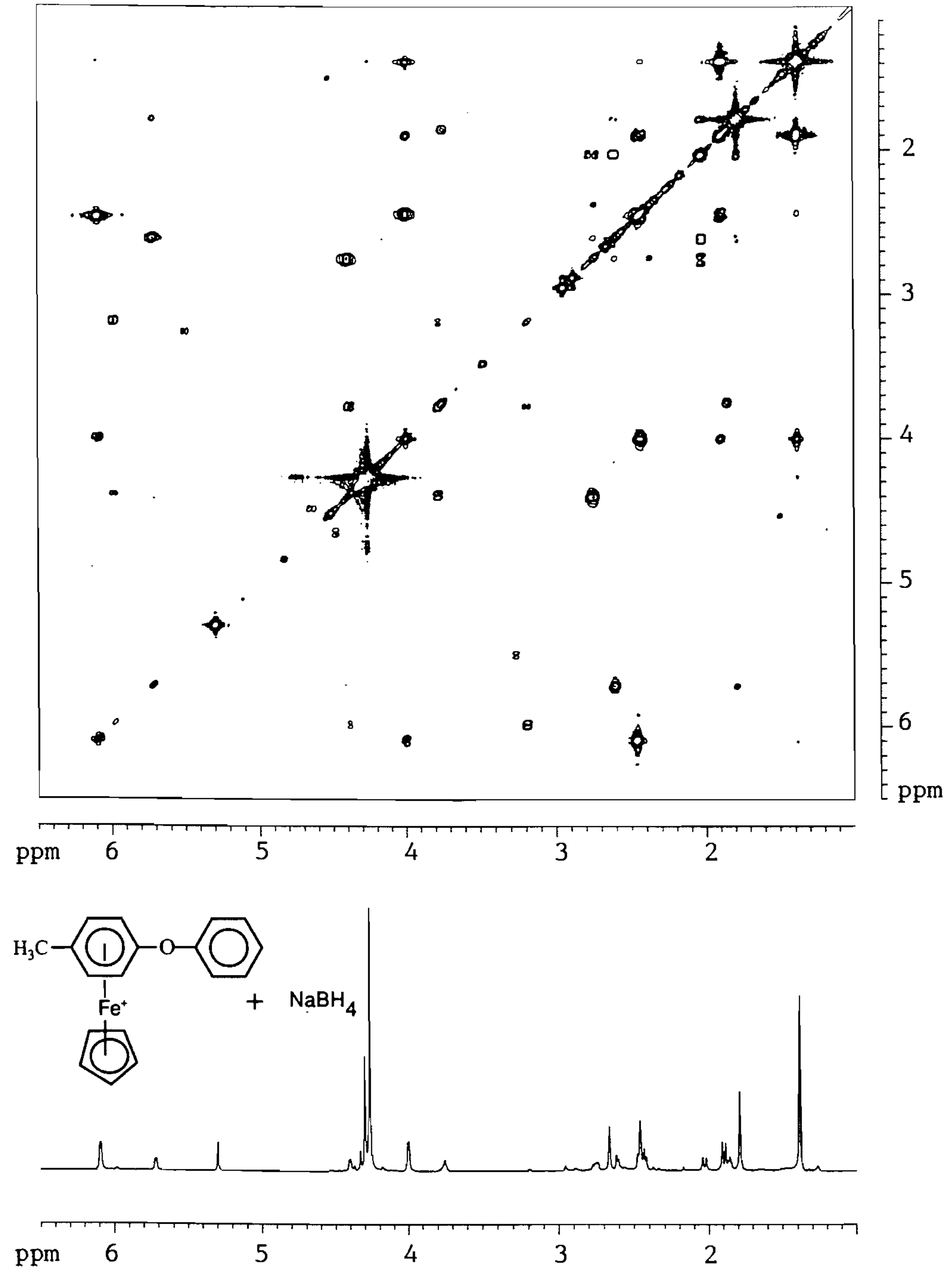
It has been established that a phenoxy substituent attached to the arene $CpFe^+$ complex directs the addition of the nucleophile to *meta* > *ortho* > *para*, whereas a methyl substituent directs *ortho* > *meta* > *para* (29–32, 37). In this study, it was very clear that the phenoxy substituent has a stronger influence on the site of addition than has the methyl substituent due to its greater strength as an electron-donating group. For clarity, we will refer to the site of addition with respect to the etheric bridge. As shown in Scheme 1, the major adduct for complex [**1**] was [**3b**] (66%), formed at the position *meta* to the phenoxy substituent. The second most abundant isomer [**3a**] (30%) displayed addition *ortho* to the phenoxy group. Trace amounts of the product *ipso* to the methyl substituent (*para* to the phenoxy substituent), [**3c**] (4%), were present; however, it was difficult to fully characterize this isomer. For complex [**2**], in which the positions *ortho* to the phenoxy substituent are hindered by methyl groups, the major addition was at the *meta* position with respect to the phenoxy group [**4b**] (60%), as illustrated in Scheme 1. Addition *para* to the phenoxy gave rise to the second most abundant isomer [**4c**] (28%). The minor isomer, [**4a**] (12%), resulted when addition *ipso* to the methyl group took place. Attempts to separate the various isomers by means of column chromatography were

Scheme 1.



1 R¹ = CH_3 R²,R³ = H	**3a** (30%)	**3b** (66%)	**3c** (4%)
2 R¹ = H R²,R³ = CH_3	**4a** (12%)	**4b** (60%)	**4c** (28%)

Fig. 1. 2D HH COSY for adducts **3a–c** in $CDCl_3$.



unsuccessful due to the instability of these products. The ^1H and ^{13}C NMR data of the addition products [**3**] and [**4**] are listed in Tables 1 and 2. For the purpose of identification, the site of hydride addition has been designated position one, and numbering proceeds around the ring, so that the phenoxy group is the lowest possible number. As an example, Fig. 1 illustrates the 2D HH COSY for the hydride addition to complex [**1**] (adducts [**3a–c**]).

Reaction of 1.0 mmol of 1,4-bis[(η^6-4-methylphenoxy-η^5-cyclopentadienyl)iron]benzene cation [**5**] with 5.0 mmol of sodium borohydride produced a mixture of isomers, as shown in Scheme 2. Since the complexed arene rings are separated from one another by a (OC_6H_4O) group, as shown in Scheme 2, the addition to each of these rings should be independent. Thus a variety of symmetrical and asymmetrical adducts should be obtained. If the addition takes place at the same site on both rings, there will be no significant change in the chemical shifts between the protons or carbons of one cyclohexadienyl ring and the other. As an example, it was not possible to distinguish between the chemical shift for the *ortho-ortho* isomer [**6a**] and the asymmetric *ortho* addition of isomer [**6c**]. The relative percentage of the addition product calculated

Table 1. ^1H NMR data for the adducts **3** and **4**.[a]

Adduct	CH_3	H(1-*exo*)	H(1-*endo*)	H(2)	H(3)	H(4)	H(5)	H(6)	Cp
3a	1.79 s	2.06 (d, 9.8, ex-en)	2.78 (dd, 9.8, en-ex; 5.9, en-6)	—	4.41 (d, 5.1)	5.73 (d, 5.1)	—	2.62 (d, 5.9, 6-en)	4.30 s
3b	1.39 s	1.93 (d, 10.7, ex-en)	2.44 m	2.46 m	—	6.11 (d, 5.1)	4.02 (d, 5.1)	—	4.27 s
4a	1.25, 1.94 s	1.86 s	—	—	—	5.80 (d, 5.9)	4.09 (t, 5.9)	2.09 (d, 5.9)	4.24 s
4b	1.30, 2.51 s	1.82 (d, 12.2, ex-en)	2.37 (dd, 12.2, en-ex; 6.1, en-6)	—	—	—	4.24 (d, 6.2)	2.03 (d, 6.2)	4.18 s
4c	1.96 s	1.57 (d, 12.8, ex-en)	2.35 (dt, 13.1, en-ex; 7.0, en-2,6)	1.79 m	—	—	—	1.79 m	4.26 s

[a] Uncomplexed aromatic peaks appear as multiplet between 6.8 and 7.5 ppm. Coupling constants (Hz) are of adjacent protons unless otherwise indicated.

Table 2. ^{13}C NMR of the adducts **3** and **4**.[a]

Adduct	CH_3	C (1)	C (2)	C (3)	C (4)	C (5)	C (6)	Cp
3a	21.75	31.71	35.99	70.71	74.15	75.11	29.07	74.78
3b	24.89	33.11	24.84	91.87	69.67	75.24	18.79	74.64
4a	29.66, 20.91	28.41	35.42	89.20	98.31	86.20	18.45	75.12
4b	19.97, 16.67	34.28	29.66	98.20	88.00	78.82	17.93	75.37
4c	20.90	28.35	20.11	86.18	94.81	86.18	20.11	76.17

[a] Uncomplexed aromatic peaks appear at 114–128 ppm.

from the NMR spectra for each isomer was based on the total amount of specific addition in each adduct. The *meta* isomer was calculated to be 59%, which was the total of the hydride addition in *meta-meta* [**6b**], *meta-ortho* [**6c**], and the trace *meta-para*. The total *ortho* addition was 35%, which represents the addition *ortho-ortho* [**6a**], *ortho-meta* [**6c**], and a trace of *ortho-para* adduct. Trace amounts of the *para* addition products were also observed (6%). It is also important to note that we did not observe diastereomers for these adducts. The ^1H and ^{13}C NMR chemical shifts are shown in Tables 3 and 4, where [**6a**] and [**6b**] represent the symmetrical *ortho* and *meta* isomers, respectively, as well as the *ortho* and *meta* addition of the asymmetrical structure [**6c**].

As part of this study, we blocked the two positions *ortho* to the etheric bridges by two methyl groups in order to enhance addition to the *meta* position. Hydride addition to 1,4-bis[(η^6-(2,6-dimethyl)phenoxy-η^5-cyclopentadienyl)iron]benzene hexafluorophosphate, [**7**], resulted in the formation of three major isomers, as well as traces of a few minor isomers, as shown in Scheme 3. Using the same strategy as described above, the predominant isomer was determined to be the *meta* adduct [**8a**] (51%); *para* [**8b**] (41%) and traces of *ortho* adducts (8%) were also present. The spectral analyses for these adducts are given in Tables 3 and 4. The position of hydride addition was found to be dependent on the substituents on the ring.

Cyanide addition

Nitrile groups are unique in their ease of transformation to other functional groups such as acids, esters, amines, and amides (49, 50). This versatility is valuable in the investigation of synthetic routes for the functionalization of organic and polymeric compounds. In the past few years, we have been involved in the synthesis and characterization of polyaromatic ethers with or without pendant metallic moieties (44–47). In this article, we report the addition of cyanide to a number of $CpFe^+$ polyaromatic ether complexes. Schemes 4 and 5 show the relative distribution of adducts obtained from cyanide addition to isomeric bis(η^6-methylphenoxy-η^5-cyclopentadienyl)ironbenzene hexafluorophosphate [**5**, **9**, and **12**] . In the case of complexes [**5**] and [**9**], single pure products [**10**] and [**11**] were obtained. Cyanide attack on [**5**] and [**9**] took place *meta* to the etheric bridge and *ortho* to the methyl group. In contrast, the *meta* isomer [**12**] gave rise to three possible adducts [**13a–c**]. These isomers displayed *ortho* addition with respect to both etheric and methyl substituents [**13a**] and addition *ortho* to the etheric bridge and *para* to the methyl group [**13b**]. As well, the asymmetrical isomer displayed addition *ortho* to one complexed arene ring with respect to both substituents and *ortho* to the etheric bridge, as well as *para* to the methyl substituent for the second complexed arene [**13c**]. The ^1H and ^{13}C NMR of the bimetallic adducts are listed in Tables 5 and 6.

Scheme 2.

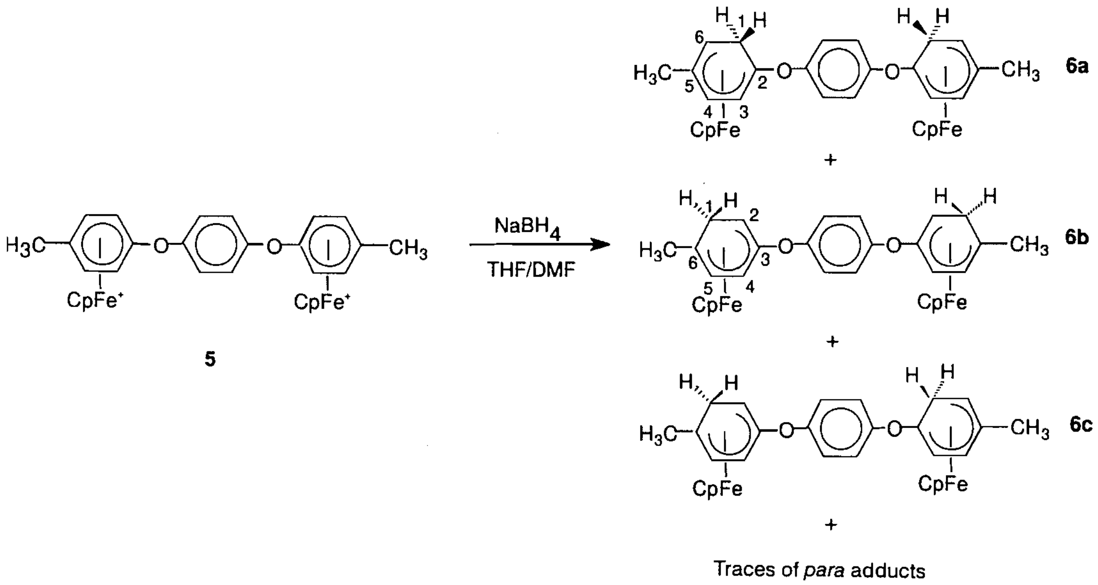


Table 3. ^{1}H NMR data for the adducts **6** and **8**.[a]

Adduct	CH$_3$	H(1-*exo*)	H(1-*endo*)	H(2)	H(3)	H(4)	H(5)	H(6)	Cp
6a	1.77 s	2.00 (d, 11.0, ex-en)	2.75 (dd, 10.8, en-ex; 5.9, en-6)	—	4.31 (d, 5.6)	5.56 (d, 5.6)	—	2.60 (d, 5.9, 6-en)	4.27 s
6b	1.36 s	1.85 (d, 10.7, ex-en)	2.41 m	2.43 (d, 6.0, 2-en)	—	6.05 (d, 5.7)	3.97 (d, 5.7)	—	4.24 s
8a	1.63, 2.70 s	1.66 (d, 12.7, ex-en)	2.39 (dd, 12.8, en-ex; 7.3, en-6)	—	—	—	4.16 m	2.03 m	4.14 s
8b	2.18 s	1.59 m	2.34 (dd, 12.1, en-ex, 7.3, en-2,6)	1.83 m	—	—	—	1.83 m	4.17 s

[a] Uncomplexed aromatic peaks appear as multiplet between 6.8 and 7.4 ppm. Coupling constants (Hz) are of adjacent aromatic protons unless otherwise indicated.

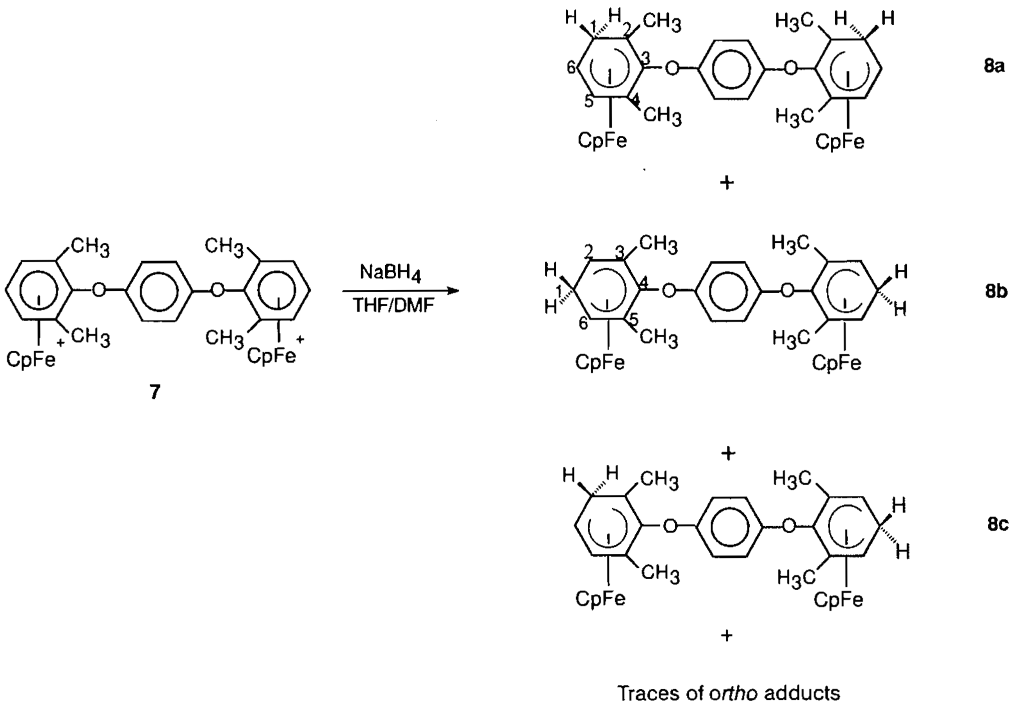
Table 4. ^{13}C NMR of the adducts **6** and **8**.[a]

Adduct	CH$_3$	C (1)	C (2)	C (3)	C (4)	C (5)	C (6)	Cp
6a	21.74	31.67	35.92	70.12	73.89	74.96	29.06	74.65
6b	24.87	33.10	18.30	93.85	68.98	75.10	18.79	74.53
8a	19.96, 16.41	34.94	29.74	97.37	89.45	78.17	16.95	75.35
8b	19.45	27.63	19.45	88.42	94.45	88.42	19.45	75.88

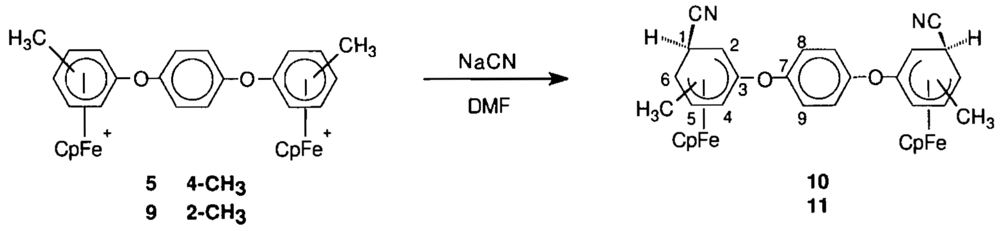
[a] Uncomplexed aromatic peaks appear at 117–128 ppm.

The higher selectivity of the cyanide addition was intriguing and prompted us to examine the polyiron systems. Polyaromatic ether complexes with pendant cyclopentadienyliron moieties [**14**]–[**19**] were treated with an excess of NaCN, as described in Scheme 6. Selective addition *meta* to the etheric bridges was obtained in all of these complexes, leading to the formation of the neutral (cyclohexadienyl)FeCp systems [**20**]–[**25**] in yields of 72–81% (based on the recovered starting cationic complexes). Separation of these adducts from their starting cationic complexes was carried out simply by

Scheme 3.



Scheme 4.



Scheme 5.

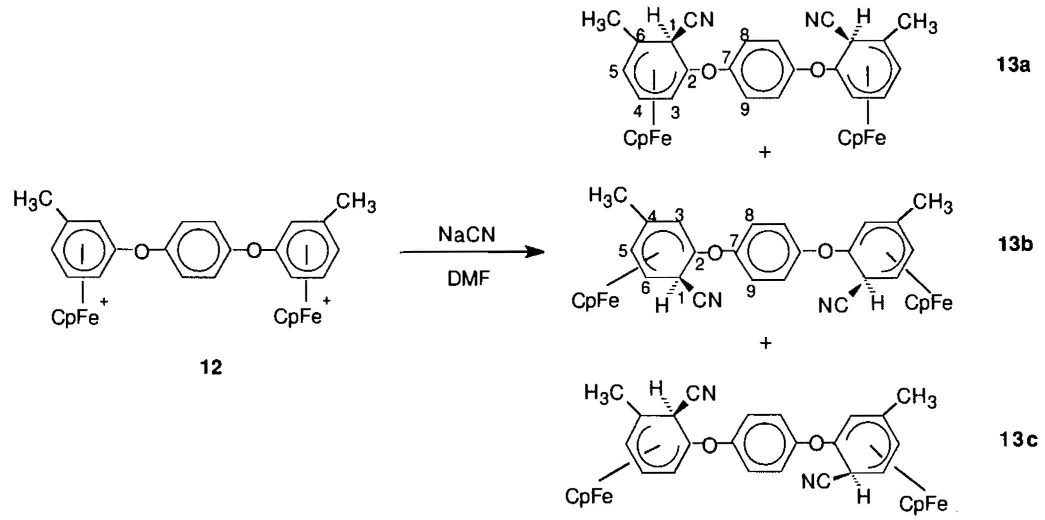


Table 5. ^{1}H NMR data for the adducts **10**, **11**, and **13**.[a]

Adduct	CH$_3$	H(1 endo)	H(2)	H(3)	H(4)	H(5)	H(6)	Cp	Ph
10	1.93	3.52	3.03	—	6.33	5.11	—	4.45	6.8–7.3
	s	(d, 5.5, en-2)	(d, 5.5, 2-en)		(d, 5.4)	(d, 5.4)		s	
11	2.19	3.54	—	—	6.33	4.79	2.96	4.44	6.8–7.3
	s	(d, 5.8, en-6)			(d, 5.6)	(t,5.6)	(t,5.6, 6-en;	s	
							t, 6.0)		
13a	1.71	3.51	—	5.08	6.25	4.57	—	4.47	6.8–7.3
	s	s		(d, 5.4)	(t, 5.4)	(d, 5.4)		s	
13b	2.58	3.46	—	5.03	—	4.77	2.98	4.49	6.8–7.3
	s	(d, 6.4, en-6)		s		(d, 6.4)	(t, 6.4)	s	

[a] Coupling constants (Hz) are of adjacent protons unless otherwise indicated.

Table 6. ^{13}C NMR of the adducts **10**, **11**, and **13**.

Adduct	**10**	**11**	**13***a*	**13***b*
CH$_3$	22.08	20.47	20.93	28.19
C (1)	28.66	28.59	33.62	23.39
C (2)	23.83	28.25	38.54	36.37
C (3)	96.66	94.49	81.14	81.76
C (4)	83.77	83.82	81.55	98.66
C (5)	79.00	80.02	78.36	80.16
C (6)	28.68	23.30	24.90	23.45
C (7)	123.38	122.77	123.61	123.42
C (8)	130.92	130.21	132.49	133.60
C (9)	128.80	126.18	129.17	128.00
CN	116.89	117.00	116.11	117.02
Cp	77.41	77.17	77.50	77.46

extracting the adducts from the mixture with chloroform. These results are consistent with those obtained for the analogous diiron complexes. Figure 2 illustrates ^{1}H NMR of the hepta-iron adduct [**24**] as an example of cyanide addition to the poly-iron series. The detailed NMR data for adducts [**20–25**] are given in Tables 7 and 8. Overall, the *meta* position is influenced by both the etheric and methyl substituents. Infrared spectroscopy was used to confirm the presence of the cyano groups. The ν_{CN} for all cyano adducts were in the range of 2228–2229 cm^{-1}. Our findings are consistant with those of Watts and co-workers, who proposed that addition is influenced by both the inductive and resonance effects of the substituents (29–32).

The free functionalized organic product can be obtained through a simple oxidative demetallation step using 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). As an example, a solution of di- or poly-iron cyclohexadienyl adducts [**10**] and [**24**] in acetonitrile was reacted with DDQ for 30 min, leading to the free organic compounds [**26**] and [**27**] in 75 and 78% yield, respectively (Scheme 6). Spectral and analytical data for these compounds are listed in the experimental section of the paper.

In conclusion, spectral data for the hydride reactions of mono- and di-iron arene complexes showed that the etheric substituent has a larger overall effect on the charge distribution on the ring in comparison to the methyl substituent(s). The proportions of the isomers for the bimetallic complexes were in agreement with their analogous monoiron species. In contrast, the reactions of the cyanide anion with di- and poly-iron arenes were selective, with addition at the *meta* position to the etheric bridges. The only isomer that gave a mixture of adducts was the bis[(η^6-3-methylphenoxy-η^5-cyclopentadienyl)iron]benzene hexafluorophosphate [**12**]. In this case, the addition was *ortho* and *para* to the methyl group and *ortho* to the etheric bridges. The oxidative demetallation proved to be successful, allowing for the liberation of the functionalized nitrile compounds from their corresponding iron moieties. The selectivity of the cyanide addition to the poly-iron system provides a unique route to the functionalization of polyaromatic ethers.

Experimental

Measurements

^{1}H and ^{13}C NMR spectra were recorded at 200 and 50 MHz (Gemini 200), respectively, while HH COSY and CH COSY were recorded on a Bruker 500 NMR spectrometer, with chemical shifts calculated from CDCl$_3$ (7.26 for proton and 77.00 for carbon). Coupling constants were measured in Hz. IR spectra were recorded with an FT-IR Bomem MB102 spectrometer.

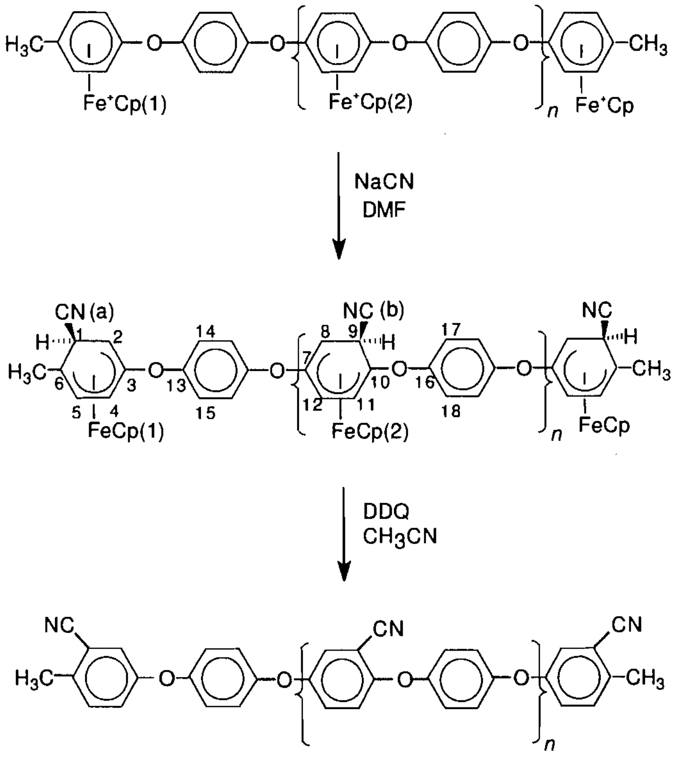
Reagents

Starting complexes [**1**, **2**, **5**, **7**, **9**, **12**, **13–28**] were prepared by established procedures (45-47). Sodium borohydride (Alfa), DDQ (Aldrich), and sodium cyanide (Aldrich) are commercially available and were used without further purification. All solvents (reagent grade) were used without further purification, with the exception of THF, which was freshly distilled. Silica gel, 60–100 mesh, was used in the column chromatographic purification of the liberated arenes.

Hydride addition reactions

In a 25 mL flask, 0.5 mmol of arene complex and 1.25 mmol of NaBH$_4$ (monoiron complexes) or 2.5 mmol of NaBH$_4$ (diiron complexes) in 10 mL of THF and 1.0 mL of DMF were stirred for 3 h under nitrogen. The bright orange product was then filtered through sintered glass, washed with 10 mL of water, and extracted with CHCl$_3$ (3 × 20 mL). The bright orange extract was washed with water, dried over MgSO$_4$, and the solvent was removed by rotary evaporation, yielding a red or orange oil.

Scheme 6.



Complex	*n*
14	1
15	2
16	3
17	4
18	5
19	6

Complex	*n*
20	1
21	2
22	3
23	4
24	5
25	6

Complex	*n*
26	0
27	5

Fig. 2. ^{1}H NMR spectrum of adduct **24** in CDCl$_3$.

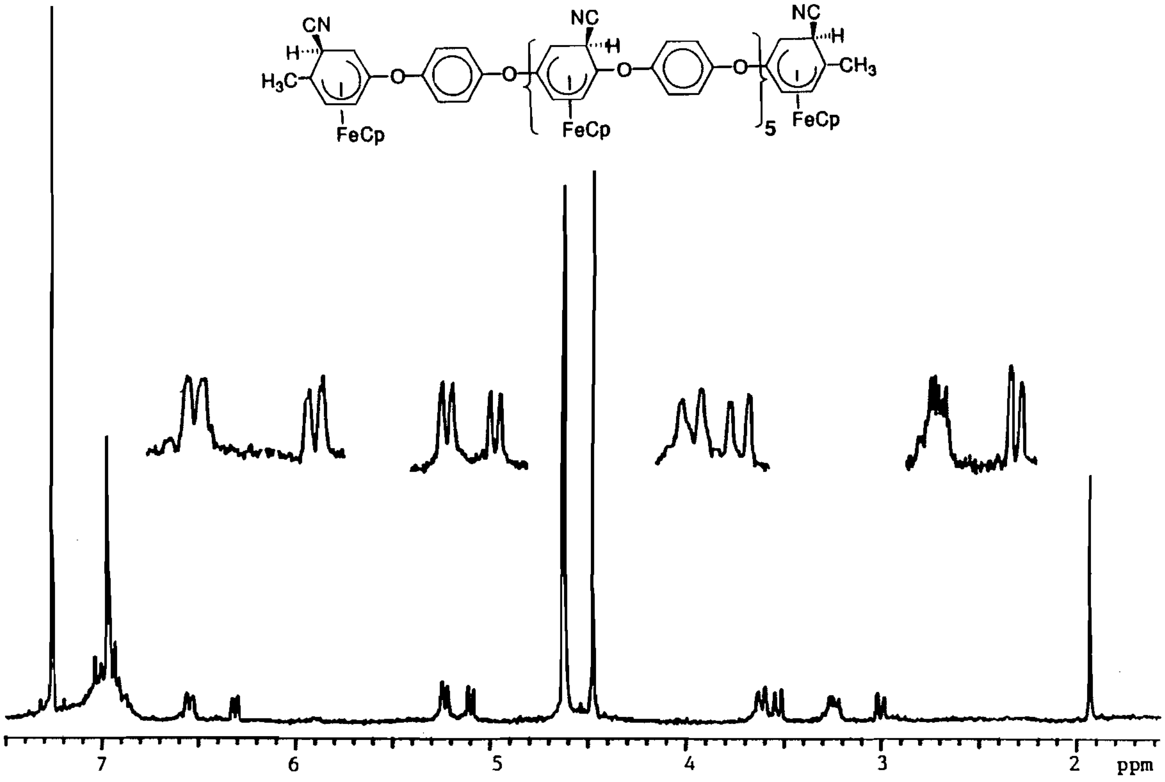


Table 7. ^{1}H NMR of the cyanide addition to the poly-iron series.[a]

Adduct	CH_3	H(1)	H(2)	H(4)	H(5)	H(8)	H(9)	H(11)	H(12)	Cp(1)	Cp(2)	Uncomp. ArH
20	1.93	3.53	3.01	6.31	5.10	3.24	3.61	5.21	6.54	4.48	4.60	6.8–7.4
	s	(d, 6.6)	(d, 6.6)	(d, 5.4)	(d, 5.4)	m	(d, 6.4)	(d, 6.1)	(d, 6.1)	s	s	m
21	1.93	3.55	3.02	6.31	5.12	3.25	3.63	5.25	6.55	4.48	4.62	6.8–7.4
	s	(d, 6.4)	(d, 6.4)	(d, 5.5)	(d, 5.5)	(d, 6.3)	(d, 6.3)	(d, 5.8)	(d, 5.8)	s	s	m
22	1.94	3.56	3.04	6.33	5.13	3.27	3.64	5.26	6.57	4.49	4.59	7.0–7.3
	s	(d, 6.8)	(d, 6.8)	(d, 5.5)	(d, 5.5)	m	(d, 5.9)	(d, 5.8)	(d, 5.8)	s	s	m
23	1.94	3.54	2.99	6.33	5.12	3.26	3.63	5.26	6.56	4.49	4.64	6.7–7.4
	s	(d, 6.7)	(d, 6.7)	(d, 6.5)	(d, 6.5)	m	(d, 6.8)	(d, 6.8)	(d, 6.8)	s	s	m
24	1.94	3.52	3.01	6.31	5.11	3.24	3.62	5.24	6.56	4.48	4.64	6.8–7.2
	s	(d, 5.8)	(d, 5.8)	(d, 5.7)	(d, 5.7)	m	(d, 6.8)	(d, 5.6)	(d, 5.6)	s	s	m
25	1.93	3.54	3.01	6.31	5.09	3.25	3.62	5.24	6.55	4.47	4.63	6.9–7.3
	s	(d, 6.7)	m	(d, 6.5)	(d, 6.5)	(d, 6.9)	(d, 6.9)	(d, 6.7)	(d, 6.7)	s	s	m

[a] Coupling constants (Hz) are of adjacent aromatic protons unless otherwise indicated.

Table 8. ^{13}C NMR of the cyanide addition to the poly-iron series.

Adduct	**20**	**21**	**22**	**23**	**24**	**25**
CN(a)	116.93	116.96	116.34	115.95	116.30	115.91
CN(b)	116.33	116.39	116.38	116.35	116.34	116.27
CH_3	22.09	22.04	22.07	22.02	20.51	20.52
Cp(1)	77.37	77.35	77.38	77.36	77.38	77.41
Cp(2)	78.18	78.17	78.19	78.18	78.19	78.16
C(1)	28.69	28.61	28.88	28.34	28.64	29.71
C(2)	26.06	26.00	25.21	26.06	25.98	25.95
C(3)	96.63	96.63	96.60	96.62	97.21	96.86
C(4)	83.74	83.72	83.68	83.59	83.57	83.58
C(5)	78.94	78.39	78.27	78.40	78.51	78.38
C(6)	29.55	28.88	28.55	28.76	28.57	28.74
C(7)	96.63	96.63	96.60	96.62	97.21	96.86
C(8)	26.00	25.99	26.08	26.04	26.12	26.39
C(9)	29.88	29.87	28.87	36.43	29.90	29.95
C(10)	33.03	29.65	29.78	29.86	29.78	29.83
C(11)	80.12	78.93	78.96	78.96	78.98	78.99
C(12)	83.67	83.64	83.74	83.72	83.72	83.74
C(13)	123.35	122.67	123.35	122.86	123.78	122.52
C(14)	129.95	129.01	129.80	129.67	128.75	128.80
C(15)	130.27	130.27	130.18	130.13	130.21	130.76
C(16)	123.35	122.67	123.35	122.86	123.78	122.52
C(17)	119.58	119.59	119.73	119.28	119.23	119.24
C(18)	119.26	120.12	119.79	119.87	119.81	119.73

Cyanide addition reactions

An example of the cyanide addition reactions: In a 25 mL flask, 0.5 mmol of 1,4-bis[(η^6-4-methylphenoxy-η^5-cyclopentadienyl)iron]benzene hexafluorophosphate and 3.0 mmol of NaCN in 5 mL of DMF and 1 drop of water were stirred for 3 h under a nitrogen atmosphere. The red solution was extracted with $CHCl_3$ (2 × 20 mL), washed with water, and dried over $MgSO_4$. The solvent was evaporated off, yielding a red oily product.

Demetallation reactions

To a solution of the adduct (0.5 mmol) in 10 mL of acetonitrile, 0.5 mmol of DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone) was added, and the resulting mixture was left to stir for 30 min at room temperature. The black solution was then filtered through sintered glass and evaporated to dryness. The product was dissolved in CH_2Cl_2, placed on a short silica gel column and eluted with $CHCl_3$ and CH_2Cl_2; the resulting solutions were dried over $MgSO_4$ and evaporated to dryness to give the free functionalized polyaromatic ethers (**26** and **27**), which have been characterized:

26: ν_{CN}: 2236 cm^{-1}. ^{1}H NMR δ: 2.50 (s, $2CH_3$), 6.90 (d, 8.6 Hz, 2H, Ar), 7.11 (d, 8.6 Hz, 2H, Ar), 7.54 (d, 7.8 Hz, 2H, Ar), 7.63 (s, 2H, Ar), 7.71 (d, 8.0 Hz, 2H, Ar); ^{13}C NMR δ: 21.66 (CH_3), 115.81 (CN), 117.74, 120.46, 130.04, 133.38, 133.88 (ArH), 112.90, 115.52, 144.70 (q). Anal. calcd. for $C_{22}H_{16}O_2N_2$: C 77.63, H 4.74, N 8.23; found: C 77.41, H 4.93, N 8.41.

27: ν_{CN}: 2234 cm^{-1}. ^{1}H NMR δ: 2.49 (s, 6H, CH_3), 7.64 (s, 2H, Ar), 7.76 (d, 8.1 Hz, 2H, Ar), 7.54 (d, 8.1 Hz, 2H, Ar), 7.63 (s, 5H, Ar), 7.57 (d, 8.1 Hz, 5H, Ar), 7.73 (d, 8.1 Hz, 5H, Ar), 6.77–7.34 (m, 24H, Ar). ^{13}C NMR δ: 21.70 (CH_3), 115.40, 115.23 (CN), 119.41, 119.82, 121.90 , 122.71, 130.53, 130.92, 134.36, 133.40 (ArH), 112.57, 115.22, 115.30, 144.31 (q). Anal. calcd. for $C_{87}H_{51}O_{12}N_7$: C 75.37, H 3.71, N 7.07; found: C 75.22, H 3.89, N 6.92.

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