

ADDITION OF THE CYANIDE ION TO CYCLOPENTADIENYLIRON COMPLEXES OF ARENES CONTAINING AN ELECTRON-WITHDRAWING SUBSTITUENT

R.G. SUTHERLAND*, R.L. CHOWDHURY, A. PIÓRKO, and C.C. LEE*

Department of Chemistry, University of Saskatchewan, Saskatoon, Saskatchewan S7N 0W0 (Canada)

(Received July 29th, 1986)

Summary

Reactions of cyclopentadienyliron (CpFe) complexes of arenes containing an electron-withdrawing substituent with NaCN in DMF resulted in a regiospecific addition of the cyanide ion at a position *ortho* to the substituent, giving rise to CpFe complexes of cyanocyclohexadienyl systems. For example, the addition of the cyanide ion to η^6 -nitrobenzene- η^5 -cyclopentadienyliron hexafluorophosphate (Ia) gave the neutral complex, 1-5- η^5 -*exo*-6-cyano-1-nitrocyclohexadienyl- η^5 -cyclopentadienyliron (IIa). Similar cyanide additions also took place with the CpFe complexes of benzophenone and of methyl benzoate. Reactions with η^6 -anthraquinone, xanthone, thioxanthone, or thioxanthone-10,10-dioxide- η^5 -cyclopentadienyliron hexafluorophosphate (IIIa, IIIb, IIIc or IIId, respectively) resulted in the addition of the cyanide ion solely to C(1), a position *ortho* to the keto substituent; for example, from IIIa, the adduct was 2,3,4,4a,9a- η^5 -*exo*-1-cyano-1*H*-anthraquinone- η^5 -cyclopentadienyliron (IVa). With the CpFe complex of fluorenone (V), however, a 3/1 mixture of products was obtained, arising from cyanide additions to C(1) and C(4a), both positions being *ortho* to the keto substituent in V. A possible explanation is suggested for the failure of the cyanide ion adding to C(4a) in reactions with IIIa to IIId.

Introduction

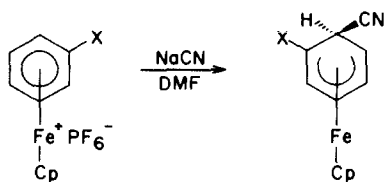
Additions of the cyanide ion to cationic manganese tricarbonyl complexes of arenes such as benzene, xylene and mesitylene to give cyanocyclohexadienyl complexes have been extensively studied by Walker and Mawby [1–3]. Similar cyanide additions to manganetricarbonyl complexes of cycloheptatriene [4,5] or thiophene [6] have also been investigated. With iron tricarbonyl complexes of derivatives of cyclohexadiene, cyanide addition to the more electron-deficient terminus of the dienyl system was observed [7,8]. An addition of the cyanide ion to one of the rings

in the bis(mesitylene)iron(II) dication has also been reported [9]. On the other hand, it is known that the cyanide ion could act as a nucleophile in an aromatic substitution reaction replacing the chloro group when it was treated with the η^6 -chlorobenzene- η^5 -cyclopentadienyliron cation [10]. Recently, we have reported [11] that the nitro group in cyclopentadienyliron (CpFe) complexes of nitroarenes could undergo nucleophilic aromatic substitution reactions (S_NAr reactions) with the nitrite ion as the leaving group when treated with a nucleophile derived from an alcohol, a thiol or an amine. However, when η^6 -nitrobenzene- η^5 -cyclopentadienyliron hexafluorophosphate (Ia) reacts with the cyanide ion, an addition rather than a substitution takes place. This paper reports our observations on the addition of the cyanide ion to CpFe complexes of arenes containing an electron-withdrawing substituent.

Results and discussion

The reaction of η^6 -nitrobenzene- η^5 -cyclopentadienyliron hexafluorophosphate (Ia) with powdered NaCN in *N,N*-dimethylformamide (DMF) at room temperature resulted in a regiospecific *exo*-addition of the cyanide ion at an *ortho* position to the NO_2 group to give the neutral complex 1-5- η^5 -*exo*-6-cyano-1-nitrocyclohexadienyl- η^5 -cyclopentadienyliron (IIa). Similarly, the addition of the cyanide ion to η^6 -benzophenone- η^5 -cyclopentadienyliron hexafluorophosphate (Ib) or η^6 -methyl benzoate- η^5 -cyclopentadienyliron hexafluorophosphate (Ic) gave rise, respectively, to 1-5- η^5 -*exo*-6-cyano-1-benzoylcyclohexadienyl- η^5 -cyclopentadienyliron (IIb) or 1-5- η^5 -*exo*-6-cyano-1-methoxycarbonylcyclohexadienyl- η^5 -cyclopentadienyliron (IIc). These behaviors are very similar to those recently reported from our laboratory [12,13] on the Janovsky reaction between carbanions derived from ketones and CpFe complexes of substituted arenes; for example, the regiospecific *exo*-addition of the acetyl anion to Ia gave rise to 1-5- η^5 -6-*exo*-(2-oxo-1-propyl)-1-nitrocyclohexadienyl- η^5 -cyclopentadienyliron. The yields, analytical data and some characteristic IR absorptions for IIa, IIb and IIc are given in Table 1.

Exo-addition of nucleophiles to CpFe complexes of arenes are well known [14,15] and the addition of the cyanide ion to complexed arenes has also been formulated as *exo* [1,9]. By analogy, the cyano group in the presently obtained products is assigned the *exo*-configuration. The magnitudes of coupling constants for the



Ia, X = NO₂

Ib, X = COC₆H₅

Ic, X = COOCH₃

IIa, X = NO₂

IIb, X = COC₆H₅

IIc, X = COOCH₃

TABLE 1

YIELDS, ANALYTICAL DATA AND SOME IR ABSORPTIONS FOR CYANO ADDUCTS DERIVED FROM CpFe COMPLEXES OF SUBSTITUTED ARENES

Complex	Yield (%)	Analysis (Found(calc) (%))			IR (cm ⁻¹)
		C	H	N	
IIa	80	53.77 (53.37)	3.95 (3.73)	10.09 (10.37)	1290,1490 (NO ₂); 2220 (CN)
IIb	82	68.96 (69.33)	4.38 (4.59)	4.38 (4.25)	1600 (CO); 2215 (CN)
IIc	75	59.49 (59.39)	4.51 (4.63)	5.12 (4.95)	1685 (CO); 2220 (CN)
IVa	85	67.98 (67.63)	3.70 (3.69)	4.09 (3.94)	1625,1660 (CO); 2220 (CN)
IVb	60	66.72 (66.50)	3.68 (3.82)	4.28 (4.08)	1640 (CO); 2220 (CN)
IVc	70	63.20 (63.53)	3.53 (3.65)	3.79 (3.90)	1640 (CO); 2220 (CN)
IVd	85	58.03 (58.33)	3.32 (3.35)	3.50 (3.58)	1645 (CO); 2220 (CN)
VIa + VIb	82	69.91 (69.75)	3.89 (4.00)	4.17 (4.28)	1660 (CO); 2220 (CN)

various cyclohexadienyl protons in IIa–IIc with the *endo*-proton at C(6) (vide infra) are quite similar to the analogous values recently reported for η^5 -cyclohexadienyl complexes [16], thus giving further support to the *exo*-configuration for the cyano group in adducts IIa–IIc.

The ¹H NMR data for IIa, IIb and IIc, obtained with a high resolution 300 MHz instrument, are summarized in Table 2. These results are consistent only with a regioselective addition of the cyanide ion to a position *ortho* to the nitro, benzoyl or methoxycarbonyl substituent in Ia, Ib, or Ic, respectively. Consider in more detail, for example, complex IIc. H(2), the proton at the C(2) position of the complexed cyclohexadienyl ring, at 5.39 ppm, is split by H(3) giving a doublet (d, *J*(2–3) 5.5 Hz) which in turn is split by H(4) and H(6) (t, *J*(2–4) = *J*(2–6) = 1.0 Hz) giving rise

TABLE 2

¹H NMR DATA FOR COMPLEXES IIa, IIb AND IIc

Complex	δ (CDCl ₃) (ppm from TMS)						
	Cp	H(2)	H(3)	H(4)	H(5)	H(6)	Others
IIa	4.47(s,5H)	5.95	6.45	5.00	3.49	4.49	
	<i>J</i> (2–3) = <i>J</i> (3–4) = 5.7 Hz; <i>J</i> (4–5) 6.5 Hz; <i>J</i> (5–6) 6.9 Hz; <i>J</i> (2–4) = <i>J</i> (3–5) = 1.2 Hz; <i>J</i> (4–6) 1.6 Hz; <i>J</i> (2–6) 0.8 Hz						
IIb	4.27(s,5H)	5.56	6.46	4.95	3.05	4.20	7.42–7.62(m,5H, uncomplexed Ar)
	<i>J</i> (2–3) = <i>J</i> (3–4) = 5.4 Hz; <i>J</i> (4–5) 6.3 Hz; <i>J</i> (5–6) 6.6 Hz						
IIc	4.33(s,5H)	5.39	6.40	4.80	2.93	3.96	3.74(s,3H,CH ₃)
	<i>J</i> (2–3) = <i>J</i> (3–4) = 5.5 Hz; <i>J</i> (4–5) 6.2 Hz; <i>J</i> (5–6) 6.6 Hz; <i>J</i> (2–4) = <i>J</i> (3–5) = <i>J</i> (2–6) = 1.0 Hz; <i>J</i> (4–6) 0.8 Hz						

TABLE 3
 ^{13}C NMR DATA FOR COMPLEXES IIa, IIb AND IIc

Complex	$\delta(\text{CDCl}_3)$ (ppm from TMS) ^a					
	Cp	C(1)	C(2,3,4)	C(5)	C(6)	Others
IIa	77.4	60.3* (127.5)	78.1, 82.4, 82.5 (83.5, 87.7, 90.0)	30.4, $J(\text{C-H})$ 179.2 Hz (80.7)	27.5, $J(\text{C-H})$ 150.4 Hz (83.5)	CN 116.5
IIb	76.0	30.7* (98.1*)	82.1, 84.2 ^b (83.7, 88.9, 89.4)	24.0, $J(\text{C-H})$ 176.4 Hz (87.7)	24.6, $J(\text{C-H})$ 148.9 Hz (88.9)	118.8 127.1, 128.6, 131.0, 139.5* (uncomplexed Ar); 202.8(CO)
IIc	75.6	22.3* (89.5*)	81.2, 83.3 ^b (89.4, 89.8, 90.8)	24.4, $J(\text{C-H})$ 172.8 Hz (89.4)	24.8, $J(\text{C-H})$ 146.8 Hz (89.8)	118.2 51.8(CH ₃ O) 174.5(CO)

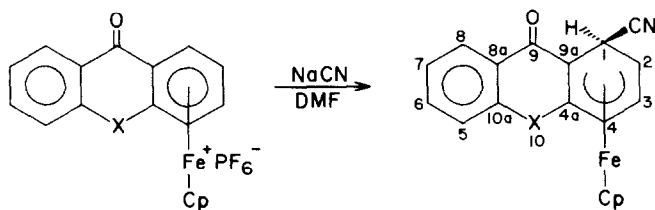
^a Asterisks denote quaternary carbons. Values given in parentheses are the chemical shifts for the corresponding carbons in the precursor complexed arenes Ia, Ib and Ic. $J(\text{C-H})$ are one bond coupling constants. ^b Overlapping chemical shifts for C(2) and C(4).

to 6 lines as a doublet of triplets. H(3), at δ 6.40 ppm, is split by H(2) and H(4) to give a triplet (t, $J(3-2) = J(3-4) = 5.5$ Hz) which in turn is split by H(5) (d, $J(3-5)$ 1.0 Hz) again giving rise to 6 lines as a triplet of doublets. H(4), at δ 4.80 ppm, is unsymmetrically split by H(3) (d, $J(4-3)$ 5.5 Hz), H(5) (d, $J(4-5)$ 6.2 Hz), H(2) (d, $J(4-2)$ 1.0 Hz) and H(6) (d, $J(4-6)$ 0.8 Hz) giving a total of 12 lines. H(5), at δ 2.93 ppm, is also unsymmetrically split by H(4) (d, $J(5-4)$ 6.2 Hz), H(6) (d, $J(5-6)$ 6.6 Hz) and H(3) (d, $J(5-3)$ 1.0 Hz) giving a doublet of doublets of doublets as 8 lines. Finally, H(6), at δ 3.96 ppm, is split by H(5) (d, $J(6-5)$ 6.6 Hz) H(2) (d, $J(6-2)$ 1.0 Hz) and H(4) (d, $J(6-4)$ 0.8 Hz) giving rise to 8 lines. These splitting patterns definitely establish the structure of IIc with the methoxycarbonyl substituent at C(1) and the cyano group at C(6).

Data from the ^{13}C NMR spectra of adducts IIa, IIb and IIc are summarized in Table 3. The assignments for C(5) and C(6) are based on the magnitudes of the C-H coupling constants, determined by gated decoupling, with the alicyclic C(6) giving lower $J(\text{C-H})$ values of around 150 Hz, while the complexed C(5), retaining some aromatic character, gave $J(\text{C-H})$ values of about 175 Hz [17,18]. The large upfield shifts [17,19] of around 65 ppm for C(1), C(5) and C(6) in IIa, IIb and IIc, when compared with the chemical shifts of the corresponding carbons in the precursor complexed arenes Ia, Ib and Ic, again support the addition of the cyanide ion at C(6), a position *ortho* to the electron-withdrawing substituent in the original complexed arene.

It has been pointed out earlier that the cyanide ion would add to the more electron deficient terminus of a cyclohexadiene system in iron tricarbonyl complexed cyclohexadienes [7,8]. A 1/1/1 ratio for the addition of the hydride ion to the *o*-, *m*- and *p*-positions of the CpFe complex of toluene (I, X = CH₃) has been reported [20], while in the hydride addition to CpFe complexed chlorobenzene [I, X = Cl] and methyl benzoate (Ic), the ratios for *o*-, *m*- and *p*-additions were found to be 4/1/0 [21] and 12.7/1/1.1 [22], respectively. It was pointed out that the methoxycarbonyl substituent of Ic, with both an electron-withdrawing inductive effect (-I) and an electron-withdrawing resonance effect (-R), was most effective in giving rise to *o*-addition of the hydride ion, suggesting that the distribution of products was controlled principally by differences in positive charge concentration at the various arene carbons occasioned by the presence of the ring substituent [22]. The presently observed regiospecific *o*-addition of the cyanide ion is most likely attributable to the strong electron-withdrawing effect of the nitro, benzoyl and methoxycarbonyl substituents in Ia, Ib and Ic.

As an extension of the work with CpFe complexes of substituted benzenes Ia, Ib and Ic, cyanide addition to a number of CpFe complexes of tricyclic aromatic systems, including the hexafluorophosphate salt of the η^6 -anthraquinone, xanthone, thioxanthone, or thioxanthone-10,10-dioxide- η^5 -cyclopentadienyliron cation (IIIa, IIIb, IIIc or IIId, respectively), was investigated. In all of these cases, regiospecific addition of the cyanide ion to C(1), which is *ortho* to an electron-withdrawing keto substituent, was observed, giving rise to 2,3,4,4a,9a- η^5 -*exo*-1-cyano-1*H*-anthraquinone- η^5 -cyclopentadienyliron (IVa), 2,3,4,4a,9a- η^5 -*exo*-1-cyano-1*H*-xanthone- η^5 -cyclopentadienyliron (IVb), 2,3,4,4a,9a- η^5 -*exo*-1-cyano-1*H*-thioxanthone- η^5 -cyclopentadienyliron (IVc), and 2,3,4,4a,9a- η^5 -*exo*-1-cyano-1*H*-thioxanthone-10,10-dioxide- η^5 -cyclopentadienyliron (IVd), respectively, from IIIa, IIIb, IIIc and IIId. The yields, analytical data and characteristic IR absorptions for these adducts



IIIa, X = CO
 IIIb, X = O
 IIIc, X = S
 IIId, X = SO₂

IVa, X = CO
 IVb, X = O
 IVc, X = S
 IVd, X = SO₂

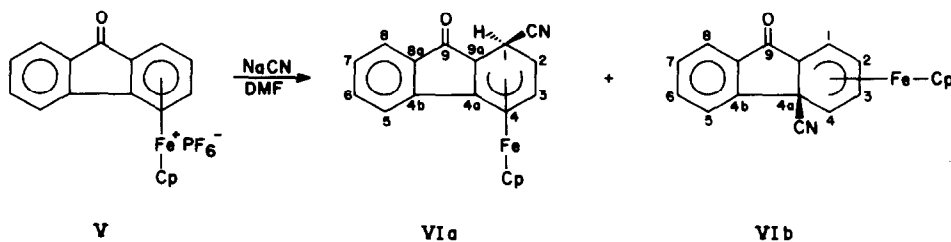
are included in Table 1. Data from the ¹H and ¹³C NMR spectra of adducts IVa, IVb, IVc and IVd are summarized in Tables 4 and 5, and these results, as discussed earlier for IIa, IIb and IIc, are consistent with the structures assigned to these neutral complexes.

When η⁶-fluorenone-η⁵-cyclopentadienyliron hexafluorophosphate (V) was treated with NaCN in DMF, a mixture of two products, 2,3,4,4a,9a-η⁵-1-*exo*-cyano-1*H*-fluorenone-η⁵-cyclopentadienyliron (VIa) and 9a,1,2,3,4-η⁵-4a-*exo*-cyano-4a*H*-fluorenone-η⁵-cyclopentadienyliron (VIb), were obtained, the ratio of VIa/VIb being about 3/1 as estimated from the ¹H NMR spectrum of the mixed products. These results indicate the addition of cyanide ion to C(1) and to C(4a), both of which are *ortho* to

TABLE 4

¹H NMR DATA FOR COMPLEXES IVa, IVb, IVc, AND IVd

Complex	δ(CDCl ₃) (ppm from TMS)					
	Cp	H(1)	H(2)	H(3)	H(4)	Uncomplexed Ar
IVa	4.20(s,5H)	4.49	3.40	5.23	7.47	7.63-7.73(m,2H), 8.11-8.17(m,2H)
		<i>J</i> (1-2) = <i>J</i> (2-3) = 6.4 Hz; <i>J</i> (3-4) 5.6 Hz, <i>J</i> (2-4) 0.8 Hz				
IVb	4.15(s,5H)	4.40	3.07	4.99	6.88	7.19-7.27(m,2H), 7.52-7.58(m,1H), 8.15-8.18(m,1H)
		<i>J</i> (1-2) = <i>J</i> (2-3) = 6.1 Hz; <i>J</i> (3-4) 5.5 Hz				
IVc	4.22(s,5H)	4.40	3.44	5.27	7.32	7.74-7.77(m,2H), 8.00-8.03(m,1H), (8.26-8.30(m,1H)
		<i>J</i> (1-2) = <i>J</i> (2-3) = 6.5 Hz; <i>J</i> (3-4) 5.5 Hz; <i>J</i> (2-4) 1.0 Hz; <i>J</i> (1-3) 0.5 Hz				
IVd	4.39(s,5H)	4.18	3.49	5.12	7.27	7.73-7.85(m,2H), 7.99-8.05(m,1H) 8.22-8.30(m,1H)
		<i>J</i> (1-2) = <i>J</i> (2-3) = 7.5 Hz; <i>J</i> (3-4) 5.7 Hz; <i>J</i> (1-3) = <i>J</i> (2-4) = 0.6 Hz				



the keto substituent in V. The yield, analytical data and some IR absorptions for this mixture of products are included in Table 1. The ^1H and ^{13}C NMR spectra definitely showed the presence of a mixture of products, and the integrated intensities of the Cp peaks in the ^1H NMR spectrum, for example, gave a ratio of 3/1 for the two products. The data from the ^1H and ^{13}C NMR spectra, as summarized in Table 6, are in agreement with structures VIa and VIb, and the relative intensities indicate that VIa is the major product.

Since reaction with V gave rise to cyanide addition at C(1) and at C(4a), the question arises as to why cyanide addition took place only at C(1) and not at C(4a) in reactions with IIIa to IIIc. As a possible explanation, it might be suggested that, with IIIa and IIIc, a positive charge developing at C(4a) would be destabilized by the presence of the electron-withdrawing CO or SO_2 group directly attached to C(4a), while with IIIb and IIIc, any positive character developing at C(4a) would be decreased by the presence of the electron-donating O or S function, again directly attached to C(4a). The overall result was that the addition of the cyanide ion took place only at the most electron-deficient center at C(1).

It may also be of interest to point out that the present results may have potential for synthetic applications. Pearson and coworkers [23] have reported that complexed cyclohexadienyl systems, when treated with ammonium ceric nitrate, could give rise to demetallation-oxidation, liberating the substituted arene ligand. A preparation of (2,5-dichlorophenyl)propanone from such a demetallation-oxidation of the Janovsky adduct obtained from addition of the acetyl anion to the CpFe complexed *p*-dichlorobenzene has been described [13]. With the presently obtained cyanide addition products, demetallation-oxidation by treatment with ammonium ceric nitrate could liberate arenes containing a cyano group *ortho* to an electron-withdrawing substituent. Such functionalization by the direct introduction of a cyano group to an aromatic ring should have potential for further synthetic applications.

Experimental

All ^1H and ^{13}C NMR spectra were obtained using a Bruker AM300 spectrometer and the IR data were recorded with a Perkin-Elmer 781 spectrometer. The elemental analyses were carried out in the Analytical Services Laboratory of the Department of Chemistry of this University.

(Continued on p. 388)

TABLE 5
 ^{13}C NMR DATA FOR COMPLEXES IVa, IVb, IVc AND IVd

Complex	$\delta(\text{CDCl}_3)$ (ppm from TMS) ^{a,b,c}									
	Cp	C(1)	C(2)	C(3)	C(4)	C(4a)	C(9a)	CN	CO	Uncomplexed Ar
IVa	78.7	21.6 $J(\text{C}-\text{H})$ 152.2 Hz	28.2 $J(\text{C}-\text{H})$ 174.5 Hz	84.7	83.2	83.7*	31.6*	117.7	188.9	126.3, 126.8, 133.5
IVb	75.6	22.7 $J(\text{C}-\text{H})$ 142.0 Hz	24.9 $J(\text{C}-\text{H})$ 172.6 Hz	78.3	71.9	129.4*	27.5*	117.8	191.3	134.4, 132.8*, 134.0*
IVc	79.2	22.0 $J(\text{C}-\text{H})$ 147.8 Hz	28.7 $J(\text{C}-\text{H})$ 175.2 Hz	82.3	81.1	98.4*	26.7*	116.9	187.4	117.3, 123.4, 126.4, 134.4, 121.7*, 156.4*
IVd	79.2	23.0 $J(\text{C}-\text{H})$ 147.5 Hz	29.0 $J(\text{C}-\text{H})$ 175.8 Hz	83.4	82.0	96.4*	28.9*	115.9	186.3	122.3, 128.2, 133.4, 133.5, 130.1*, 140.7*
									185.5	123.8, 127.8, 128.2, 133.1, 133.2*, 140.6*

^a Asterisks denote quaternary carbons. ^b The chemical shift values for the parent cations have previously been published in [25] and [26]. ^c $J(\text{C}-\text{H})$ are one-bond coupling constants.

TABLE 6
 ^1H AND ^{13}C NMR DATA FOR COMPLEXES VIa AND VIb

Complex	$\delta(\text{CDCl}_3)$ (ppm from TMS) ^{a,b,c}	H(1) or C(1)	H(2) or C(2)	H(3) or C(3)	H(4) or C(4)	C(4a)	C(9a)	Others	Uncomplexed Ar
$^1\text{H NMR}$									
VIa	4.10(s,5H)	4.15	3.18	5.09	7.02				7.10–7.24(m,1H),7.40–8.00(m,3H) (overlapping with VIb)
	$J(1-2) = J(2-3) = 6.3 \text{ Hz}; J(3-4) 5.2 \text{ Hz}; J(2-4) 0.5 \text{ Hz}$								
VIb	4.18(s,5H)	5.64	6.55	5.07	3.38				7.10–7.24(m,1H),7.40–8.00(m,3H) (overlapping with VIa)
	$J(1-2) = J(2-3) = 5.2 \text{ Hz}; J(3-4) 6.3 \text{ Hz}; J(2-4) 0.8 \text{ Hz}$								
$^{13}\text{C NMR}$									
VIa	77.7	22.7 $J(\text{C-H})$ 147.8 Hz	28.3 $J(\text{C-H})$ 169.3 Hz	81.4	78.7	93.7*	31.7*	117.8(CN) 201.0(CO)	119.3,122.3,128.3, 133.3,131.8*,145.1*
VIb	77.4	81.8	85.1	74.6	34.7 $J(\text{C-H})$ 173.6 Hz	38.0*	36.6*	118.6(CN) 194.9(CO)	122.8,124.3,129.5, 132.9,140.1*,147.5*

^a Asterisks denote quaternary carbon in the ^{13}C NMR spectrum. ^b The chemical shift values for the parent cations have previously been published in [25] and [26].
^c $J(\text{C-H})$ are one-bond coupling constants.

Arene complexes

The various CpFe complexes of substituted arenes employed in the reactions with cyanide ion were prepared using known procedures. The nitrobenzene complex Ia was obtained from oxidation of the CpFe complex of aniline [24]. The methyl benzoate complex Ic was prepared as described by McGreer and Watts [22]. The CpFe complexes of benzophenone (Ib), anthraquinone (IIIa) and fluorenone (V) were obtained from the in situ KMnO_4 oxidation of the corresponding CpFe complexed diphenylmethane, anthracene and fluorene as these latter complexes were prepared from ligand exchange reactions [25]. Similarly, the CpFe complexes of xanthone (IIIb), thioxanthone (IIIc) and thioxanthone-10,10-dioxide (IIId) were obtained from the in situ KMnO_4 oxidation of the CpFe complex of xanthene or thioxanthene [26].

Cyanide addition reactions

The same procedure applies to the addition of the cyanide ion to all of the arene complexes studied in the present work. The following are illustrations of typical experiments.

To a stirred solution of 500 mg (1.29 mmol) of η^6 -nitrobenzene- η^5 -cyclopentadienyliron hexafluorophosphate (Ia) in 5.0 ml of DMF, 300 mg (6.12 mmol) powdered NaCN was introduced and 1 or 2 drops of H_2O was added to bring the mixture into solution. The material was then stirred vigorously at room temperature for 30–40 min when the initially yellow solution became very dark in color. The cyanide addition product was recovered by extraction with CHCl_3 (4×50 ml), the extract washed with H_2O (3×50 ml) and dried over MgSO_4 . The solvent was removed by a rotary evaporator at about 40°C under reduced pressure and the residual oil was crystallized from ether/pentane at about -20°C to give 277 mg (80%) of adduct IIa as a dark purple solid.

A similar reaction between 500 mg (1.05 mmol) of η^6 -anthraquinone- η^5 -cyclopentadienyliron hexafluorophosphate (IIIa) and 300 mg (6.12 mmol) of powdered NaCN in 5.0 ml of DMF, using the same work-up procedure as described above for the preparation of IIa, gave 317 mg (85%) of adduct IVa as a dark green solid.

When 500 mg (1.12 mmol) of η^6 -fluorenone- η^5 -cyclopentadienyliron hexafluorophosphate (V) was treated with 300 mg (6.12 mmol) of powdered NaCN and the reaction mixture worked up in the same way, the product (300 mg, 82%) was recovered as an oil which was characterized by high resolution NMR as a 3/1 mixture of VIa and VIb.

Acknowledgment

The financial support given by the Natural Sciences and Engineering Research Council of Canada is sincerely acknowledged.

References

- 1 P.J.C. Walker and J.R. Mawby, *Inorg. Chem.*, 10 (1971) 404.
- 2 P.J.C. Walker and J.R. Mawby, *J. Chem. Soc., Dalton Trans.*, (1973) 622.
- 3 P.J.C. Walker and J.R. Mawby, *Inorg. Chim. Acta*, 7 (1973) 621.
- 4 F. Haque, J. Miller, P.L. Pauson, and J.B. Pd. Tripathi, *J. Chem. Soc. (C)*, (1971) 743.

- 5 E.D. Honig, M. Quin-jin, W.T. Robinson, P.G. Williard, and D.A. Sweigart, *Organometallics*, 4 (1985) 871.
- 6 D.A. Lesch, J.W. Richardson, Jr., R.A. Jacobson, and R.J. Angelici, *J. Am. Chem. Soc.*, 106 (1984) 2901.
- 7 A.J. Pearson, *J. Chem. Soc., Chem. Commun.*, (1977) 339.
- 8 A.J. Pearson, *J. Chem. Soc., Perkin Trans. I*, (1978) 495.
- 9 J.F. Helling and G.G. Cash, *J. Organomet. Chem.*, 173 (1974) C10.
- 10 A.N. Nesmeyanov, N.A. Vol'kenau, and I.N. Bolesova, *Dokl. Akad. Nauk SSSR*, 175 (1967) 606.
- 11 R.L. Chowdhury, C.C. Lee, A. Piórko and R.G. Sutherland, *Synth. React. Inorg. Met.-Org. Chem.*, 15 (1985) 1237.
- 12 R.G. Sutherland, R.L. Chowdhury, A. Piórko, and C.C. Lee, *J. Chem. Soc., Chem. Commun.*, (1985) 1296.
- 13 R.G. Sutherland, R.L. Chowdhury, A. Piórko, and C.C. Lee, *Can. J. Chem.*, in press.
- 14 S.G. Davies, M.L.H. Green, and D.M.P. Mingos, *Tetrahedron*, 34 (1978) 3047.
- 15 P.L. Pauson, *J. Organomet. Chem.*, 200 (1980) 207.
- 16 S.L. Grundy and P.M. Maitlis, *J. Organomet. Chem.*, 272 (1984) 265.
- 17 A.N. Nesmeyanov, E.I. Fedin, P.V. Petrovskii, B.V. Lokshin, L.S. Kotova, and N.A. Vol'kenau, *Koord. Khim.*, 1 (1975) 550.
- 18 E. Breitmaier and W. Voelter, ¹³C NMR Spectroscopy, 2nd Ed., Verlag Chemie, New York, 1978, pp. 93-99.
- 19 D. Astruc, J.-R. Hamon, E. Román, and P. Michaud, *J. Am. Chem. Soc.*, 103 (1981) 7502.
- 20 I.U. Khand, P.L. Pauson, and W.E. Watts, *J. Chem. Soc. (C)*, (1968) 2257.
- 21 I.U. Khand, P.L. Pauson, and W.E. Watts, *J. Chem. Soc. (C)*, (1968) 2261.
- 22 J. McGreer and W.E. Watts, *J. Organomet. Chem.*, 110 (1976) 103.
- 23 A.J. Pearson, P.R. Bruhn, and I.C. Richards, *Israel J. Chem.*, 24 (1984) 93.
- 24 C.C. Lee, U.S. Gill, M. Iqbal, C.I. Azogu, and R.G. Sutherland, *J. Organomet. Chem.*, 231 (1982) 151.
- 25 C.C. Lee, K.J. Demchuk, U.S. Gill, and R.G. Sutherland, *J. Organomet. Chem.*, 247 (1983) 71.
- 26 C.C. Lee, U.S. Gill, and R.G. Sutherland, *J. Organomet. Chem.*, 267 (1984) 157.