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Studies on some mono- and di-substitution reactions with cyclopentadienyliron complexes of *o*-, *m*- and *p*-dichlorobenzenes

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Abstract

Reaction of the cyclopentadienyliron (CpFe) complex of *o*-, *m*- or *p*-dichlorobenzene (Ia, Ib or Ic, respectively) with an excess of n-butylamine gave only monosubstitution of one of the two chloro groups, while a similar reaction carried out in the presence of some added HOAc resulted in disubstitution of both chloro groups. On the other hand, in the reaction of Ia, Ib or Ic with one equivalent or with an excess of pyrrolidine, respectively, mono- or di-substitution took place. These observations support the previous suggestion that, under the basic conditions of the reaction, deprotonation of the monosubstitution product from a reaction with a primary amine would render the second chloro group incapable of undergoing another nucleophilic substitution, while for a reaction with a secondary amine, there could be no deprotonation with the monosubstitution product, thus allowing disubstitution to occur. When Ia, Ib or Ic was treated with an excess of NaCN in DMF for up to 4 days, only monosubstitution was observed, a pure product being obtained with Ia, while with Ib or Ic, the product was contaminated with a large amount of starting material. When the same reaction of Ia, Ib or Ic with NaCN was carried out for 30 min and then worked up without any added aqueous NH_4PF_6, cyclohexadienyl complexes from the nucleophilic addition of a cyanide ion were obtained. Under similar reaction conditions but with the reaction time extended to 2 days, Ia could also give rise to products derived from monosubstitution and cyanide addition. Mechanistic implications of these results are discussed.

Introduction

In a previous study on nucleophilic substitution reactions with the cyclopentadienyliron (CpFe) complex of *o*-dichlorobenzene (Ia) [1], it was found that with an excess of an O- or S-containing nucleophile, such as phenol or *p*-thiocresol, in the presence of K_2CO_3, disubstitution of both chloro groups of Ia would take place,

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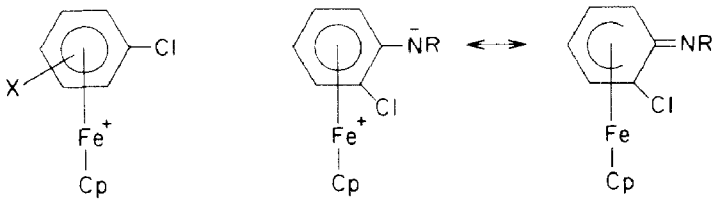
while for a similar reaction with one equivalent of the nucleophile and under conditions of high dilution, monosubstitution of one of the two chloro groups could occur. On the other hand, with a nucleophile containing an NH_2 group, such as methylamine or benzylamine, only the monosubstitution product was obtained even if the nucleophile was used in excess. It was suggested that, under the basic conditions of the reaction, the monosubstitution product from a reaction with RNH_2 would deprotonate to give a Zwitterion-cyclohexadienyl complex (II) [1], similar to the deprotonation of the CpFe complex of aniline as reported by Helling and Hendrickson [2]. Such a deprotonated species would be electron-rich and the chloro group in II would not undergo a further nucleophilic substitution reaction. If this explanation for monosubstitution with a primary amine were valid, for a similar reaction with a secondary amine, there would be no H on the N for deprotonation and disubstitution should be possible. In the present work, nucleophilic substitution reactions for a primary and a secondary amine with the CpFe complexes of *o*-, *m*- and *p*-dichlorobenzenes (Ia, Ib and Ic, respectively) were investigated.



II

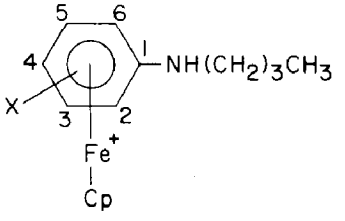
Ia, X = *o* - Cl
Ib, X = *m* - Cl
Ic, X = *p* - Cl

In a recent study on possible steric hindrance effects in nucleophilic addition reactions to CpFe complexes of substituted benzenes, it was found that in the reaction of the cyanide ion with the CpFe complex of *o*-chlorotoluene or 2,6-dimethylchlorobenzene, both a nucleophilic addition and the substitution of the chloro group by the nucleophile took place [3]. The present work also included some studies on the reaction of the cyanide ion with Ia, Ib and Ic.

Results and discussion

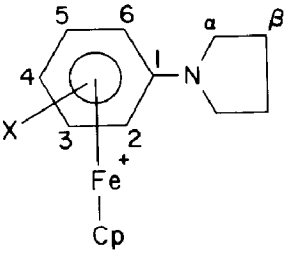
The reaction of 2.0 mmol of the hexafluorophosphate of Ia, Ib or Ic with 10 mmol of n-butylamine in tetrahydrofuran (THF) or in a 1/1 mixture of THF/dimethylsulfoxide (DMSO) at room temperature or under reflux for 12 h gave rise to only monosubstitution, the product being the hexafluorophosphate of IIIa, IIIb or IIIc, respectively. These results are in agreement with previous observations on reactions of Ia with an excess of primary amines [1]. When the same reaction was carried ou in 1/1 THF/DMSO under reflux for 12 h, but with 1.0 ml (about 17 mmol) of glacial acetic acid added to the reaction mixture, disubstitution took place giving rise to the hexafluorophosphate of IVa, IVb or IVc, respectively, from Ia, Ib or Ic. Apparently, the presence of the acetic acid suppressed the possibility of deprotonation, allowing disubstitution to occur, again supporting the suggestion that deprotonation to give a species such as II could be the explanation for the occurrence of only monosubstitution upon treatment of a CpFe complex of a

dichlorobenzene with an excess of a primary amine. It may also be pointed out that if the reaction of Ia, Ib or Ic with n-butylamine in the presence of added HOAc were carried out at room temperature, very little product was obtained, and if the reaction were effected under reflux in THF instead of THF/DMSO, a mixture of mono- and di-substitution products would result.. Possibly, the presence of the more polar DMSO may be of assistance in the formation of the disubstitution product.



IIIa, X = *o* - Cl
IIIb, X = *m* - Cl
IIIc, X = *p* - Cl
IVa, X = *o* - $NH(CH_2)_3CH_3$
IVb, X = *m* - $NH(CH_2)_3CH_3$
IVc, X = *p* - $NH(CH_2)_3CH_3$

n-Butylamine and pyrrolidine were among the nucleophiles recently employed in our studies on nucleophilic substitution reactions with CpFe complexes of chloroarenes and nitroarenes [4]. In the present work, pyrrolidine was utilized in the investigation of the behavior of a secondary amine in its reactions with Ia, Ib and Ic. When a THF solution of pyrrolidine was added dropwise at room temperature to a stirred THF solution of 1.0 molar equivalent of the hexafluorophosphate of Ia, Ib or Ic in the presence of an excess of K_2CO_3, such conditions would maintain a high degree of dilution for the amine and the product obtained was Va, Vb or Vc, respectively, derived from monosubstitution. This behavior is similar to that previously observed for the reaction of Ia with one equivalent of an O- or S-containing nucleophile [1]. When Ia, Ib or Ic and an excess of pyrrolidine in 1/1 THF/DMSO was heated under reflux for 12 h, the disubstitution product, VIa, VIb or VIc, respectively, was formed, and this result was in accord with anticipation since the substitution product from a secondary amine would have no H on N and could not undergo deprotonation, thus allowing disubstitution to take place.



Va, X = *o* - Cl
Vb, X = *m* - Cl
Vc, X = *p* - Cl
VIa, X = *o* - NC_4H_8
VIb, X = *m* - NC_4H_8
VIc, X = *p* - NC_4H_8

From the studies with n-butylamine and with pyrrolidine described above, 12 new CpFe complexes have been prepared. The spectral data, obtained with a Bruker AM 300 NMR spectrometer, in support of the assigned structures for these complexes, are summarized in Tables 1 and 2. Since reactions with a primary and a secondary amine have been carried out, it seemed worthwhile to test whether a tertiary amine could also act as a nucleophile in similar substitution reactions. When η^6-chlorobenzene-η^5-cyclopentadienyliron hexafluorophosphate and an excess of triethylamine in THF in the presence of added K_2CO_3 was heated under reflux for 12 h, no substitution product was obtained and the starting material, the CpFe

Table 1

^{1}H NMR data for cyclopentadienyliron complexes from nucleophilic substitution reactions (δ(Acetone-d_6)(ppm from TMS) [b])

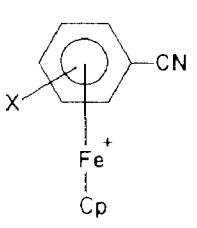
Complex [a]	Cp [b]	Complexed Ar [c]	Substituents [d]
IIIa	5.04	6.09–6.21(m,4H,H4,H5,H6,NH), 6.61(d,J 5.9,1H,H3)	0.99(t,J 7.4,3H,δ-CH_3),1.48(sextet,J 7.4,2H,γ-CH_2), 1.77(quintet,J 7.4,2H,β-CH_2),3.46–3.53(m,2H,-α-CH_2)
IIIb	5.08	5.84(d,J 5.9,1H,H6),6.22(s,1H,H2) 6.26(t,J 5.9,1H,H5),6.40(d,J 5.9,1H,H4)	0.97(t,J 7.4,3H,δ-CH_3),1.48(sextet,J 7.4,2H,γ-CH_2), 1.71(quintet,J 7.4,2H,β-CH_2),3.35–3.41(m,2H,α-CH_2), 5.53(broad s,1H,NH)
IIIc	5.08	5.89(d,J 6.3,2H,H2,H6), 6.50(d,J 6.3,2H,H3,H5)	0.96(t,J 7.4,3H,δ-CH_3),1.45(sextet,J 7.4,2H,γ-CH_2), 1.68(quintet,J 7.4,2H,β-CH_2),3.26–3.34(m,2H,α-CH_2), 6.16(broad s,1H,NH)
IVa	4.75	5.69–5.74(A_2B_2 m,2H,H3,H6), 5.88–5.92(A_2B_2 m,2H,H4,H5)	0.98(t,J 7.4,6H,δ-CH_3),1.50(sextet,J 7.4,4H,γ-CH_2), 1.72–1.80(m,4H,β-CH_2),3.32–3.43(m,4H,α-CH_2), 5.02(broad s,2H,NH)
IVb	4.77	5.48–5.60(m,4H,H2,H4,H6,NH), 5.91(t,J 6.6,1H,H5)	0.97(t,J 7.4,6H,δ-CH_3),1.47(sextet,J 7.4,4H,γ-CH_2), 1.68(quintet,J 7.4,4H,β-CH_2),3.24–3.31(m,4H,α-CH_2)
IVc	4.91	5.61(s,4H,H2,H3,H5,H6)	0.97(t,J 7.4,6H,δ-CH_3),1.47(sextet,J 7.4,4H,γ-CH_2), 1.67(quintet,J 7.4,4H,β-CH_2),3.21–3.29(m,4H,α-CH_2), 5.16(broad s,1H,NH)
Va	5.13	5.97(d,J 6.1,1H,H6), 6.17–6.19(m,2H,H4,H5), 6.49(d,J 5.5,1H,H3)	2.03–2.08(m,4H,β-CH_2) 3.77–3.82(m,4H,α-CH_2)

Vb	5.11	5.72(d,*J* 6.4,1H,6H),6.10(s,1H,H2), 6.28(t,*J* 6.4,1H,H5),6.42(d,*J* 6.4,1H,H4)	2.04–2.13(m,4H,β-CH_2), 3.48–3.58(m,4H,α-CH_2)
Vc	5.12	5.78(d,*J* 6.8,2H,H2,H6), 6.51(d,*J* 6.8,2H,H3,H5)	2.04–2.11(m,4H,β-CH_2), 3.48–3.54(m,4H,α-CH_2)
VIa	5.07	6.00–6.03(A_2B_2 m,2H,H3,H6), 6.07–6.10(A_2B_2 m,2H,H4,H5)	1.97–2.04(m,8H,β-CH_2), 3.27–3.35(m,8H,α-CH_2)
VIb	4.86	5.19(s,1H,H2),5.46(d,*J* 6.4,2H,H4,H6), 5.94(t,*J* 6.4,1H,H5)	1.97–2.04(m,8H,β-CH_2), 3.48–3.53(m,8H,α-CH_2)
VIc	4.92	5.48(s,4H,H2,H3,H5,H6)	1.97–2.04(m,8H,β-CH_2), 3.39–3.44(m,8H,α-CH_2)
VIIa	5.61	6.86,6.94(2t,*J* 6.2,2H,H4,H5), 7.22,7.24(2d,*J* 6.2,2H,H3,H6)	–
VIIb	5.61	7.03–7.05(m,2H,H4,H6), 7.23(t,1H,H5),7.36(s,1H,H2)	–
VIIc	5.63	7.20–7.24(m,4H,H2,H3,H5,H6)	–

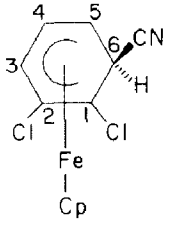
[a] IIIa, IIIb or IIIc, respectively, is the η^6-*o*-, -*m*- or -*p*-chloro-n-butylaminobenzene-η^5-cyclopentdienyliron cation; IVa, IVb or IVc, respectively, is the η^6-*o*-, -*m*- or -*p*-di-n-butylaminobenzene-η^5-cyclopentadienyliron cation; Va, Vb or Vc, respectively, is the η^6-*o*-, -*m*- or -*p*-chloro-*N*-pyrrolidinylbenzene-η^5-cyclopentadienyliron cation; VIa, VIb or VIc, respectively, is the η^6-*o*-, -*m*-, -*p*-di-*N*-pyrrolidinylbenzene-η^5-cyclopentadienyliron cation; and VIIa, VIIb or VIIc, respectively, is the η^6-*o*-, -*m*- or -*p*-chlorobenzonitrile-η^5-cyclopentadienyliron cation; all of these cationic complexes were obtained as their hexafluorophosphates. [b] All Cp absorptions are 5 H singlets. [c] H*x* designates the proton on carbon *x* of the complexed benzene ring; all *J* values are in Hz. [d] The 4 carbon positions of the n-butylamino substituents of IIIa–IIIc and IVa–IVc are designated as α, β, γ and δ; the carbon positions of the *N*-pyrrolidinyl substituents of Va–Vc and VIa–VIc are designated as α or β to the N. No protons are present in the substituents of VIIa–VIIc.

complex of chlorobenzene, was recovered in 85% yield. If a substitution reaction with a tertiary amine were to take place, a quaternary ammonium ion would result and the complexed product would be a dication. Apparently, such a dicationic product was not formed from triethylamine and the CpFe complex of chlorobenzene.

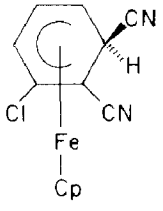
When a mixture of *o*-dichlorobenzene complex Ia and an excess of powdered NaCN in one drop of H_2O was stirred in dimethylformamide (DMF) at room temperature for 2 days and then worked up after the addition of an aqueous solution of NH_4PF_6, monosubstitution product VIIa was isolated as its hexafluorophosphate. No disubstitution product could be obtained even when the reaction time was extended to 4 days. When the same reaction was carried out for 30 min or for 2 days and the reaction mixture worked up without the addition of aqueous NH_4PF_6, the products were, respectively, cyanide adduct VIII or a 13/1 mixture of IX and X derived from cyanide substitution and addition. Essentially the same mixture of IX and X, in a ratio of 14/1, was obtained when the monosubstitution product VIIa was treated with NaCN in DMF for 30 min. Since the 2-h reaction, with or without the presence of added aqueous NH_4PF_6, gave VIIa or IX and X, respectively, the aqueous NH_4PF_6 must have caused a reversal of IX and X to cationic complex VIIa which then gave rise to its hexafluorophosphate.



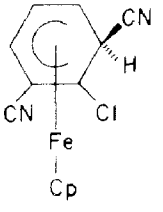
VIIa, X = *o*-Cl
VIIb, X = *m*-Cl
VIIc, X = *p*-Cl



VIII



IX



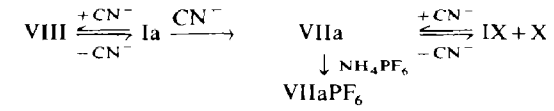
X

In our laboratory, we have found that CpFe complexes of cyclohexadienyl systems from nucleophilic additions could be converted back to the complexed arene, especially under acidic conditions, and we have utilized the addition of the acetonyl anion to a complexed sulfone followed by acidification to regenerate the sulfone complex as a means for its purification [5]. In the 2-h reaction of Ia with NaCN in DMF to give substitution product VIIa, apparently the added aqueous NH_4PF_6 was sufficiently acidic to cause a ready reversal of IX and X to VIIa, while in the absence of aqueous NH_4PF_6, the products were IX and X. As summarized in Scheme 1, initially, Ia would undergo a rapid and reversible cyanide addition to give VIII. Competing with the addition reaction would be a slower substitution to give VIIa. Substitution product VIIa, once formed, would also undergo rapid and reversible cyanide addition to give IX and X, the major adduct, IX, being derived from addition of the cyanide ion *ortho* to the more electron-withdrawing cyano group, while the minor adduct, X, resulted from addition *ortho* to the chloro group. In the presence of added aqueous NH_4PF_6, IX and X would revert back to VIIa and then giving rise to the hexafluorophosphate salt of VIIa.

Table 2
^{13}C NMR data for cyclopentadienyliron complexes from nucleophilic substitution reactions ((δ-Acetone-d_6)(ppm from TMS)

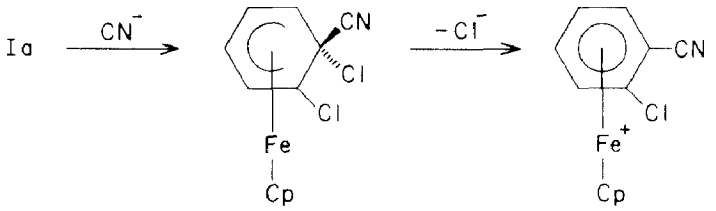
Complex	Cp	Complexed Ar [a]	Substituents
IIIa	78.3	66.7,80.7,85.9,87.1,89.3*(C2),125.3*(C1)	13.9(δ-CH_3),20.5(γ-CH_2), 31.1(β-CH),43.5(α-CH_2)
IIIb	78.1	66.5,69.0,81.1,85.6,106.6*(C3),127.3*(C1)	13.8(δ-CH_3),20.3(γ-CH_2), 30.8(β-CH_2),43.1(α-CH_2)
IIIc	78.4	66.9(2C),86.7(2C),101.4*(C4),127.0*(C1)	13.8(δ-CH_3),20.4(γ-CH_2), 31.0(β-CH_2),43.4(α-CH_2)
IVa	75.0	67.8(2C),78.0(2C),110.2*(2C,C1,C2)	13.9(2C,δ-CH_3),20.5(2C,γ-CH_2), 31.2(2C,β-CH_2),43.8(2C,α-CH_2)
IVb	74.6	53.8,62.1(2C),83.4,125.1*(2C,C1,C3)	13.9(2C,δ-CH_3),20.5(2C,γ-CH_2), 31.4(2C,β-CH_2),43.5(2C,α-CH_2)
IVc	75.0	65.5(4C),122.1*(2C,C1,C4)	14.0(2C,δ-CH_3),20.6(2C,γ-CH_2), 31.5(2C,β-CH_2),43.8(2C,α-CH_2)
Va	78.1	69.1,81.9,85.9,89.2,88.7*(C2),126.9*(C1)	26.0(2C,β-CH_2),52.0(2C,α-CH_2)
Vb	77.9	66.8,69.0,81.1,85.7,106.9*(C3),126.1*(C1)	25.5(2C,β-CH_2),48.8(2C,α-CH_2)
Vc	77.9	66.8(2C),86.5(2C),101.4*(C4),125.5*)(C1)	25.6(2C,β-CH_2),48.7(2C,α-CH_2)
VIa	74.8	75.3(2C),81.6(2C),115.6*(2C,C1,C4)	25.0(4C,β-CH_1),51.0(4C,α-CH_2)
VIb	73.4	53.5,62.2(2C),83.4,123.5*(2C,C1,C3)	25.5(4C,β-CH_2),48.5(4C,α-CH_2)
VIc	74.5	65.8(4C),120.0*(2C,C1,C4)	25.5(4C-β-CH_2),48.6(4C,α-CH_2)
VIIa	82.7	76.0*(C1),89.0,90.5,90.9,109.0*(C2)	114.8(CN)
VIIb	82.8	77.6*(C1),82.6,89.9,90.0,91.5,109.0*(C3)	116.5(CN)
VIIc	82.6	73.7(C1),90.0(2C),91.2(2C),109.2*(C4)	115.7(CN)

[a] Asterisks designate quaternary carbons.



Scheme 1

When *m*- or *p*-dichlorobenzene complex Ib or Ic was treated with an excess of NaCN in DMF and the reaction mixture worked up in the presence of added aqueous NH_4PF_6, some monosubstitution product, VIIb or VIIc, respectively, was formed. However, even after a reaction time of 4 days, more than one-half of the recovered material was the unreacted starting complex Ib or Ic. Although no pure substitution product VIIb or VIIc could be isolated, from the spectra of the mixtures of Ib and VIIb or Ic and VIIc, the spectral data for VIIb and VIIc could be deduced, and these data, as well as those for VIIa, are included in Tables 1 and 2. The finding that Ib or Ic could not give rise to a substitution reaction as readily as Ia possibly might be explained by the addition-elimination mechanism for aromatic nucleophilic substitutions [6]. If addition to give an *ipso*-adduct, such as XI from Ia, followed by loss of the leaving group, were the mechanism for the overall substitution, the presence of the second chloro group at the *ortho*-position, with its electron-withdrawing effect, would enhance the ease for the formation of *ipso*-adduct XI more than similar effects of the second chloro group at the *m*- or *p*-position, thus leading to a more facile overall substitution for Ia.



XI VIIa

It is of interest to note that reaction of Ia, Ib or Ic with the cyanide ion could only give rise to monosubstitution products VIIa, VIIb or VIIc, respectively, and no disubstitution product was ever obtained. As shown in Scheme 1 for reactions of Ia, monosubstitution product VIIa, once formed, would undergo rapid and reversible additions to give IX and X. Since IX and X would be more electron-rich than a complexed arene such as VIIa, the chloro group in adducts IX and X could not undergo another nucleophilic substitution reaction and only monosubstitution was observed for Ia. Although VIIb or VIIc was not isolated from reaction with Ib or Ic,

Table 3

^{1}H NMR data for cyclohexadienyl complexes from nucleophilic addition or substitution and addition reactions with the cyanide ion ($\delta(CDCl_3)$(ppm from TMS) [b])

Complex [a]	Cp	H2	H3	H4	H5	H6
VIII	4.61		6.46(d of d, J(3–4) 5.2, J(3–5) 1.2)	4.54(t of d, J(4–3) = J(4–5) 5.2, J(4–6) 0.4)	2.88(d of d of d, J(5–6) 6.3, J(5–4) 5.2, J(5–3) 1.2)	3.95(d, J(6–5) 6.3)
IX	4.63	–	6.70(d of d, J(3–4) 5.4, J(3–5) 0.7)	4.91(t, J(4–3) = J(4–5) 5.4)	3.02(d of d, J(5–6) 6.5, J(5–4) 5.4)	3.67(d, J(6–5) 6.5)
X	4.67	–	6.56(d of d, J(3–4) 52, J(3–5) 1.2)	[c]	3.12(d of d, J(5–6) 7.0, J(5–4) 6.4)	3.97(d, J(6–5) 7.0)
XII	4.53	4.77(d of d, J(2–3) 5.3, J(2–4) 1.1)	5.99(t, J(3–2) = J(3–4) 5.3)	4.77(d of d, J(4–3) 5.3, J(4–2) 1.1)	–	4.23(t, J(6–2) = J(6–4) 1.1)
XIII	4.51	4.71(s)	–	[c]	3.02(d of d, J(5–6) 6.2, J(5–4) 5.4)	3.65(d, J(6–5) 6.2)
XIV	4.51	4.81(d of d, J(2–3) 5.5, J(2–6) 1.5)	6.34(d of d, J(3–2) 5.5, J(3–5) 1.8)	–	3.31(d of d, J(5–6) 6.9, J(5–3) 1.8)	3.87(d of d, J(6–5) 6.9 J(6–2) 1.5)

[a] Complexes VIII, IX, X, XII, XIII and XIV, respectively, are 1–5-η^5-1,2-dichloro-*exo*-6-cyanocyclohexadienyl-η^5-cyclopentadienyliron, 1–5-η^5-2-chloro-1,*exo*-6-dicyanocyclohexadienyl-η^5-cyclopentadienyliron, 1–5-η^5-1-chloro-2,*exo*-6-dicyanocyclohexadienyl-η^5-cyclopentadienyliron, 1–5-η^5-1,5-dichloro-*exo*-6-cyanocyclohexadienyl-η^5-cyclopentadienyliron, 1–5-η^5-1,3-dichloro-*exo*-6-cyanocyclohexadienyl-η^5-cyclopentadienyliron, and 1–5-η^5-1,4-dichloro-*exo*-6-cyanocyclohexadienyl-η^5-cyclopentadienyliron. [b] All Cp absorptions are 5H singlets; H2 to H6 are the protons on cyclohexadienyl carbons 2 to 6, respectively. The J values are in Hz, and $J(a-b)$ is the coupling constant for Ha and Hb. [c] Hidden under other peaks.

Table 4

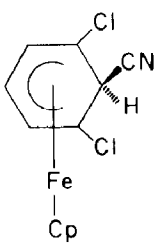
^{13}C NMR data for cyclohexadienyl complexes from nucleophilic addition or substitution and addition reactions with the cyanide ion ($\delta(CDCl_3)$(ppm from TMS) [a])

Complex	Cp	C1	C2	C3	C4	C5 [b]	C6 [c]	CN [d]
VIII	79.0	53.1*	106.5*	81.0	80.3	24.4	29.8	115.9
						J(C–H) 175.7	J(C–H) 147.9	J(C–H) 6.8
IX	79.3	8.8*	103.2*	83.8	79.3	24.3	29.9	116.1, J(C–H) 6.7
						J(C–H) 175.6	J(C–H) 147.7	120.9, J(C–H) 4.0
X	80.0	52.0*	61.7*	83.3	82.1	26.6 [e]	36.3 [e]	115.5, J(C–H) 6.5
								118.2, J(C–H) 3.8
XII	79.4	57.1*	76.2	77.3	76.2	57.1*	46.3	114.5
							J(C–H) 152.5	J(C–H) 5.9
XIII	79.3	50.9*	83.7	106.5*	81.5	24.4	29.8	116.1
						J(C–H) 179.1	J(C–H) 148.4	J(C–H) 5.2
XIV	79.2	52.5*	75.0	79.8	101.9*	28.1	38.1	115.8
						J(C–H) 176.9	J(C–H) 149.5	J(C–H) 6.3

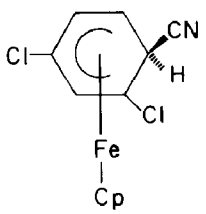
[a] Asterisks designate quaternary carbons; all J values are in Hz. Assignments for C3 and C4 of VIII, IX and X, for C2 and C4 of XIII, and for C2 and C3 of XIV may be reversed. [b] J(C–H) values of about 175–179 Hz confirm the assignment of C5 as a carbon with some aromatic character. [c] J(C–H) values of about 147–152 Hz confirm the assignment of C6 as a tetrahedral carbon. [d] Two-bond C–H coupling constant of about 5–7 Hz indicates the absorption of CN at the C6 position; the second CN signal with J(C–H) of about 4 Hz is due to the CN at C1 or C2, respectively, of IX or X. [e] Weak signals as X is the minor component in the mixture of IX and X and no J(C–H) can be evaluated.

presumably, similar behaviors as observed for VIIa could occur, and VIIb or VIIc, once formed, would also undergo rapid and reversible addition reactions with the cyanide ion, rendering the second chloro group incapable of giving rise to another nucleophilic substitution reaction.

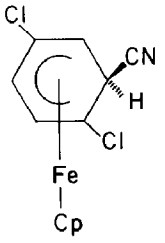
Similar to the addition of the cyanide ion to Ia to give VIII, when Ib or Ic was treated with NaCN in DMF for 30 min and then worked up without any added aqueous NH_4PF_6, a 9/1 ratio of XII and XIII was obtained from Ib, while only one adduct, XIV, was formed from the symmetrical Ic. The formation of XII as the major adduct from Ib in spite of possible steric hindrance effects again pointed to the importance of the electron-withdrawing effect of the chloro group in promoting nucleophilic addition at the *ortho* position, XII being derived from cyanide addition at a position *ortho* to both chloro groups. The spectral data for these cyclohexadienyl complexes, XII, XIII and XIV, as well as for VIII, IX and X from Ia, are given in Tables 3 and 4.



XII



XIII



XIV

It has been found that DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone) is an effective reagent for the demetallation–rearomatization of CpFe complexed cyclo-

hexadienyl systems and thereby providing a method for the synthesis of the liberated substituted arenes [7]. From the DDQ treatment of VIII or XIV, which was the sole product from the cyanide addition to Ia or Ic, 2,3-dichlorobenzonitrile or 2,5-dichlorobenzonitrile, respectively, was obtained. Similar DDQ treatments were also carried out with mixtures of cyclohexadienyl complexes, the 14/1 mixture of IX and X from Ia giving rise to 3-chlorophthalonitrile contaminated with a small amount of 2-chloroisophthalonitrile, while the 9/1 mixture of XII and XIII from Ib gave 2,6-dichlorobenzonitrile contaminated with some 2,4-dichlorobenzonitrile. Although pure products were not obtained in these experiments with mixtures of cyclohexadienyl complexes, spectral data for the individual components of the mixed products could be deduced as given in the Experimental Section.

Experimental

η^6-o-, m- or p-Chloro-n-butylaminobenzene-η^5-cyclopentadienyliron hexafluorophosphate ($IIIaPF_6$, $IIIbPF_6$ or $IIIcPF_6$)

The η^6-*o*-, *m*-, and *p*-dichlorobenzene-η^5-cyclopentadienyliron cations (Ia, Ib and Ic) were prepared from ligand exchange reactions as previously reported [8] and were isolated as their hexafluorophosphates. A mixture of 826 mg (2.0 mmol) of the hexafluorophosphate of Ia, Ib or Ic and 731 (10.0 mmol) of n-butylamine in 30 ml of THF or 1/1 THF/DMSO was stirred at room temperature for 12 h. In this and in subsequent experiments, the reaction was carried out under an atmosphere of N_2 and the reaction flask was wrapped with foil to minimize any possible effect of light. The resulting solution was concentrated by a rotary evaporator to remove essentially all of the solvent and the residue was redisolved in CH_2Cl_2. A solution of 326 mg (2.0 mmol) of NH_4PF_6 in 20 ml of H_2O was then added and the product was recovered by extraction with CH_2Cl_2 (4×25 ml). The combined extract was washed with H_2O and then dried over $MgSO_4$. Upon removal of most of the CH_2Cl_2 by a rotary evaporator, addition of ether gave a precipitate of the hexafluorophosphate of IIIa, IIIb or IIIc, in yields of 84, 77 or 72%, respectively. (Found for $IIIaPF_6$, $IIIbPF_6$ and $IIIcPF_6$, respectively: C, 39.82, 39.78 and 39.87; H, 4.11, 4.18 and 4.33; N, 3.12, 3.11 and 3.16. $C_{15}H_{19}NClFePF_6$ calcd.: C, 40.04; H, 4.26; N, 3.11%. The elemental analyses for these and other compounds were carried out by the analytical laboratory of the University of Saskatchewan).

η^6-o-, m- or p-Di-n-butylaminobenzene-η^5-cyclopentadienyliron hexafluorophosphate ($IVaPF_6$, $IVbPF_6$ or $IVcPF_6$)

A mixture of 826 mg (2.0 mmol) of the hexafluorophosphate of Ia, Ib or Ic, 731 mg (10.0 mmol) of n-butylamine and 1.0 ml of glacial acetic acid in 20 ml of a 1/1 mixture of THF/DMSO was heated under reflux for 12 h. The resulting reaction mixture was then worked up as described above for the similar experiment without the added HOAc. Disubstitution product $IVaPF_6$, $IVbPF_6$ or $IVcPF_6$ was obtained in a yield of 65, 71 or 68%, respectively. (Found for $IVaPF_6$, $IVbPF_6$ and $IVcPF_6$, respectively: C, 46.90, 46.78 and 46.95; H, 5.95, 6.06 and 6.10; N, 5.65, 5.80 and 5.68. $C_{19}H_{29}N_2FePF_6$ calcd.: C, 46.93; H, 6.01, N, 5.76%).

η^6-o-, m- or p-Chloro-N-pyrrolidinylbenzene-η^6-cyclopentadienyliron hexafluorophosphate ($VaPF_6$, $VbPF_6$ or $VcPF_6$)

A mixture of 826 mg (2.0 mmol) of the hexafluorophosphate of Ia, Ib or Ic and 690 mg (5.0 mmol) of $K_2CO_3$2 in 100 ml of THF was stirred at room temperature and a solution of 142 mg (2.0 mmol) of pyrrolidine in 30 ml of THF was added dropwise over a period of 1 h. Stirring was continued for 5 h and the resulting material was filtered, concentrated by a rotary evaporator and then worked up as described in the preparation of $IIIaPF_6$, $IIIbPF_6$ or $IIIcPF_6$. Monosubstitution product $VaPF_6$, $VbPF_6$ or $VcPF_6$ was obtained in a yield of 77, 73 or 82%, respectively. (Found for $VaPF_6$, $VbPF_6$ and $VcPF_6$, respectively: C, 40.28, 40.35 and 40.38; H, 3.92, 4.00 and 3.98; N, 3.25, 3.10 and 3.02. $C_{15}H_{17}NClFePF_6$ calcd.: C, 40.25; H, 3.83; N, 3.13%).

η^6-o-, m- or p-Di-N-pyrrolidinylbenzene-η^5-cyclopentadienyliron hexafluorophosphate ($VIaPF_6$, $VIbPF_6$ or $VIcPF_6$)

A mixture of 826 mg (2.0 mmol) of the hexafluorophosphate of Ia, Ib or Ic and 711 mg (10.0 mmol) of pyrrolidine in 20 ml of 1/1 THF/DMSO was heated under reflux for 12 h and then worked up the usual way to give a 72, 75 or 75% yield of $VIaPF_6$, $VIbPF_6$ or $VIcPF_6$, respectively. (Found for $VIaPF_6$, $VIbPF_6$ and $VIcPF_6$, respectively: C, 47.42, 47.19 and 47.39; H, 5.31, 5.23 and 5.32; N, 5.78, 5.78 and 5.70. $C_{19}H_{25}N_2FePF_6$ calcd.: C, 47.32; H, 5.23; N, 5.80%).

η^6-o-, m- or p-Chlorobenzonitrile-η^5-cyclopentadienyliron hexafluorophosphate ($VIIaPF_6$, $VIIbPF_6$ or $VIIcPF_6$)

A mixture of 826 mg (2.0 mmol) of the hexafluorophosphate of Ia, Ib or Ic, 1.0 g (20 mmol) of powdered NaCN and one drop of H_2O in 10 ml of DMF was stirred at room temperature for 2 or 4 days. A solution of 1.0 g (6.1 mmol) of NH_4PF_6 in 20 ml of H_2O was then added and the resulting material extracted with a 1/1 mixture of CH_2Cl_2/CH_3NO_2 (4×100 ml). The combined extract was washed with H_2O and dried over $MgSO_4$. After removal of the solvent, the residue was redissolved in acetone and upon addition of ether, the product precipitated. From $IaPF_6$, 403 mg (50%) of $VIIaPF_6$ was obtained as a yellow powder. (Found: C, 35.90; H, 2.13; N, 3.60. $C_{12}H_9NClFePF_6$ calcd.: C, 35.72; H, 2.25; N, 3.47%). From the hexafluorophosphate of Ib or Ic, even after a reaction time of 4 days, the product contained a large amount of unreacted material as indicated by NMR. An approximately 3/1 mixture of $IbPF_6$ and $VIIbPF_6$ or a mixture of about 3/2 $IcPF_6$ and $VIIcPF_6$ was obtained, respectively, from $IbPF_6$ or $IcPF_6$, and no pure $VIIbPF_6$ or $VIIcPF_6$ could be isolated.

Nucleophilic addition reactions with the cyanide ion

A mixture of 413 mg (1.0 mmol) of the hexafluorophosphate of Ia, Ib or Ic, 500 mg (10 mmol) of powdered NaCN and one drop of H_2O in 5.0 ml of DMF was stirred at room temperature for 30 min. Water (50 ml, without any NH_4PF_6) was then added and the resulting material extracted with $CHCl_3$ (4×50 ml). The combined extract was washed with H_2O, dried over $MgSO_4$, and the solvent removed to give 176 mg (60%) of 1–5-η^5-1,2-dichloro-*exo*-6-cyanocyclohexadienyl-η^5-cyclopentadienyliron (VIII) from Ia as a red oil; 214 mg (73%) of a 9/1 mixture of 1-5-η^5-1,5-dichloro-*exo*-6-cyanocyclohexadienyl-η^5-cyclopentadienyliron (XII) and

1–5-η^5-1,3-dichloro-exo-6-cyanocyclohexadienyl-η^5-cyclopentadienyliron (XIII) from Ib as a red powder; or 235 mg (80%) of 1–5-η^5-1,4-dichloro-*exo*-6-cyanocyclohexadienyl-η^5-cyclopentadienyliron (XIV) from Ic as a red powder. (Found for VIII, XII/XIII and XIV, respectively: C, 48.95, 48.98 and 49.10; H, 3.15, 3.17 and 3.20; N, 4.68, and 4.87 and 4.90. $C_{12}H_9NCl_2Fe$ calcd.: C, 49.03; H, 3.09; N, 4.76%).

When the same reaction between 413 mg (1.0 mmol) of IaPF$_6$, 500 mg (10 mmol) of powdered NaCN and one drop of H_2O was stirred at room temperature for 48 h instead of 30 min and the resulting material worked up as described above, 151 mg (53%) of a 13/1 mixture of 1–5-η^5-2-chloro-1,*exo*-6-dicyanocyclohexadienyl-η^5-cyclopentadienyliron (IX) and 1–5-η^5-1-chloro-2,*exo*-dicyanocyclohexadienyl-η^5-cyclopentadienyliron (X) was obtained as a red solid. (Found: C, 55.20; H, 3.25; N, 9.98. $C_{13}H_9N_2ClFe$ calcd.: C, 54.88; H, 3.19; N, 9.84%).

In another experiment when a mixture of 403 mg (1.0 mmol) of the hexafluorophosphate of VIIa, 500 mg (10 mmol) of powdered NaCN and one drop of H_2O in 5.0 ml of DMF was stirred at room temperature for 30 min and worked up as described above, the products obtained were a 14/1 mixture of IX and X, very similar to the 13/1 mixture of IX and X from the 48 h reaction between Ia and NaCN.

Reactions with DDQ

Demetallation-rearomatization of cyclohexadienyl complexes by treatment with DDQ was carried out as previously described [7]. Typically, a solution of 1.0 mmol of the complex and 1.0 mmol of DDQ in 10 ml of CH_3CN was stirred at room temperature for 30 min. The resulting material was filtered through a sintered glass filter and the filtrate evaporated to dryness. The residue was redissolved in 5.0 ml of CH_2Cl_2 and the solution passed through a short (about 20 cm) alumina column, with elution by CH_2Cl_2. Removal of the solvent from the eluate gave the liberated substituted arene.

From cyclohexadienyl complex VIII, a 50% yield of 2,3-dichlorobenzonitrile was obtained, m.p. 56–57 °C (lit. [9] m.p. 56–57 °C). ^{1}H NMR: $\delta(CDCl_3)$ 7.36 (t, 1H, H at C5), 7.62 (d, *J* 7.2 Hz, 1H), 7.71 (d, *J* 8.0 Hz, 1H) (H at C4 and C6); ^{13}C NMR: $\delta(CDCl_3)$ 115.2 (CN), 115.3 (quat.), 127.9, 132.2, 133.9 (quat.), 134.1 (quat.), and 134.7 ppm (arene carbons).

From the 14/1 mixture of IX and X, a 73% yield of 3-chlorophthalonitrile (XV) contaminated by a small amount of 2-chloroisophthalonitrile (XVI) was obtained. The mixture melted at 107–109 °C. The preparation of XV has been mentioned [10], but little data were available. For XV, ^{1}H NMR: $\delta(CDCl_3)$ 7.71 (t, *J* 7.7 Hz, 1H, H at C5), 7.74 (d, *J* 7.7 Hz, 1H), 7.80 (d, *J* 7.7 Hz, 1H) (H at C4 and C6); ^{13}C NMR: $\delta(CDCl_3)$ 116.2, 117.5 (CN), 112.8 (quat.), 114.5 (quat.), 131.6, 134.1, 134.2, 138.7 (quat.) ppm (arene carbons). For XVI, ^{1}H NMR: $\delta(CDCl_3)$ 7.57 (t, *J* 7.8 Hz, 1H, H at C5), 7.93 (d, *J* 7.8 Hz, 2H, H at C4 and C6) ppm.

From the 9/1 mixture of XII and XIII, a 72% yield of 2,6-dichlorobenzonitrile (XVII) containing about 8% 2,4-dichlorobenzonitrile (XVIII) was obtained. The mixture melted at 134–137 °C. The reported m.p. of XVII and XVIII, respectively, were 142.5–143.5 °C [11] and 61–62 °C [12]. For XVII, ^{1}H NMR: $\delta(CDCl_3)$ 7.42–7.52 (m, A_2B, 3H); ^{13}C NMR: $\delta(CDCl_3)$ 113.3 (2C, CN and quat. C1), 128.1 (2C, C3 and C5), 133.9 (C4), 138 (2C, quat. C2 and C6) ppm. For XVIII, ^{1}H NMR: $\delta(CDCl_3)$ 7.61–7.81 (m, ABC, 3H) ppm.

From XIV, a 70% yield of 2,5-dichlorobenzonitrile was obtained, m.p. 129–130° (lit. [12] m.p. 129–130°C). ^{1}H NMR: $\delta(CDCl_3)$ 7.46 (d, J 8.7 Hz, 1H), 7.53 (d, J 8.7 Hz, 1H) (H at C3 and C4), 7.66 (s, 1H, H at C6); ^{13}C NMR: $\delta(CDCl_3)$ 114.6 (2C, CN and quat. C1), 131.1, 133.2 (quat.), 133.4, 134.1, 135.1 (quat.) ppm (arene carbons).

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