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STUDIES ON NUCLEOPHILIC SUBSTITUTION REACTIONS WITH η^6-*o*-DICHLOROBENZENE-η^5-CYCLOPENTADIENYLIRON HEXAFLUOROPHOSPHATE

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Summary

Reaction of η^6-*o*-dichlorobenzene-η^5-cyclopentadienyliron hexafluorophosphate (IPF_6) with an excess of phenol or *p*-thiocresol in the presence of K_2CO_3 could give disubstitution of both chloro groups of I, while a similar reaction with one equivalent of the nucleophile, and under conditions of high dilution, monosubstitution of only one of the chloro groups of I could be obtained. Similarly, di- or monosubstitution could be brought about under appropriate conditions with benzyl or methyl alcohol as the source of the nucleophile. While no reaction could take place between IPF_6 and aniline, a reaction did occur between IPF_6 and *o*-anisidine (*o*-methoxyaniline), but only the monosubstitution product was obtained, even in the presence of an excess of *o*-anisidine. Similar results of monosubstitution were observed with other nucleophiles containing the NH_2 group, including NH_3, NH_2NH_2, CH_3NH_2 and $C_6H_5CH_2NH_2$. These findings are consistent with the reported differences in yields when IPF_6 was treated with two nucleophilic groups (OH, SH and/or NH_2) located in the 1,2-positions of a benzene ring to give CpFe complexes of heterocyclic systems related to 9,10-dihydroanthracene with two hetero-atoms at the 9,10-positions [15]. Reactions were also carried out between IPF_6 and the carbanion-enolate anion derived from acetylacetone, α-benzoylacetophenone, diethyl malonate or ethyl acetoacetate. In these cases, only monosubstitution of one of the chloro groups of I was observed, leading to the formation of a C–C bond. A possible explanation for the formation of only monosubstitution products in reactions with N- or C-containing nucleophiles is discussed.

Introduction

The ready substitution of the chlorine atom in the η^6-chlorobenzene-η^5-cyclopentadienyliron cation by various nucleophiles was first reported in 1967 by Nesmeyanov and coworkers [1] and it was estimated that the "mobility" of the chlorine atom in the cyclopentadienyliron (CpFe) complex of chlorobenzene was similar to that of the chlorine atom in 2,4-dinitrochlorobenzene [2]. Subsequently,

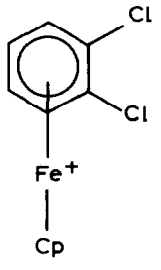
other studies on such nucleophilic aromatic substitutions (S_NAr reactions) on CpFe complexes of chloroarenes and their synthetic applications have been reported [3–9] and kinetic studies on such reactions have been carried out [10–14]. In 1982, it was reported from this laboratory that reactions between η^6-*o*-dichlorobenzene-η^5-cyclopentadienyliron hexafluorophosphate (IPF_6) and two nucleophilic groups (OH, SH and/or NH_2) located in the 1,2-positions of a benzene ring, carried out in the presence of K_2CO_3, could give rise to CpFe complexes of heterocyclic systems related to 9,10-dihydroanthracene with 2 heteroatoms at the 9,10-positions, and upon demetallation by pyrolytic sublimation, the free heterocyclic compound could be liberated [15]. Good yields were obtained when the two nucleophilic groups utilized in the reaction were OH and/or SH, but when one of the two nucleophilic groups was NH_2, the yield was low, and when both nucleophiles were NH_2, no reaction took place. In the present work, further investigations on nucleophilic substitution reactions of IPF_6 are carried out in order to study its reactivities with different nucleophiles and possibly to provide some clarification on the differences in yields obtained in the synthesis of the heterocyclic systems.

Results and discussion

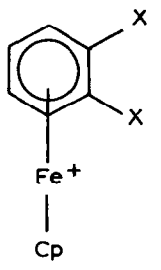
Reaction of IPF_6 with an excess of phenol or *p*-thiocresol in the presence of K_2CO_3 in tetrahydrofuran (THF) resulted in the substitution of both chloro groups of I, giving rise to the hexafluorophosphate salt of the η^6-*o*-diphenoxybenzene-η^5-cyclopentadienyliron cation (IIa) or the η^6-*o*-di-*p*-tolylthiobenzene-η^5-cyclopentadienyliron cation (IIb). Substitution of only one of the two chloro groups of I could also be effected under conditions of high dilution by the dropwise addition of a THF solution of one equivalent of phenol or *p*-thiocresol to IPF_6 and K_2CO_3 in THF. The product obtained was the hexafluorophosphate salt of the CpFe complex of *o*-chlorophenoxybenzene (IIIa) or *o*-chloro-*p*-tolylthiobenzene (IIIb).

Similar results were obtained with methanol or phenylmethanol (benzyl alcohol) as the source of nucleophile. Instead of using K_2CO_3 to generate the nucleophile, the phenylmethoxide ion was obtained from treatment of benzyl alcohol with NaH, and reaction of IPF_6 with an excess or with 1 equiv. of the phenylmethoxide ion gave, respectively, the disubstituted complex IIc or the monosubstituted complex IIIc. The methoxide ion was generated by reaction of methanol with Na. To ensure disubstitution, IPF_6 was heated under reflux for 3 h with an excess of $NaOCH_3$-CH_3OH followed by the introduction of a further portion of $NaOCH_3$-CH_3OH with further refluxing to give the hexafluorophosphate of the η^6-*o*-dimethoxybenzene-η^5-cyclopentadienyliron cation (IId). When IPF_6 was treated with 1 equiv. of $NaOCH_3$ in CH_3OH, besides the monosubstituted IIId-PF_6, some unreacted IPF_6 remained as a contaminant. Pure IIId-PF_6, however, could be prepared from a separate synthesis involving methylation of the *o*-chlorophenol complex by treatment with diazomethane.

When IPF_6 was treated with aniline, no substitution reaction took place. This finding is similar to that reported by Pauson and Segal [16] that no nucleophilic substitution occurred when the CpFe complex of chlorobenzene was treated with aniline. A substitution reaction did occur between IPF_6 and *o*-anisidine (*o*-methoxyaniline), presumably because the presence of an electron-donating *o*-substituent would increase the nucleophilic character of the aromatic amine. However, only monosubstitution took place even in the presence of an excess of *o*-anisidine,



(I)



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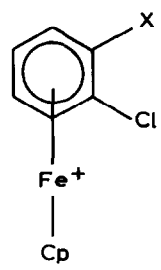
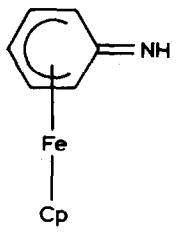


(III)

For IIa, IIb, IIc and IId, X = OC_6H_5, $SC_6H_4CH_3$-*p*, $OCH_2C_6H_5$, and OCH_3, respectively. For IIIa, IIIb, IIIc, IIId, IIIe, IIIf, IIIg, IIIh, IIIi, IIIj, IIIk, IIIl and IIIm, X = OC_6H_5, $SC_6H_4CH_3$-*p*, $OCH_2C_6H_5$, OCH_3, $NHC_6H_4OCH_3$-*o*, NH_2, $NHNH_2$, $NHCH_3$, $NHCH_2C_6H_5$, CH_2COCH_3, $CH(COC_6H_5)_2$, $CH(COOC_2H_5)_2$, and $CH(COCH_3)COOC_2H_5$, respectively.

the product obtained being the hexafluorophosphate of the η^6-*o*-chloro-2-methoxyphenylaminobenzene-η^5-cyclopentadienyliron cation (IIIe). Reactions with other N-containing nucleophiles, including ammonia, hydrazine, methylamine and benzylamine, all gave monosubstitution products even in the presence of an excess of the nucleophile, the products obtained being the hexafluorophosphate salts of the CpFe complexes of *o*-chloroaniline, *o*-chlorophenylhydrazine, *o*-chloro-*N*-methylaniline and *o*-chloro-*N*-benzylaniline, respectively (IIIf to IIIi). The yields as well as the analytical and spectral data for disubstituted products IIa to IId and monosubstituted products IIIa to IIIi are summarized in Tables 1–3.

Since all the N-containing nucleophiles used in the present study contained at least one NH_2 group and all of these nucleophiles gave only monosubstitution on reaction with IPF_6, it would be of interest to consider a possible explanation for such behaviors. Under basic conditions, loss of a proton from the α-position to a CpFe complexed arene is known to give a Zwitterionic species which may be formulated as a cyclohexadienyl complex with an exocyclic double bond, as illustrated by IV from the deprotonation of the CpFe complex of aniline reported by Helling and Hendrickson [3,17]. Formation of similar cyclohexadienyl complexes with an exocyclic double bond to the NH group has also been studied by Michaud and Astruc [18] and by Moinet and Raoult [19]. In studies carried out in this laboratory on ring opening reactions with CpFe complexed heterocyclic systems [20], it was found that the presence of an NH group in the heterocycle, such as the η^6-phenoxazine-η^5-cyclopentadienyliron cation (V), failed to give ring opening when treated with a nucleophile, and it was suggested that deprotonation with V would give rise to an electron-rich cyclohexadienyl type of complex VI which would not react with a nucleophile.



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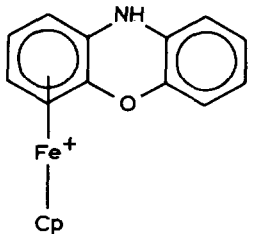

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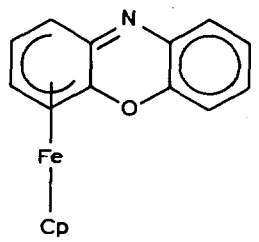


(VI)

TABLE 1

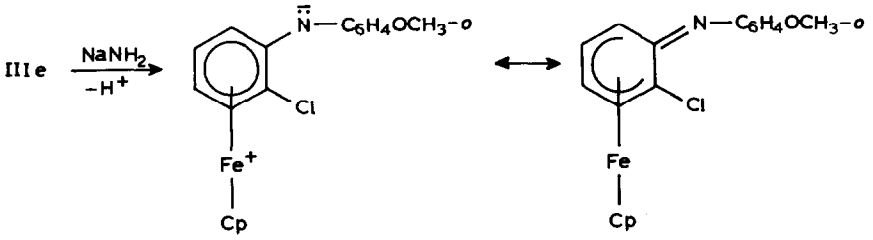
YIELDS AND ANALYTICAL DATA FOR DI- AND MONO-SUBSTITUTION PRODUCTS FROM REACTIONS WITH η^6-*o*-DICHLOROBENZENE-η^5-CYCLOPENTADIENYLIRON HEXAFLUOROPHOSPHATE (IPF_6)

Complex [a]	Yield (%)	Analysis (Found (calcd.)(%))		
		C	H	N
o-$(C_6H_5O)_2C_6H_4FeCp^+$ (IIa)	76	52.27 (52.30)	3.74 (3.62)	–
o-(*p*-$CH_3C_6H_4S)_2C_6H_4FeCp^+$ (IIb)	80	50.33 (51.03)	3.92 (3.94)	–
o-$(C_6H_5CH_2O)_2C_6H_4FeCp^+$ (IIc)	58	53.26 (53.88)	4.13 (4.16)	–
o-$(CH_3O)_2C_6H_4FeCp^+$ (IId)	80	38.80 (38.54)	3.71 (3.73)	–
o-$Cl(C_6H_5O)C_6H_4FeCp^+$ (IIIa)	68	43.54 (43.39)	3.12 (2.99)	–
o-Cl(*p*-$CH_3C_6H_4S)C_6H_4FeCp^+$ (IIIb)	84	42.50 (43.18)	3.42 (3.22)	–
o-$Cl(C_6H_5CH_2O)C_6H_4FeCp^+$ (IIIc)	50	43.99 (44.52)	3.32 (3.32)	–
o-$Cl(CH_3O)C_6H_4FeCp^+$ (IIId)	75	35.27 (35.19)	3.10 (2.95)	–
o-Cl(*o*-$CH_3OC_6H_4NH)C_6H_4FeCp^+$ (IIIe)	60	43.55 (43.27)	3.51 (3.43)	2.95 (2.80)
o-$Cl(NH_2)C_6H_4FeCp^+$ (IIIf)	83	33.07 (33.48)	2.75 (2.81)	2.52 (2.55)
o-$Cl(NH_2NH)C_6H_4FeCp^+$ (IIIg)	46	32.34 (32.18)	2.96 (3.02)	6.86 (6.54)
o-$Cl(CH_3NH)C_6H_4FeCp^+$ (IIIh)	85	35.37 (35.34)	3.22 (3.39)	3.44 (3.36)
o-$Cl(C_6H_5CH_2NH)C_6H_4FeCp^+$ (IIIi)	65	44.91 (45.31)	3.59 (3.65)	2.89 (3.04)
o-$ClC_6H_4CH_2COCH_3FeCp^+$ (IIIj)	81	38.63 (38.69)	3.54 (3.25)	–
o-$ClC_6H_4CH(COC_6H_5)_2FeCp^+$ (IIIk)	70	51.75 (51.98)	3.56 (3.35)	–
o-$ClC_6H_4CH(COOC_2H_5)_2FeCp^+$ (IIIl)	71	40.47 (40.29)	3.97 (3.76)	–
o-$ClC_6H_4CH(COCH_3)COOC_2H_5FeCp^+$ (IIIm)	80	40.10 (40.31)	3.35 (3.58)	–

[a] As the hexafluorophosphate salt.

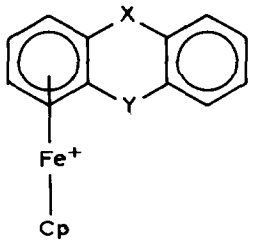
In the present preparation of IIIe from the reaction of IPF_6 with *o*-anisidine, the cyclohexadienyl complex VII (1-5-η^5-1-chloro-6-*o*-methoxyphenyliminocyclohexadienyl-η^5-cyclopentadienyliron) was actually isolated from the basic reaction mixture, and a pure sample of VII was prepared directly from the deprotonation of IIIe. Since VII is derived from deprotonation, it would be more electron-rich than a CpFe complexed chloroarene, and, therefore, the chloro group in VII would not undergo further nucleophilic substitution to give a disubstituted product. A similar explanation may also apply in the preparation of monosubstituted products IIIf to IIIi, which under the basic reaction conditions could deprotonated to give cyclo-

hexadienyl type of complexes and, therefore, could not give rise to nucleophilic substitution of both chloro groups of IPF_6.



(VII') (VII)

The present results on the formation of mono- and disubstitution products are consistent with the differences in yields observed in the preparation of CpFe complexes of heterocyclic systems VIII [15]. The ready substitution of both chloro



(VIII)

groups in I by O- or S-containing nucleophiles, such as the phenoxide ion or the *p*-methylthiophenoxide ion to give IIa or IIb, respectively, is in agreement with the good yields obtained in the synthesis of VIII with X and Y being both O, both S, or one O and one S [15]. With a N-containing nucleophile, such as *o*-anisidine, substitution of only one of the two chloro groups in I could take place to give IIIe. On the assumption that the chloro group in a cyclohexadienyl complex such as VII would be inert towards nucleophilic substitution, it may be suggested that in the synthesis of VIII, with X = O or S and Y = NH, substitution must take place first with an O- or S-containing nucleophile, followed by substitution with the N-containing nucleophile. If the first substitution were to involve the N-nucleophile, no complexed heterocycle would be formed thus accounting for a lower yield of VIII when X = O or S and Y = NH, and no complexed heterocyclic product would be obtained if both X and Y in VIII were to be NH groups (see Scheme 1).

One of us (U.S.G.) in his post-doctoral work has carried out similar nucleophilic aromatic substitutions and has recently reported the use of carbanions-enolate anions as nucleophiles in S_NAr reactions with CpFe complexed chloroarenes [8]. Since CpFe complexes of nitroarenes are also activated towards such substitutions with the nitrite ion as the leaving group [21], we have shown that carbanions-enolate anions could also act as nucleophiles in S_NAr reactions with CpFe complexes of both chloroarenes and nitroarenes leading to the formation of a C–C bond to the aromatic ring [9]. In the present work, reactions of IPF_6 with acetylacetone (1,3-pentanedione), α-benzoylacetophenone (1,3-diphenyl-1,3-propanedione), diethyl

(Continued on p. 88)

TABLE 2

DATA FROM THE ^{1}H NMR AND IR SPECTRA OF DI- AND MONO-SUBSTITUTION PRODUCTS FROM REACTIONS WITH η^6-*o*-DICHLOROBENZENE-η^5-CYCLOPENTADIENYLIRON HEXAFLUOROPHOSPHATE (IPF_6)

Complex [a]	δ (ppm from TMS)				IR (cm^{-1})
	Solvent	Cp	Complexed Ar	Others	
IIa	CD_3CN	5.06 (s,5H)	5.84–6.34 (m,4H)	7.10–7.80 (m,10H,uncomplexed Ar)	
IIb	CD_3COCD_3	4.97 (s,5H)	5.85–6.13 (m,4H)	7.30–7.80 (m,8H,uncomplexed AR); 2.46 (s,6H,two CH_3)	
IIc	CD_3COCD_3	4.83 (s,5H)	6.16–6.40 (m,2H); 5.73–5.96 (m,2H)	7.40–7.70 (m,10H,uncomplexed Ar); 5.26 (s,4H,two CH_2)	
IId	CD_3COCD_3	5.10 (s,5H)	6.26–6.56 (m,2H); 5.83–6.16 (m,2H)	4.10 (s,3H, CH_3O)	
IIIa	CD_3CN	5.10 (s,5H)	6.60–6.78 (m,1H); 6.00–6.35 (m,3H)	7.06–7.78 (m,5H,uncomplexed Ar)	
IIIb	CD_3COCD_3	5.30 (s,5H)	6.08–6.85 (m,4H)	7.36–7.90 (m,4H,uncomplexed Ar); 2.50 (s,3H,CH_3)	
IIIc	CD_3COCD_3	5.26 (s,5H)	6.73–7.10 (m,2H); 6.33–6.66 (m,2H)	7.40–7.96 (m,5H,uncomplexed Ar); 5.60 (s,2H,CH_2)	
IIId	CD_3COCD_3	5.13 (s,5H)	6.40–6.76 (m,2H); 6.10–6.33 (m,2H)	4.10 (s,3H,CH_3O)	

IIIe	CD_3CN	5.02 (s,5H)	6.65–6.75 (m,1H); 6.14 (br s,2H); 5.85 (br s, 1H)	7.10–7.53 (m, 4H, uncomplexed Ar); 7.99 (s,1H,NH); 3.93 (s,3H,CH_3O)	3380 (NH)
IIIf	CD_3COCD_3	5.03 (s,5H)	6.00–6.35 (m,4H)	6.50–6.70 (m,2H,NH_2)	3475 (NH)
IIIg	CD_3COCD_3	4.93 (s,5H)	5.66–6.13 (m,4H)	6.23–6.90 (m,3H,$NHNH_2$)	3450 (NH)
IIIh	CD_3COCD_3	4.83 (s,5H)	5.76–6.40 (m,4H)	6.00–6.40 (m,1H,NH); 3.00 (s,3H,CH_3)	3450 (NH)
IIIi	CD_3COCD_3	4.83 (s,5H)	6.60–7.10 (m,1H); 6.10–6.33 (m,3H)	7.40–7.86 (m,5H,umcomplexed Ar); 6.60–7.10 (m,1H,NH); 2.90 (s,2H,CH_2)	3430 (NH)
IIIj [b]	CD_3COCD_3	5.30 (s,5H)	6.47 (t,1H); 6.55 (d, 1H); 6.62 (t,1H); 6.68(d,1H) (J's about 6.3 Hz)	2.34 (s,3H,CH_3); 4.36, 4.63 (AB quartet,2H,CH_2 J 18.1 Hz)	1715 (CO)
IIIj [c]	CD_3COCD_3	5.28 (s,5H)	6.44–6.59 (m,3H) 6.83 (d,1H)	2.34 (s,3H,CH_3); 4.29, 4.39, 4.59, 4.68 (AB,2H,CH_2,J 20 Hz)	1690 (CO)
IIIk	CD_3SOCD_3	4.80 (s,5H)	6.60 (br s,4H)	6.95 (s,1H,CH); 7.35–7.90 (m,6H) 8.03–8.35 (m,4H) (uncomplexed Ar)	1700 (CO)
IIIl	CD_3SOCD_3	5.31 (s,5H)	6.60–7.00 (m,4H)	1.36 (t,6H,two CH_3); 4.40 (q,4H,two CH_2); 5.53 (s,1H,CH)	1730 (CO)
IIIm	CD_3SOCD_3	5.30 (s,5H)	6.40–6.96 (m,4H)	1.43 (t,3H,CH_3CH_2); 2.60 (s,3H,CH_3CO); 4.66 (q,2H,CH_3CH_2); 5.73 (s,1H,CH)	1712 1730 (CO)

[a] As the hexafluorophosphate salt. [b] ^1H NMR data obtained using a 300 MHz instrument. [c] As reported by Moriarty and Gill [8].

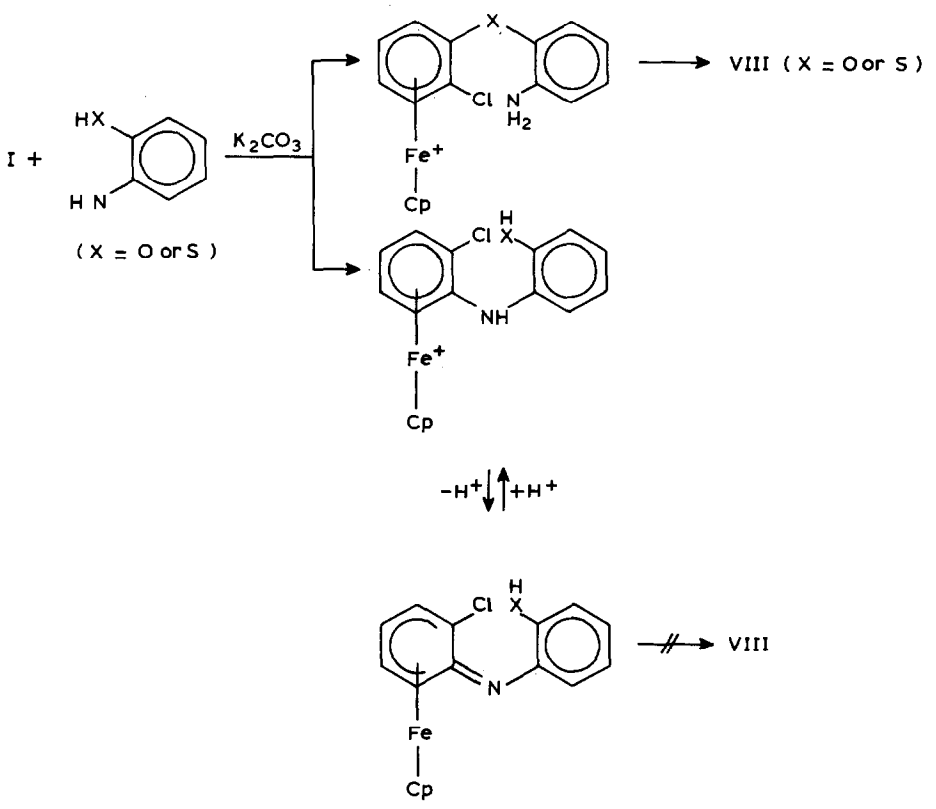
TABLE 3

DATA FROM THE ^{13}C NMR SPECTRA OF DI- AND MONO-SUBSTITUTION PRODUCTS FROM REACTIONS WITH η^6-*o*-DICHLOROBENZEN-η^5-CYCLOPENTADIENYLIRON HEXAFLUOROPHOSPHATE (IPF_6)

Complex [a]	δ (ppm from TMS) [b]				
	Solvent	Cp	Complexed Ar	Uncomplexed Ar	Others
IIa	CD_3CN	77.3	77.2, 82.5, 123.0*	119.2, 125.6, 130.2, 153.7*	
IIb	CD_3COCD_3	78.6	84.8, 84.9, 106.6*	130.8, 134.5, 124.7*, 141.0*	20.0 (CH_3)
IIc	CD_3COCD_3	77.5	74.7, 82.4, 125.5*	129.2, 129.8, 129.8, 136.5*	73.3 (CH_2)
IId	CD_3COCD_3	75.2	71.0, 80.1, 124.3*		55.9 (CH_3O)
IIIa	CD_3CN	78.6	75.8, 84.0, 85.0, 87.5, 96.8*, 129.8*	119.8, 126.3, 130.4, 152.7*	
IIIb	CD_3COCD_3	81.0	84.6, 86.6, 86.8, 87.3, 103.8*, 113.1*	132.6, 137.0, 124.0*, 142.9*	21.4 (CH_3)
IIIc	CD_3SOCD_3	75.9	72.8, 78.1, 78.1 80.7, 92.4*, 123.3*	123.3, 128.5, 128.5, 135.1*	71.1 (CH_2)
IIId	CD_3COCD_3	77.6	71.0, 82.8, 84.6, 87.0, 95.5*, 131,1*		56.7 (CH_3O)

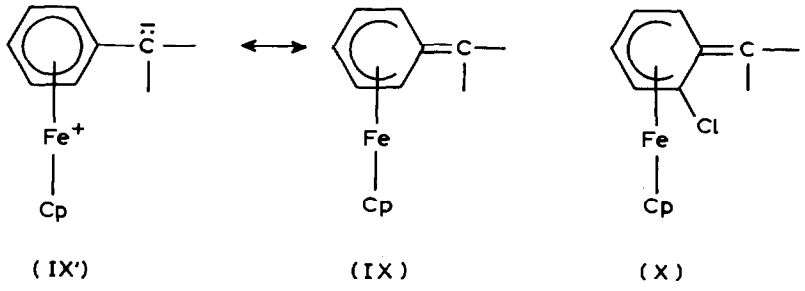
IIIe	CD_3COCD_3	78.9	71.6, 82.1, 86.0, 87.6, 90.5*, 126.4*	113.5, 122.2, 128.0 129.5, 122.1*, 155.1*	56.2 (CH_3O)
IIIf	CD_3COCD_3	78.9	71.3, 84.1, 86.5, 87.4, 90.6*, 124.5*		
IIIg	CD_3COCD_3	79.0	70.8, 82.4, 86.4, 87.4, 90.9*, 119.9*		
IIIh	CD_3COCD_3	78.4	66.8, 81.0, 86.1 87.3, 90.2*, 125.9*		29.9 (CH_3)
IIIi	CD_3COCD_3	76.4	65.0, 79.2, 83.8, 85.4, 88.0*, 122.8*	127.2, 127.2, 128.0, 136.0*	45.0 (CH_2)
IIIj	CD_3SOCD_3	78.9	87.0, 87.4, 85.5, 89.2, 98.9*, 107.6*		29.6 (CH_3), 46.5 (CH_2), 203.1 (CO)
IIIk	CD_3SOCD_3	78.8	86.6, 87.5, 87.9, 88.7, 99.0*, 106.7*	128.3, 129.2, 134.5, 135.5*	56.7 (CH), 193.0 (CO)
IIIl	CD_3CN	79.3	86.5, 86.6, 87.7, 88.6, 96.6*, 107.1*		12.8 (CH_3), 53.6 (CH), 63.0 (CH_2), 164.8 (CO)
IIIm	CD_3SOCD_3	79.5	87.03, 87.04, 88.1, 89.0, 97.6*, 106.9*		13.7 (CH_3CH_2), 29.6 (CH_3CO), 60.2 (CH), 63.0 (CH_2) 166.1 ($COOEt$), 199.0 (CH_3CO)

[a] As the hexafluorophosphate salt. [b] Asterisks denote quaternary carbons.



SCHEME 1

malonates, and ethyl acetoacetate in dimethylformamide (DMF) in the presence of K_2CO_3 were investigated, and in all of these cases only monosubstitution took place. Before discussing the nature of these substitution products, it may be pointed out that studies on deprotonation in CpFe complexes of substituted arenes from an α-carbon position to give Zwitterionic-cyclohexadienyl complexes with an exocyclic double bond to carbon (IX) have been reported [3,17,22,23]. In S_NAr reactions of IPF_6 with C-nucleophiles, under the basic conditions employed, formation of cyclohexadienyl complex X would render the second chloro group of I unreactive in nucleophilic substitution, and similar to reactions with NH_2-containing nucleophiles, only monosubstitution product would be obtained.



(IX') (IX) (X)

One of the reactions carried out in the present work and by Moriarty and Gill [8] is that between IPF_6 and acetylacetone. The product reported by Moriarty and Gill was the hexafluorophosphate salt of the η^6-*o*-chlorophenylacetone-η^5-cyclopentadienyliron cation (IIIj, with X in III = CH_3COCH_2), which must have resulted from deacetylation of the substitution product between IPF_6 and the carbanion derived from acetylacetone. In our earlier studies on carbanions as nucleophiles in S_NAr reactions with the CpFe complex of chlorobenzene or nitrobenzene [9], it was noted that, in the reaction with acetylacetone, deacetylation occurred when the work-up procedure was that used by Moriarty and Gill [8] and it involved the removal of solvent by heating under acidic conditions at about 50°C. When heating under acidic conditions in the work-up was avoided, no deacetylation took place [9]. In the present work, from the reaction of IPF_6 and acetylacetone, when the work-up did not involve heating under acidic conditions, an impure product, presumably a mixture of products with and without deacetylation, was obtained. Using the work-up procedure as described by Moriarty and Gill [8], pure IIIj resulted, but its ^1H NMR and IR spectral data showed some slight differences from those reported by Moriarity and Gill (see Table 2).

In the reaction of IPF_6 with α-benzoylacetophenone, diethyl malonate, or ethyl acetoacetate, using our work-up procedure without heating under acidic conditions, the products obtained, respectively, was the CpFe complex of α-*o*-chlorophenyl-α-benzoylacetophenone (IIIk), diethyl *o*-chlorophenylmalonate (III1), or ethyl α-*o*-chlorophenylacetoacetate (IIIm). It may be pointed out further that Moriarty and Gill also reported the reaction between IPF_6 and ethyl acetoacetate, and their product was that derived from deacetylation of IIIm. As noted previously [8,9], these S_NAr reactions with carbanions as nucleophiles gave arylations leading to the formation of a C–C bond, and demetallation by pyrolytic sublimation [15] would liberate the synthetically useful substituted arenes. The yields and analytical and spectral data for IIIj to IIIm are included in Tables 1 to 3.

Experimental

Disubstitution products IIa, IIb, IIc and IId

In the preparation of IIa, a mixtue of 1.24 g (3.0 mmol) of η^6-*o*-dichlorobenzene-η^5-cyclopentadienyliron hexafluorophosphate (IPF_6), 846 mg (9.0 mmol) of phenol and 1.24 g (9.0 mmol) of K_2CO_3 in 50 ml of tetrahydrofuran (THF) was heated at 50°C under reflux and under N_2 for 15 h. The resulting material was treated with 20 ml of H_2O and 20 ml of 10% HCl and then 3.0 mmol of NH_4PF_6 was introduced. The product was recovered by extraction with CH_2Cl_2 (4 × 50 ml), the extract washed with H_2O (2 × 50 ml) and dried over $MgSO_4$. The solvent was then removed under reduced pressure by a rotary evaporator and the residual oil was redissolved in a small amount CH_2Cl_2 or acetone. Upon addition of ether, 1.20 g (76%) of the hexafluorophosphate salt of the η^6-*o*-diphenoxybenzene-η^5-cyclopentadienyliron cation (IIa) precipitated as a brown powder.

Using the same procedure and starting with 3.0 mmol of IPF_6, 9.0 mmol of *p*-thiocresol, and 9.0 mmol of K_2CO_3, the hexafluorophosphate salt of the η^6-*o*-di-*p*-tolylthiobenzene-η^5-cyclopentadienyliron cation (IIb) was obtained as a light yellow powder in 80% yield.

In the preparation of IIc, a mixture of 2.0 ml of benzyl alcohol and 86 mg (3.6 mmol) of NaH was stirred under N_2 for 10 min and then 1.0 mmol of IPF_6 in 10 ml

of THF was introduced. The reaction mixture was heated at 50°C under reflux and under N_2 for 12 h and then worked up as described in the preparation of IIa to give 320 mg (58%) of the hexafluorophosphate salt of the η^6-*o*-di(phenylmethoxy)benzene-η^5-cyclopentadienyliron cation (IIc).

For the preparation of IId, 1.0 mmol of IPF_6 in an excess of $NaOCH_3$-CH_3OH (from 200 mg of Na and 200 ml of CH_3OH) was heated under reflux and under N_2 for 3 h. Another portion of $NaOCH_3/CH_3OH$ (from 100 mg of Na and 50 ml CH_3OH) was added and the mixture refluxed for an additional 3 h. The resulting material was neutralized with 10% HCl. Most of the CH_3OH was then removed by a rotary evaporator and the aqueous residue was extracted with CH_2Cl_2 and worked up the usual way to give an 80% yield of the hexafluorophosphate salt of the η^6-*o*-dimethoxybenzene-η^5-cyclopentadienyliron cation (IId).

Monosubstitution products IIIa, IIIb, IIIc and IIId

In the preparation of IIIa, to a stirred and refluxing mixture of 413 mg (1.0 mmol) of IPF_6 and 165 mg (1.2 mmol) of K_2CO_3 in 50 ml of THF was added dropwise over a period of 30 min a solution of 94 mg (1.0 mmol) of phenol in 50 ml of THF. Heating and stirring under a N_2 atmosphere was continued for 4 h and then 20 ml of H_2O, 10 ml of 10% HCl and 1.0 mmol of NH_4PF_6 were added. The product was recovered by extraction with CH_2Cl_2 and then worked up as described in the preparation of IIa to give 360 mg (68%) of the hexafluorophosphate salt of the η^6-*o*-chlorophenoxybenzene-η^5-cyclopentadienyliron cation (IIIa). In a similar way, reaction between equimolar amounts of IPF_6 and *p*-thiocresol gave the hexafluorophosphate of the η^6-*o*-chloro-*p*-tolylthiobenzene-η^5-cyclopentadienyliron cation (IIIb) in 84% yield.

In the preparation of IIIc, to a mixture of 1.0 mmol of IPF_6 and 1.2 mmol of NaH in 100 ml of THF, heated at 40–50°C under reflux and with stirring, was added dropwise over a period of 30 min a solution of 1.0 mmol of benzyl alcohol in 50 ml of THF. The reaction mixture was heated under N_2 at about 40°C for 15 h and then worked up the usual way to give a 55% yield of the hexafluorophosphate salt of the η^6-*o*-chlorophenylmethoxybenzene-η^5-cyclopentadienylrion cation (IIIc).

The preparation of pure IIId was effected by the diazomethane treatment of the *o*-chlorophenol complex derived from basic hydrolysis of IPF_6. A mixture of 413 mg (1.0 mmol) of IPF_6 and 500 mg (12 mmol) and NaOH in 30 ml of 50% aqueous acetone was stirred at room temperature under N_2 for 15 h. The resulting material was made slightly acidic with 10% HCl and then about 7 mmol of diazomethane in ether was introduced. Stirring was continued for an additional 3 h. The organic solvents were then removed under reduced pressure by a rotary evaporator. To the aqeous residue, 1.0 mmol of NH_4PF_6 was added and the mixture was extracted with CH_2Cl_2 and worked up the usual way to give a 75% yield of the hexafluorophosphate salt of the η^6-*o*-chloromethoxybenzene-η^5-cyclopentadienyliron cation (IIId), which was recrystallized from a turbid solution in acetone/ether clarified by a few drops of CH_2Cl_2.

η^6-o-Chloro-2-methoxyphenylaminobenzene-η^5-cyclopentadienyliron hexafluorophosphate (IIIe-PF_6)

A mixture of 6.0 mmol of IPF_6, 30 mmol of *o*-anisidine and 10 mmol of K_2CO_3 in 50 ml of THF was heated with stirring under gentle reflux and under N_2 for 15 h. The resulting mixture was filtered and the filtrate evaporated to dryness under

reduced pressure by a rotary evaporator. The residual material was dissolved in CH_2Cl_2 and 6.0 mmol of NH_4PF_6 was added. The mixture was neutralized with 10% HCl, extracted with CH_2Cl_2, and worked up the usual way to give a 60% yield of the hexafluorophosphate salt of IIIe which was recrystallized form absolute ethanol.

1–5-η^5-1-Chloro-6-o-methoxyphenyliminocyclohexadienyl-η^5-cyclopentadienyliron (VII)

A mixture of 500 mg (1.0 mmol) of IIIe-PF_6 and 390 mg (10 mmol) of $NaNH_2$ in 40 ml of CH_2Cl_2 was stirred at room temperature under N_2 for 2 h. The deep red solution was filtered through a sinter glass filter and the filtrate evaporated to dryness. The residual solid was washed with $CHCl_3$ and the $CHCl_3$ solution decanted from any insoluble material. Removal of the solvent from the $CHCl_3$ solution gave 220 mg (62%) of VII as a brownish powder, m.p. 76–78°C. Its mass spectrum gave a molecular ion at *m/e* 353. Its ^1H NMR showed the following absorptions: $\delta(CDCl_3)$ in ppm, 3.84 (s, 3H, CH_3O); 4.53 (s, 5H, Cp); 4.43 (d, 1H), 5.04 (t, 1H), 5.46 (t, 1H), 5.68 (d, 1H) (cyclohexadienyl protons); 6.86–7.08 (m, 4H, uncomplexed Ar). Its ^{13}C MNR spectrum gave the following data: $\delta(CDCl)_3$ in ppm, 55.6 (CH_3O); 75.4 (Cp); 60.9, 73.5, 82.3, 84.5, 86.0 (quat), 155.2 (quat, a previously reported [18] C=NH quaternary C gave an absorption at 156.5 ppm) (cyclohexadienyl); 111.9 121.3, 123.1 123.7, 112.9 (quat), 152.3 (quat) (uncomplexed Ar). (Found: C, 61.21; H, 4.18; N, 3.62. $C_{18}H_{16}ONClFe$ calcd.: C, 61.13; H, 4.46; N, 3.96%).

A crude sample of VII was also isolated from the reaction mixture in the preparation of IIIe. After 6.0 mmol of IPF_6, 30 mmol of *o*-anisidine and 10 mmol of K_2CO_3 in 50 ml of THF was gently refluxed overnight, filtered, and the filtrate evaporated to dryness, instead of dissolving in CH_2Cl_2 followed by treatment with 10% HCl, the residual material was washed with $CHCl_3$ and the $CHCl_3$ solution was decanted from the undissolved material. The washing with $CHCl_3$ was repeated until the $CHCl_3$ solution was colorless. The combined $CHCl_3$ washings was evaporated to dryness to give a reddish brown solid the ^1H NMR spectrum of which showed the presence of all the peaks of VII plus some unknown impurities.

Preparations of monosubstitution products IIIf, IIIg, IIIh and IIIi

A mixture of 2.0 mmol of IPF_6 and 6.0 mmol of NH_3 (as conc. NH_4OH), NH_2NH_2, CH_3NH_2 or $C_6H_5CH_2NH_2$ in 10 ml of CH_2Cl_2 was stirred at room temperature under N_2. A dark red solution developed after about 5 min and stirring was continued for 5 h. The solution was evaporated to dryness and the residue redissolved in CH_2Cl_2. H_2O (about 5 ml) and NH_4PF_6 (2.0 mmol) were added and the mixture was stirred and neutralized with 10% HCl. The product was recovered by extraction with CH_2Cl_2, the extract dried over $MgSO_4$, and upon removal of most of the CH_2Cl_2, addition of ether gave a precipitate of the product, the hexafluorophosphate salt of the CpFe complex of *o*-chloroaniline (IIIf), *o*-chlorophenylhydrazine (IIIg), *o*-chloro-*N*-methylaniline (IIIh) or *o*-chloro-*N*-benzylaniline (IIIi), respectively.

Monosubstitution products from reactions with carbanion nucleophiles

A mixture of 2.0 mmol of IPF_6, 2.2 mmol of acetylacetone, α-benzoylacetophenone, diethyl malonate, or ethyl acetoacetate, and 5.0 mmol of K_2CO_3 in 10 ml of *N,N*-dimethylformamide (DMF) was stirred at room temperature and under

N_2 for 5 h. The resulting material was filtered into 10 ml of 10% HCl. The reaction flask was washed with CH_2Cl_2 and the washing also filtered into the 10% HCl. H_2O (40 ml) and NH_4PF_6 (2.0 mmol) were added and the product was then recovered from the DMF/H_2O solution by extraction (3 × 50 ml) with a 4/1 mixture of CH_2Cl_2/CH_3NO_2. The extract was washed with H_2O (5 × 25 ml), dried over $MgSO_4$, and the solvent removed under reduced pressure by a rotary evaporator. The residue was washed with ether to remove any traces of DMF before being crystallized from absolute ethanol. From the reactions with α-benzoylacetophenone, diethyl malonate and ethyl acetoacetate, the pure monosubstitution products, namely, the hexafluorophosphate salts of the CpFe complexes of α-*o*-chlorophenyl-α-benzoylacetophenone (IIIk), diethyl *o*-chlorophenylmalonate (III1) and ethyl α-*o*-chlorophenylacetoacetate (IIIm), respectively, were obtained.

From the reaction with acetylacetone, an impure product, presumably due to partial deacetylation, was formed. In a work-up procedure similar to that used by Moriarty and Gill [8], after the reaction mixture was filtered into 10% HCl, the reaction flask was washed with ethanol instead of CH_2Cl_2 and then treated with NH_4PF_6. The mixture was then heated at about 50°C for 0.5 h in a rotary evaporator to remove the ethanol before being extracted with CH_2Cl_2/CH_3NO_2. The product obtained was the pure deacetylated η^6-*o*-chlorophenylacetone-η^5-cyclopentadienyliron hexafluorophosphate (IIIj-PF_6).

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