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SOME RING REPLACEMENT AND NUCLEOPHILIC SUBSTITUTION REACTIONS OF η^6-SUBSTITUTED ARENE-η^5-CYCLOPENTADIENYLIRON HEXAFLUOROPHOSPHATES

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Summary

A number of nitroarene and aminoarene complexes, including the PF_6^- salts of $NO_2C_6H_5FeCp^+$, *o*-, *m*- or *p*-$CH_3(NO_2)C_6H_4FeCp^+$, $NH_2C_6H_5FeCp^+$ and *o*-, *m*-, or *p*-$CH_3(NH_2)C_6H_4FeCp^+$, when heated with an excess of $P(OC_2H_5)_3$ all gave rise to the ring replacement product, $CpFe(P(OC_2H_5)_3)_3^+$ PF_6^- (I). Similarly, the thermal reaction of $NO_2C_6H_5Fe(CH_3)Cp^+$ PF_6^- or $NH_2C_6H_5Fe(CH_3)Cp^+$ PF_6^- with $P(OC_2H_5)_3$ gave $CH_3CpFe(P(OC_2H_5)_3)_3^+$ PF_6^- (VII). With *m*-$CH_3(Cl)C_6H_4$-$FeCp^+$ PF_6^- (XIV), heating with $P(OC_2H_5)_3$ also gave rise to I, while the same treatment with $P(OC_2H_5)_3$ at room temperature in CH_2Cl_2 showed no nucleophilic substitution of the chlorine atom of XIV by $P(OC_2H_5)_3$. On the other hand, the chlorine atom of a number of chloroarene complexes could be readily displaced at room temperature with various amines acting as nucleophiles. Such nucleophilic substitutions were carried out on $ClC_6H_5FeCp^+$ PF_6^- and *o*-, *m*- or *p*-$CH_3(Cl)C_6H_4FeCp^+$ PF_6^- with methylamine, ethylenediamine, cyclohexylamine, benzylamine and pyrrolidine to give rise to 20 *N*-substituted aminoarene complexes.

Introduction

Recently, Gill and Mann [1] report a number of synthetic applications arising from ring replacement reactions when the η^6-*p*-xylene-η^5-cyclopentadienyliron cation was photolyzed in the presence of suitable two-electron or six-electron donor ligands. Among the results obtained was the formation of the previously unknown η^6-tris(triethyl phosphite)-η^5-cyclopentadienyliron hexafluorophosphate, $CpFe(P(OC_2H_5)_3)_3^+$ PF_6^- (I), when the photolysis was carried out in the presence of triethyl phosphite. We wish to report that I can also be obtained under thermolysis conditions. Because we recently investigated the photolysis and thermolysis of the η^6-azidobenzene-η^5-cyclopentadienyliron cation which

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TABLE 1

DATA ON THE NITROARENE COMPLEXES FROM THE H_2O_2 OXIDATION OF THE CORRESPONDING AMINOARENE COMPLEXES

Product	Yield (%)	Analysis (found (calcd.) (%))			^{1}H NMR (δ(acetone-d_6) (ppm) from TMS)		
		C	H	N	CH_3	Cp	Aromatic
$NO_2C_6H_5FeCp^+ PF_6^-$ (II)	39	33.72 (33.96)	2.79 (2.59)	3.57 (3.60)		5.2(s)(5H)	6.7—7.0(m)(3H), 7.4—7.6(m)(2H)
o-$CH_3(NO_2)C_6H_4FeCp^+ PF_6^-$ (III)	26	35.90 (35.76)	3.05 (3.00)	3.40 (3.48)	2.8(s)(3H)	5.5(s)(5H)	6.8—7.7(m)(4H)
m-$CH_3(NO_2)C_6H_4FeCp^+ PF_6^-$ (IV)	29	35.49 (35.76)	3.17 (3.00)	3.41 (3.48)	2.8(s)(3H)	5.4(s)(5H)	6.8—7.6(m)(4H)
p-$CH_3(NO_2)C_6H_4FeCp^+ PF_6^-$ (V)	34	35.44 (35.76)	3.03 (3.00)	3.47 (3.48)	2.7(s)(3H)	5.4(s)(5H)	6.9(d)(2H), 7.5(d)(2H)
$NO_2C_6H_5FeCH_3Cp^+ PF_6^-$ (VI)	48	35.37 (35.76)	3.04 (3.00)	3.49 (3.48)	2.0(s)(3H)	5.3(s)(4H)	6.7—6.9(m)(3H), 7.4—7.6(m)(2H)

gave rise to a ring contraction product, cyanoferrocene, via an intermediate nitrene complex [2], it would be of interest to attempt to generate the nitrene by an alternative method. Cadogan [3,4] has shown that nitrenes may be generated as reaction intermediates from the deoxygenation of nitro compounds upon treatment with triethyl phosphite. The present paper reports on the preparation of a number of η^6-nitroarene-η^5-cyclopentadienyliron cations and their reactions with triethyl phosphite. Since only the ring replacement product I, instead of a nitrene, was obtained, we have included in this paper the results from some other displacement reactions with η^6-chloroarene-η^5-cyclopentadienyliron cations.

Results and discussion

The η^6-nitroarene-η^5-cyclopentadienyliron hexafluorophosphates were prepared from the corresponding aminoarene complexes by oxidation with H_2O_2 in trifluoroacetic acid. The method is similar to that reported by Sheats and Rausch [5] in their oxidation of aminocobalticinium hexafluorophosphate to give the nitrocobalticinium salt. Attempts were also made using various concentrations of an aqueous solution of $KMnO_4$ as oxidizing agent, but they failed to give the desired conversion of the aminoarene complex to the nitro compound. Summarized in Table 1 are the data for the various nitroarene complexes prepared from the H_2O_2 oxidation.

When η^6-nitrobenzene-η^5-cyclopentadienyliron hexafluorophosphate (II) or the isomeric η^6-*o*-, -*m*- or -*p*-nitrotoluene-η^5-cyclopentadienyliron hexafluorophosphate (III, IV or V, respectively) was heated in an excess of triethyl phosphite at 130—140°C for 18 h, conditions similar to those used in deoxygenation reactions [3], the product obtained in all cases was the ring replacement product, η^6-tris(triethyl phosphite)-η^5-cyclopentadienyliron hexafluorophosphate (I). The same treatment with triethyl phosphite on η^6-nitrobenzene-η^5-methylcyclopentadienyliron hexafluorophosphate (VI) again resulted in the replacement of the nitrobenzene ligand to give η^6-tris(triethyl phosphite)-η^5-methylcyclopentadienyliron hexafluorophosphate (VII). Indeed when the aminoarene complexes that were used in the preparation of the nitroarene complexes, namely, the hexafluorophosphate salts of η^6-aniline-η^5-cyclopentadienyliron, η^6-*o*,-*m*- or -*p*-toluidine-η^5-cyclopentadienyliron, and η^6-aniline-η^5-methylcyclopentadienyliron cations (VIII, IX, X, XI and XII, respectively) were heated with triethyl phosphite at 150°C for 16—20 h, the ring replacement product I or VII was also obtained. The yields of I or VII from these reactions are given in Table 2.

It is of interest to point out that Gill and Mann [1] have shown that control thermal reactions with η^6-*p*-xylene-η^5-cyclopentadienyliron hexafluorophosphate in the presence of various ligands including triethyl phosphite at room temperature or in refluxing CH_2Cl_2 resulted only in the recovery of the unreacted starting material. The results given in Table 2, however, were obtained at much higher temperatures of 130—150°C. Control experiments carried out in complete darkness at these higher temperatures also gave results similar to those recorded in Table 2. It is, therefore, concluded that similar to the photolysis results obtained by Gill and Mann [1], the ring replacement product, I or VII, can also be formed by thermolysis at temperatures of 130—150°C.

TABLE 2

YIELDS OF $CpFe(P(OCH_2CH_3)_3)_3^+ PF_6^-$ (I) OR $CH_3CpFe(P(OCH_2CH_3)_3)_3^+ PF_6^-$ (VII) FROM VARIOUS ARENE COMPLEXES

Product	Yield (%) from reaction with [a]										
	II	III	IV	V	VI	VIII	IX	X	XI	XII	XIV
I	47	14	48	7 [b]	—	60	48	47	46	—	40
VII	—	—	—	—	36	—	—	—	—	60	—

[a] II, III, IV, V and VI, respectively, are the hexafluorophosphate salts of $NO_2C_6H_5FeCp^+$, *o*-, *m*-, or *p*-$CH_3(NO_2)C_6H_4FeCp^+$ and $NO_2C_6H_5FeCH_3Cp^+$; VIII, IX, X, XI and XII, respectively, are the hexafluorophosphate salts of $NH_2C_6H_5FeCp^+$, *o*-, *m*-, or *p*-$CH_3(NH_2)C_6H_4FeCp^+$, and $NH_2C_6H_5FeCH_3Cp^+$; XIV is *m*-$CH_3(Cl)C_6H_4FeCp^+ PF_6^-$. [b] Another product, as yet unidentified, was obtained in about 20% yield.

Nesmeyanov and coworkers [6,7] have shown that the chlorine atom in η^6-chlorobenzene-η^5-cyclopentadienyliron tetrafluoroborate (XIII) could be readily replaced by a number of nucleophiles such as the ethoxy, thiophenoxy, *n*-butylthio, phthalimido and cyano groups. The "mobility" of the chlorine atom in XIII was estimated to be similar to the chlorine in 2,4-dinitrochlorobenzene [7]. Such nucleophilic substitution reactions have also been studied in the chromium tricarbonyl complexes of aryl halides [8] and in the η^6-halogenobenzenetricarbonylmanganese salts [9]. In order to ascertain whether the chlorine atom in a chloroarene complex would be replaced by triethyl phosphite as a nucleophile, η^6-*m*-chlorotoluene-η^5-cyclopentadienyliron hexafluorophosphate (XIV) was heated with an excess of $P(OC_2H_5)_3$ at 150°C for 18 h, and a 40% yield of the ring replacement product I was obtained, a finding that is similar to those observed for the nitroarene and aminoarene complexes (Table 2). When the treatment of XIV in the presence of $P(OC_2H_5)_3$ was carried out in refluxing CH_2Cl_2, the reactants were recovered unchanged, indicating no nucleophilic displacement of the chlorine atom by $P(OC_2H_5)_3$.

When amines were used as nucleophiles, displacement of the chlorine atom in the η^6-chloroarene-η^5-cyclopentadienyliron hexafluorophosphate by the nucleophile occurred readily to give various aminoarene complexes in good yield. Reactions of five amines with four chloroarene complexes were investigated. The chloroarene complexes employed included the η^6-chlorobenzene-η^5-cyclopentadienyliron hexafluorophosphate (XV) and the isomeric η^6-*o*-, -*m*-, or -*p*-chlorotoluene-η^5-cyclopentadienyliron hexafluorophosphate (XVI, XIV or XVII, respectively), and the amine reagents utilized were methylamine, ethylenediamine, cyclohexylamine, benzylamine and pyrrolidene. Twenty nucleophilic substitution products were obtained and these were characterized by their ^1H and ^{13}C NMR spectra. Given in Table 3 are the yields obtained and the ^{13}C NMR data for these products.

The ^{13}C NMR data in Table 3 are all consistent with the structures of the products. For example, in the first entry, the η^6-*N*-methylaniline-η^5-cyclopentadienyliron hexafluorophosphate shows, besides the Cp and CH_3NH peaks, 4 aromatic absorptions, 3 for the *o*-, *m*- and *p*-carbons and one for a quaternary carbon linked to the methylamino substituent. For the second entry, the η^6-*N*-

methyl-*o*-toluidine-η^5-cyclopentadienyliron hexafluorophosphate, there are two CH_3 absorptions at 15.7 and 28.1 ppm, the one at lower field being bonded to the more electronegative N. All 6 aromatic carbons of the *N*-methyl-*o*-toluidine ligand are different, giving rise to 6 peaks. Of the 2 quaternary aromatic peaks, the one at 82.1 ppm is the *o*-carbon bonded to the CH_3 substituent, while the quaternary carbon linked to the more electronegative N substituent appears at 124.8 ppm. Similar interpretations can be made with all of the other ^{13}C NMR data, and these data thus constitute support for the assigned structures of the various nucleophilic substitution products.

Recently, we have utilized the neutral zwitterionic species from the deprotonation of η^6-arene-η^5-cyclopentadienyliron cations as nucleophiles in a variety of synthetic applications [11,12]. When the isomeric η^6-*o*-, -*m*- or -*p*-toluidine-η^5-cyclopentadienyliron cation was deprotonated, it was a H on the amino group, rather than a H on the methyl group, that was removed, and reaction of the resulting zwitterion with, for example, substrates such as CH_3I or CH_3COCl would give rise to alkylated or acylated aminobenzene complexes [12]. The present results obtained from nucleophilic substitutions on η^6-chloroarene-η^5-cyclopentadienyliron hexafluorophosphates with different amines thus constitute a further extension of the synthetic approaches to a variety of *N*-substituted aminoarene complexes.

Experimental

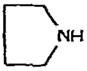
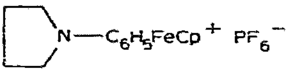
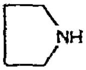
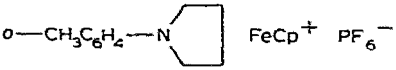
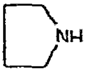
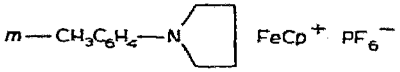
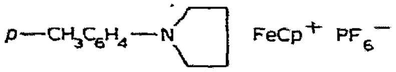
η^6-Nitroarene-η^5-cyclopentadienyliron hexafluorophosphates

η^6-Aniline-η^5-cyclopentadienyliron hexafluorophosphate (VIII) and η^6-*o*, -*m*- or -*p*-toluidine-η^5-cyclopentadienyliron hexafluorophosphate (IX, X or XI, respectively) were obtained by ligand exchange reactions between the aminoarene and ferrocene as previously described [12]. η^6-Aniline-η^5-methylcyclopentadienyliron hexafluorophosphate (XII) was also prepared by a similar ligand exchange reaction between aniline and a commercially obtained 1,1′-dimethylferrocene. The various nitroarene complexes, $NO_2C_6H_5FeCp^+ PF_6^-$ (II), *o*-, *m*- or *p*-$CH_3(NO_2)C_6H_4FeCp^+ PF_6^-$ (III, IV or V, respectively), and $NO_2C_6H_5Fe(CH_3)Cp^+ PF_6^-$ (VI) were prepared from the oxidation of the corresponding aminoarene complex with H_2O_2 in trifluoroacetic acid [5]. A typical experiment is given below.

The aniline complex VIII (3.35 g, 9.0 mmol) was added with stirring to 80 ml of a 1/1 solution of 30% H_2O_2 and trifluoroacetic acid. The mixture was heated at 75°C for 30 min. The resulting orange-yellow solution was cooled, diluted with 25 ml of H_2O and extracted four times of 25 ml aliquots of a 1/4 mixture of CH_3NO_2/CH_2Cl_2. The combined extract was dried over $MgSO_4$ and the solvent was removed under reduced pressure, giving a residual yellow-brown oil. Water (15 ml) was then introduced and acetone was gradually added until a homogeneous solution was obtained. Upon addition with stirring of a concentrated aqueous solution of NH_4PF_6, the nitrobenzene complex II appeared as a yellow precipitate. It was collected by filtration and crystallized from acetone/ether. The yield was 1.43 g (39%); its analysis and ^1H NMR data are given in Table 1.

(*continued on p. 158*)

TABLE 3. DATA ON THE SUBSTITUTION PRODUCTS FROM THE REACTION OF η^6-CHLOROBENZENE-η^5-CYCLOPENTADIENYLIRON HEXAFLUOROPHOSPHATE (XV) OR η^6-*o*-, -*m*- OR -*p*-

Reagent [a]	Substrate	Product [b]	Yield (%)
CH_3NH_2	XV	$CH_3NHC_6H_5FeCp^+ PF_6^-$ [d]	81
CH_3NH_2	XVI	*o*-$CH_3(CH_3NH)C_6H_4FeCp^+ PF_6^-$	86
CH_3NH_2	XIV	*m*-$CH_3(CH_3NH)C_6H_4FeCp^+ PF_6^-$	86
CH_3NH_2	XVII	*p*-$CH_3(CH_3NH)C_6H_4FeCp^+ PF_6^-$	85
$H_2NCH_2CH_2NH_2$	XV	$H_2NCH_2CH_2NHC_6H_5FeCp^+ PF_6^-$	70
$H_2NCH_2CH_2NH_2$	XVI	*o*-$CH_3(H_2NCH_2CH_2NH)C_6H_4FeCp^+ PF_6^-$ [d]	65
$H_2NCH_2CH_2NH_2$	XIV	*m*-$CH_3(H_2NCH_2CH_2NH)C_6H_4FeCp^+ PF_6^-$	69
$H_2NCH_2CH_2NH_2$	XVII	*p*-$CH_3(H_2NCH_2CH_2NH)C_6H_4FeCp^+ PF_6^-$	84
c-$C_6H_{11}NH_2$	XV	c-$C_6H_{11}NHC_6H_5FeCp^+ PF_6^-$	68
c-$C_6H_{11}NH_2$	XVI	*o*-CH_3(c-$C_6H_{11}NH)C_6H_4FeCp^+ PF_6^-$	48
c-$C_6H_{11}NH_2$	XIV	*m*-CH_3(c-$C_6H_{11}NH)C_6H_4FeCp^+ PF_6^-$	75
c-$C_6H_{11}NH_2$	XVII	*p*-CH_3(c-$C_6H_{11}NH)C_6H_4FeCp^+ PF_6^-$	72
$C_6H_5CH_2NH_2$	XV	$C_6H_5CH_2NHC_6H_5FeCp^+ PF_6^-$	70
$C_6H_5CH_2NH_2$	XVI	*o*-$CH_3(C_6H_5CH_2NH)C_6H_4FeCp^+ PF_6^-$	80
$C_6H_5CH_2NH_2$	XIV	*m*-$CH_3(C_6H_5CH_2NH)C_6H_4FeCp^+ PF_6^-$	81
$C_6H_5CH_2NH_2$	XVII	*p*-$CH_3(C_6H_5CH_2NH)C_5H_4FeCp^+ PF_6^-$	78
	XV		89
	XVI		85
	XIV		77
	XVII		77

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[a] As this work was in progress, Nesmeyanov and coworkers [10] reported briefly that they have carried out an analogous substitution reaction between XV and piperidine. [b] Satisfactory C, H, N analyses were obtained for all of the products. [c] ^1H NMR spectra consistent with the structures of the products were also

CHLOROTOLUENE-η^5-CYCLOPENTADIENYLIRON HEXAFLUOROPHOSPHATE (XVI, XIV OR XVII, RESPECTIVELY) WITH VARIOUS NUCLEOPHILES

^{13}C NMR (δ(acetone-d_6) (ppm) from TMS) ^{c}		
Cp	Aromatic	Others
74.7	67.1, 79.9, 85.1; 126.1(quat) ^{e}	28.4 (CH_3NH)
74.5	64.1, 78.6, 83.3, 86.8; 82.1(quat), 124.8(quat)	15.7 (CH_3); 28.1 (CH_3NH)
74.5	65.3, 68.1, 79.9, 84.0; 100.2(quat), 125.7(quat)	18.9 (CH_3); 28.1 (CH_3NH)
74.7	66.0, 84.9; 94.8(quat), 124.9(quat)	17.8 (CH_3); 28.1 (CH_3NH)
74.3	66.8, 79.3, 84.7; 125.4(quat)	42.7, 48.5 (CH_2)
75.4	65.4, 79.2, 83.9, 87.6; 82.5(quat), 124.7(quat)	16.6 (CH_3); 43.5, 49.3 (CH_2)
74.7	65.4, 68.3, 79.8, 84.0; 100.2(quat), 125.0(quat)	18.9 (CH_3); 42.7, 48.6 (CH_2)
74.9	66.2, 85.1; 94.6(quat), 124.4(quat)	17.9 (CH_3); 43.0, 48.7 (CH_2)
74.7	66.2, 79.1, 85.0; 125.4(quat)	23.4, 24.4, 31.4 (CH_2); 50.2 (CH)
74.8	64.3, 78.2, 83.3, 87.1; 80.7(quat), 123.9(quat)	15.9 (CH_3); 23.6, 24.2, 31.2 (CH_2); 50.6 (CH)
75.3	65.1, 67.9, 79.9, 84.4; 100.7(quat), 125.0(quat)	19.4 (CH_3); 23.8, 24.7, 31.7 (CH_2); 50.5 (CH)
75.9	66.3, 85.9; 95.2(quat), 125.0(quat)	18.6 (CH_3) 24.2, 25.1, 32.2 (CH_2); 52.0 (CH)
74.4	67.0, 79.6, 84.9; 125.1(quat) (complexed ring) 127.0, 127.2, 128.0; 136.8(quat) (uncomplexed ring)	45.4 (CH_2)
74.5	64.4, 78.5, 83.0, 87.0; 81.9(quat), 123.9(quat) (complexed ring) 126.8, 127.0, 127.9; 136.9(quat) (uncomplexed ring)	15.9 (CH_3); 45.2 (CH_2)
74.5	65.3, 68.3, 79.9, 83.9; 100.1(quat), 124.5(quat) (complexed ring) 126.8, 127.0, 127.8; 136.7(quat) (uncomplexed ring)	18.8 (CH_3); 45.2 (CH_2)
74.8	66.2, 84.8; 94.7(quat), 123.7(quat) (complexed ring) 126.8, 127.0, 127.8; 136.6(quat) (uncomplexed ring)	17.8 (CH_3); 45.2 (CH_2)
73.9	66.5, 79.1, 84.7; 124.1(quat)	23.9, 46.8 (CH_2)
74.7	64.7, 79.9, 83.3, 88.8; 83.7(quat), 127.4(quat)	20.9 (CH_3); 24.4, 49.7 (CH_2)
74.0	64.9, 68.0, 79.7, 83.8; 83.7(quat), 127.4(quat)	19.0 (CH_3); 23.8, 46.7 (CH_2)
74.2	65.8, 84.8; 94.2(quat), 122.8(quat)	17.8 (CH_3); 23.7, 46.7 (CH_2)

obtained. ^{d} The ^{13}C NMR spectra were obtained using CD_3CN instead of acetone-d_6 as solvent. ^{e} (quat) denotes quaternary carbons with much lower peak intensities.

Reactions with triethylphosphite

The nitroarene complex II, III, IV or V was heated under reflux with 4 equivalents of $P(OC_2H_5)_3$ at 130—140° C under N_2 for 18 h. The excess $P(OC_2H_5)_3$ was removed under reduced pressure. The solid residue was taken up in acetone and chromatographed through an alumina column. Elution with a 1/1 mixture of acetone/CH_2Cl_2 gave the ring replacement product, $CpFe(P(OC_2H_5)_3)_3^+ PF_6^-$ (I). After crystallization from CH_2Cl_2/ether, the yields obtained are given in Table 2. Typically, from the reactions of 0.64 g (1.6 mmol) of $NO_2C_6H_5$-$FeCp^+ PF_6^-$ (II) with 1.10 g (6.4 mmol) of $P(OC_2H_5)_3$, 0.50 g (47%) of I was obtained. The ^1H NMR spectrum of I is the same as reported by Gill and Mann [1]. (Found: C, 36.18; H, 6.48. $C_{23}H_{50}O_9FeP_4F_6$ calcd.: C, 36.13; H, 6.54%).

When the same reaction was carried out under the same conditions with $NO_2C_6H_5Fe(CH_3)Cp^+ PF_6^-$ (VI), a 36% yield of $CH_3CpFe(P(OCH_2CH_3)_3)_3^+ PF_6^-$ (VII) was obtained; ^1H NMR, δ(acetone-d_6) 1.17(*t*, 27H, $9CH_3$), 1.93(*s*, 3H, CH_3Cp), 3.97—4.45(*m*, 18H, $9CH_2$), 4.52—4.82(m, 4H, Cp). (Found: C, 36.72; H, 6.81. $C_{24}H_{52}O_9FeP_4F_6$ calcd.: C, 37.03; H, 6.73%).

When the aminoarene complex VIII, IX, X or XI was heated with 4 equivalents of $P(OC_2H_5)_3$ at 145—150°C for 16 h and the resulting material worked up as described above, the ring replacement product I was obtained in yields as given in Table 2. With $NH_2C_6H_5Fe(CH_3)Cp^+ PF_6^-$ (XII), the heating at 145—150°C was extended to 20 h, and a 60% yield of VII was obtained.

Reactions of chloroarene complexes with amines

The chloroarene complexes, $ClC_6H_5FeCp^+ PF_6^-$ (XV) and the *o*-, *m*- or *p*-$CH_3(Cl)C_6H_4FeCp^+ PF_6^-$ (XVI, XIV or XVII, respectively) were prepared from ligand exchange reactions between ferrocene and the chloroarene as previously reported [13—15]. A general procedure for the nucleophilic substitution of the chlorine atom in XV, XVI, XIV and XVII with various amines as nucleophiles is given below.

A solution of 2—4 mmol of the chloroarene complex and an excess of the amine (6—10 equiv.) in 30 ml of CH_2Cl_2 was stirred at room temperature for 10—12 h. To the resulting material, a concentrated aqueous solution of NH_4PF_6 was added and the mixture was extracted with CH_2Cl_2. After drying over $MgSO_4$ and removal of most of the solvent, addition of ether precipitated the product which was recrystallized from CH_2Cl_2/ether. In a typical reaction, a solution of 1.57 g (4.0 mmol) of $ClC_6H_5FeCp^+ PF_6^-$ (XV) and 3.90 g (36.4 mmol) of benzylamine in 30 ml of CH_2Cl_2 was stirred overnight (about 12 h) and worked up as described above to give 1.44 g (78%) of η^6-*N*-benzylaniline-η^5-cyclopentadienyliron hexafluorophosphate as listed in Table 3.

The above general procedure was used for the reaction of XV, XVI, XIV and XVII with methylamine, cyclohexylamine, benzylamine and pyrrolidine except that in the reaction of *o*-$CH_3(Cl)C_6H_4FeCp^+ PF_6^-$ (XVI) with cyclohexylamine or benzylamine, CH_3CN instead of CH_2Cl_2 was used as solvent. In the reactions with ethylenediamine as nucleophile, a prolonged reaction time gave rise to poor yields and impure products, probably because of the possibility of further reaction of the second amino group with more chloroarene substrate. In the reaction of $ClC_6H_5FeCp^+ PF_6^-$ (XV) with a 10 molar equivalent of $H_2NCH_2CH_2$-NH_2 in CH_2Cl_2, the reaction mixture was stirred for only 10 min, while in the reaction of *o*-, *m*-, or *p*-$CH_3(Cl)C_6H_4FeCp^+ PF_6^-$ with $H_2NCH_2CH_2NH_2$, the reaction time was 1.0 h.

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