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Ring opening reactions of some epoxides with cyclopentadienyliron complexed aminoarenes

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Abstract

Treatment of a number of CpFe complexed aminoarenes under basic conditions with propylene oxide resulted in ring opening reactions at the primary methylene carbon of the epoxide, leading to the preparation of CpFe complexed *N*-(2-hydroxypropyl)aminoarenes. Of interest is the formation of a pair of diastereomers in the reaction with the CpFe complex of *o*-toluidine, demonstrating that besides the chiral center in the *N*-(2-hydroxylpropyl) group, the CpFe complexed unsymmetrical *o*-toluidine is also chiral. Similar reactions of the CpFe complexed *p*-toluidine with cyclohexene oxide or with *cis*- or *trans*-2,3-butylene oxide led to ring opening products with the expected stereochemistry from a direct nucleophilic displacement reaction.

Introduction

Ring opening reactions of epoxides with a variety of nucleophiles have been extensively studied and these reactions have been included in a number of reviews [1–5]. For such ring openings with amines, it has been pointed out that while aliphatic amines react with relative ease, aromatic amines show decreased reactivity and may require the use of an excess of amine and elevated temperatures [6,7]. Modifications to allow for more ready reactions with aromatic amines, such as the use of aryldiethylaluminium amides [6] or the employment of hexamethylphosphoramide as solvent [7], have been reported. In our laboratory, we have shown that treatment of the η^6-*o*-, *m*- or *p*-toluidine-η^5-cyclopentadienyliron cation with t-BuOK in THF resulted in the loss of a proton from the amino group, giving rise to a zwitterionic species which could be utilized directly in nucleophilic substitution reactions [8]. Such zwitterionic species from deprotonation of cyclopentadienyliron (CpFe) complexed aromatic amines should be capable of undergoing ring opening reactions with epoxides more readily than the corresponding uncomplexed aromatic amines. In the present work, reactions of some epoxides with a number of CpFe

complexed aromatic amines under basic conditions were investigated and the results provided ready syntheses of CpFe complexes of aminoarenes with a β-hydroxyalkyl substituent on the amino nitrogen.

Results and discussion

Reaction of 1.0 mmol of the hexafluorophosphate salt of the η^6-aniline-η^5-cyclopentadienyliron cation (Ia) and 2.0 mmol of t-BuOK with an excess of propylene oxide at room temperature in 10 or 30 ml of tetrahydrofuran (THF) for 48 h gave a 60 or 45% yield, respectively, of the η^6-*N*-(2-hydroxypropyl)aniline-η^5-cyclopentadienyliron cation (Ib), obtained as its hexafluorophosphate. An analogous reaction of an excess of the uncomplexed aniline with propylene oxide at 125 °C for 8 h was reported to give a 70% yield of *N*-(2-hydroxypropyl)aniline [9]. While this yield of 70% was higher, the temperature of 125 °C that was required was also considerably higher. In the present work, similar reactions of 5 other CpFe complexed substituted anilines, IIa–VIa, with propylene oxide readily gave the corresponding products IIb–VIb, the results being summarized in Table 1. As an illustration of a reaction with a sulfur analog, the results from treatment of the CpFe complex of *p*-toluidine (IIIa) with propylene sulfide are included in Table 1.

It is seen that all the products listed in Table 1 are the "normal" products [1] derived from ring opening reactions at the primary carbon of the propylene oxide or propylene sulfide, and no "abnormal" product from reaction at the secondary carbon was detectable. This finding is in agreement with expectation for an S_N2 reaction, the less sterically hindered primary methylene group being the preferred site of reaction. Under the basic conditions employed, presumably the nucleophile in these reactions would be the zwitterionic species from deprotonation of the

Table 1

Products and yields from reactions of CpFe complexed anilines with propylene oxide [a]

Aniline complex [b]	Product complex [b]	Yield (%) [c]	
		concentrated	dilute
$C_6H_5(NH_2)FeCp^+$ (Ia)	$C_6H_5[NHCH_2CH(OH)CH_3]$-$FeCp^+$ (Ib)	60	45
p-$(CH_3)_2NC_6H_4(NH_2)FeCp^+$ (IIa)	*p*-$(CH_3)_2NC_6H_4[NHCH_2CH$-$(OH)CH_3]FeCp^+$ (IIb)	70	70
p-$CH_3C_6H_4(NH_2)FeCp^+$ (IIIa)	*p*-$CH_3C_6H_4[NHCH_2CH$-$(OH)CH_3]FeCp^+$ (IIIb)	72	73
o-$CH_3C_6H_4(NH_2)FeCp^+$ (IVa)	*o*-$CH_3C_6H_4[NHCH_2CH$-$(OH)CH_3]FeCP^+$ (IVb) [d]	65	50
2,6-$(CH_3)_2C_6H_3(NH_2)FeCp^+$ (Va)	2,6-$(CH_3)_2C_6H_3[NHCH_2CH$-$(OH)CH_3]FeCp^+$ (Vb)	40	20
p-$ClC_6H_4(NH_2)FeCp^+$ (VIa)	*p*-$ClC_6H_4[NHCH_2CH(OH)CH_3]$-$FeCp^+$ (VIb)	45	32
IIIa [e]	*p*-$CH_3C_6H_4[NHCH_2CH$-$(SH)CH_3]FeCp^+$ (VII)	31	25

[a] Reaction of 1.0 mmol of the complexed aniline and 2.0 mmol of t-BuOK with an excess of propylene oxide at room temperature for 48 h in 10 or 30 ml of THF. [b] As the hexafluorophosphate. [c] Yields from reactions carried out in 10 or 30 ml of THF, respectively, being designated as concentrated or dilute reactions. [d] As a pair of diastereomers. [e] Reaction of IIIa with propylene sulfide.

complexed aromatic amines [8]. The yields of various products as summarized in Table 1 are also of interest. For complex IIa or IIIa with an electron-donating *p*-substituent, the yield obtained under either dilute or more concentrated solution of the reactants was essentially the same. On the other hand, reactions of Ia and IVa–VIa all gave higher yields when the reactions were carried out at higher reactant concentrations. Apparently, complex IVa or Va with the methyl group at the *o*- or 2,6-positions providing some steric hindrance, and complex VIa with an inductively electron-withdrawing *p*-chloro group, all would give rise to less reactive nucleophiles for the S_N2 ring opening reaction, which was reflected by the generally lower yields, with these yields being somewhat higher when the reactions were carried out at higher reactant concentrations. Similarly, propylene sulfide has been found to be less reactive than propylene oxide towards aniline [10], and thus reaction of IIIa with propylene sulfide to give VII followed the same pattern as the reaction of IVa–VIa with propylene oxide.

In view of the above finding that no ring opening reaction took place at the secondary carbon of propylene oxide, it is of interest to investigate possible reactions with the epoxy group linked to two secondary carbons. When *p*-toluidine complex IIIa was treated with cyclohexene oxide under similar conditions as in its reaction with propylene oxide, ring opening occurred only with still higher reactant concentration of 1.0 mmol of IIIa in 5.0 ml of THF to give the η^6-*N-trans*-(2-hydroxycyclohexyl)-*p*-toluidine-η^5-cyclopentadienyliron cation (VIII), isolated as its hexafluorophosphate. For the analogous reaction of uncomplexed *p*-toluidine with cyclohexene oxide, *N-trans*-(2-hydroxycyclohexyl)-*p*-toluidine was obtained when the reactants were heated in the presence of $NaHCO_3$ in hexamethylphosphoramide as solvent [7]. When IIIa was similarly treated with *cis*- or *trans*-2,3-butylene oxide, the η^6-*threo*- or *erythro*-*N*-(3-hydroxy-2-butyl)-*p*-toluidine-η^5-cyclopentadienyliron cation (IX or X, respectively) was obtained as its hexafluorophosphate, as expected from the direct nucleophilic substitution mechanism for the ring opening reaction. The same stereochemical results have been reported that upon reaction with NH_3 or NH_2NH_2, *cis*- or *trans*-2,3-butylene oxide gave rise to the *threo*- or *erythro*-product, respectively [11]. Thus the presently observed formation of VIII, IX and X, as well as the products from reactions with propylene oxide (Table 1), indicate that these ring opening reactions of epoxides could be readily utilized for the preparation of CpFe complexed aminoarenes with a β-hydroxyalkylamino side chain containing both the hydroxy and amino functions.

Summarized in Tables 2 and 3 are the ^1H and ^{13}C NMR spectral data in support of the assigned structures for the various products obtained in the present studies. It may be of interest to point out that, in theory, the *threo*- and *erythro*-diastereomers IX and X may be differentiated by the magnitudes of the vicinal coupling constants of the C2 and C3 protons of the butyl group [11,12]. Unfortunately, these coupling constants could not be evaluated because of poor resolution. However, the assignment of IX and X as *threo* and *erythro*, respectively, was based on the conformational analysis of Maurette and coworkers [12], which indicated that for the *threo*-isomer, the two methyl groups of the 2-butyl system, being *trans* in the most stable conformation, would show two well separated doublets as observed for IX, while for the *erythro*-isomer, these methyl groups being *gauche*, would give two overlapping doublets as observed for X. It is also of interest to note that except for IVb, all the products obtained are racemic (*R,S*)-pairs showing one set of ^1H or ^{13}C

Table 2. ^{1}H NMR data for products from reactions of CpFe complexed aminoarenes with epoxides.

Product complex [a]	δ(acetone-d_6) (ppm from TMS)		
	Cp [b]	Complexed Ar [c]	Substituents [c]
Ib	4.99	5.92(t, *J* 5.8,2H,H2,6), 6.02(t, *J* 5.9,1H,H4), 6.14(d of d, *J* 5.9,7.2, 2H,H3.5)	1.23(d, *J* 6.0,3H,CH_3), 3.17–3.23,3.36–3.42(2m,2H,CH_2), 4.02–4.08(m,2H,CH,OH) 6.05(br.s,1H,NH)
IIb	4.91	5.48–5.61(m,5H, H2,3,5,6,NH)	1.24(d, *J* 5.5,3H,CH_3), 3.04 [d](s,6H,$(CH_3)_2N$), 3.04–3.12 [d],3.28–3.36(2m,2H,CH_2), 3.96–4.08(m,2H,CH,OH)
IIIb	4.95	5.85,5.87(2d, *J* 5.5,2H,H2,6), 6.08(d, *J* 6.8,2H,H3,5)	1.24(d, *J* 5.8,3H,CH_3), 2.41(s,3H,CH_3Ar), 3.17–3.21,3.36–3.40(2m,2H,CH_2) 3.98–4.08(m,2H,CH,OH), 5.95(br.s,1H,NH)
IVb	4.89 4.90	5.89–5.94,6.05–6.15 (2m,4H,H3,4,5,6)	1.24,1.26(2d, *J* 6.2,3H,CH_3), 2.41,2.42(2s,3H,CH_3Ar), 3.24–3.32,3.40–3.48(2m,2H,CH_2), 4.00–4.20(m,2H,CH,OH), 5.47,5.55(2br.s,1H,NH)
Vb	4.90	5.90(t, *J* 6.0,1H,H4), 6.14(d, *J*5.6,2H,H3,5)	1.17(d, *J* 6.2,3H,CH_3), 2.56,2.57(2s,6H,2,6-$(CH_3)_2$Ar), 3.14–3.22,3.38–3.46(2m,2H,CH_2), 3.85–3.95(m,1H,CH), 4.10(d, *J* 4.8,1H,OH),4.68(br.s,1H,NH)
VIb	5.08	5.95,5.97(2d, *J* 5.9,2H,H2,6), 6.49(d, *J* 7.1,2H,H3,5)	1.22(d, *J* 6.1,3H,CH_3), 3.14–3.22,3.36–3.44(2m,2H,CH_2), 3.98–4.18(m,2H,CH,OH), 6.25(br.s,1H,NH)
VII [e]	4.98	5.86–5.90(m,2H,H_2,6), 6.06–6.16(m,3H,H3,5,NH)	1.40(br.s,1H,SH), 1.45(d, *J* 6.5,3H,CH_3), 2.43(s,3H,CH_3Ar), 2.80–3.00(m,2H,CH_2), 4.18–4.22(m,1H,CH)
VIII	4.92	5.82–5.92 [f](m,2H,H2,6), 5.98–6.06(m,2H,H3,5)	1.26–1.46,1.67–1.75,2.00–2.14 (3m,8H,H3′,4′,5′,6′), 2.39(s,3H,CH_3Ar), 3.32–3.46(m,2H,H1′,2′), 4.19(d, *J* 4.2,1H,OH), 5.78 [f](d, *J* 6.9,1H,NH)
IX	4.93	5.74–5.86(m,3H,H2,6,NH), 6.04–6.10(m,2H,H3,5)	1.22,1.27(2d, *J* 6.4,6.5,6H,2CH_3), 2.41(s,3H,CH_3Ar), 3.58–3.64[m,1H,C*H*(NH)], 3.78–3.84[m,1H,C*H*(OH)], 4.15(d, *J* 4.4,1H,OH)
X	4.94	5.80–5.92(m,3H,H2,6,NH), 6.06–6.12(m,2H,H3,5)	1.21,1.23(2d,overlapping,6H,2CH_3), 2.41(s,3H,CH_3Ar), 3.72–3.78[m,1H,C*H*(NH)], 3.96–4.02[m,1H,C*H*(OH)], 4.10(d, *J* 4.5,1H,OH)

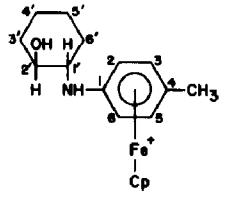
[a] As the hexafluorophosphate; for structures Ib–VIb and VII, see Table 1; VIII is the CpFe complex of *N*-(*trans*-2-hydroxycyclohexyl)-*p*-toluidine, IX and X, respectively, are the CpFe complexes of *threo*- and *erythro*-*N*-(3-hydroxy-2-butyl)-*p*-toluidine. [b] The Cp absorptions are 5H singlets. [c] *J* values are in Hz; the OH and NH signals were confirmed by exchange with D_2O. [d] Some overlap between these peaks. [e] From reaction of the CpFe complex of *p*-toluidine with propylene sulfide instead of an epoxide. [f] Some overlap between these peaks.

Table 3

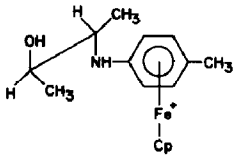
^{13}C NMR data for products from reactions of CpFe complexed aminoarenes with epoxides

Product complex [a]	δ(acetone-d_6) (ppm from TMS)		
	Cp	Complexed Ar	Substituents
Ib	76.2	68.7(C2,6),81.1(C4) 86.6(C3,5),127.6(Cl),	21.4(CH_3),50.9(CH_2), 66.2(CH)
IIb	75.1	65.5(C2,6),65.9(C3,5), 122.1(C4),122.6(C1)	21.4(CH_3),40.2[(CH_3)$_2$N], 51.4(CH_2),66.2(CH)
IIIb	76.7	68.0(C2,6),86.8(C3,5), 96.4(C4),126.5(C1)	19.7(CH_3Ar),21.4(CH_3), 51.0(CH_2),66.2(CH)
IVb	76.47 76.50	66.40,66.72(C6), 80.24,80.31(C4) 83.36,83.44(C2), 85.00,85.05(C5) 88.64,88.66(C3), 126.11,126.36(C1)	17.60,17.67(CH_3Ar), 21.24,21.45(CH_3), 50.84,51.13(CH_2) 66.01,66.31(CH)
Vb	77.5	82.0(C4),88.4,88.5(C3,5), 89.0(C2,6),125.8(C1)	19.4,19.6[2,6-(CH_3)$_2$Ar] 21.3(CH_3),55.4(CH_2),67.3(CH)
VIb	78.6	67.3(C2,6),86.7(C3,5), 101.6(C4),127.5(C1)	21.3(CH_3),50.9(CH_2), 66.2(CH)
VII [b]	77.1	68.3(C2,6),87.0(C3,5), 96.9(C4),124.6(C1)	19.6(CH_3Ar),20.3(CH_3), 46.1(CH_2),24.8(CH)
VIII	76.8	67.7,68.0(C2,6), 86.7(C3,5),95.9(C4) 126.7(C1)	19.6(CH_3Ar),24.8,24.9(C4′,5′), 32.1,35.2(C3′,6′), 59.1(C1′),74.1(C2′)
IX	76.8	67.5,67.7(C2,6) 86.8,86.9(C3,5), 96.1(C4),127.0(C1)	17.2,17.4(CH_3),19.7(CH_3Ar), 54.8[CH(NH)],70.3[CH(OH)]
X	76.8	67.4,67.6(C2,6), 86.8,86.9(C3,5) 96.1(C4),126.7(C1)	15.0,19.2(CH_3),19.6(CH_3Ar), 54.1[CH(NH)],69.5[CH(OH)]

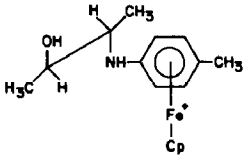
[a] As the hexafluorophosphate; structures as stated in footnote *a* of Table 2. [b] From reaction of the CpFe complex of *p*-toluidine with propylene sulfide instead of an epoxide.



VIII



IX



X

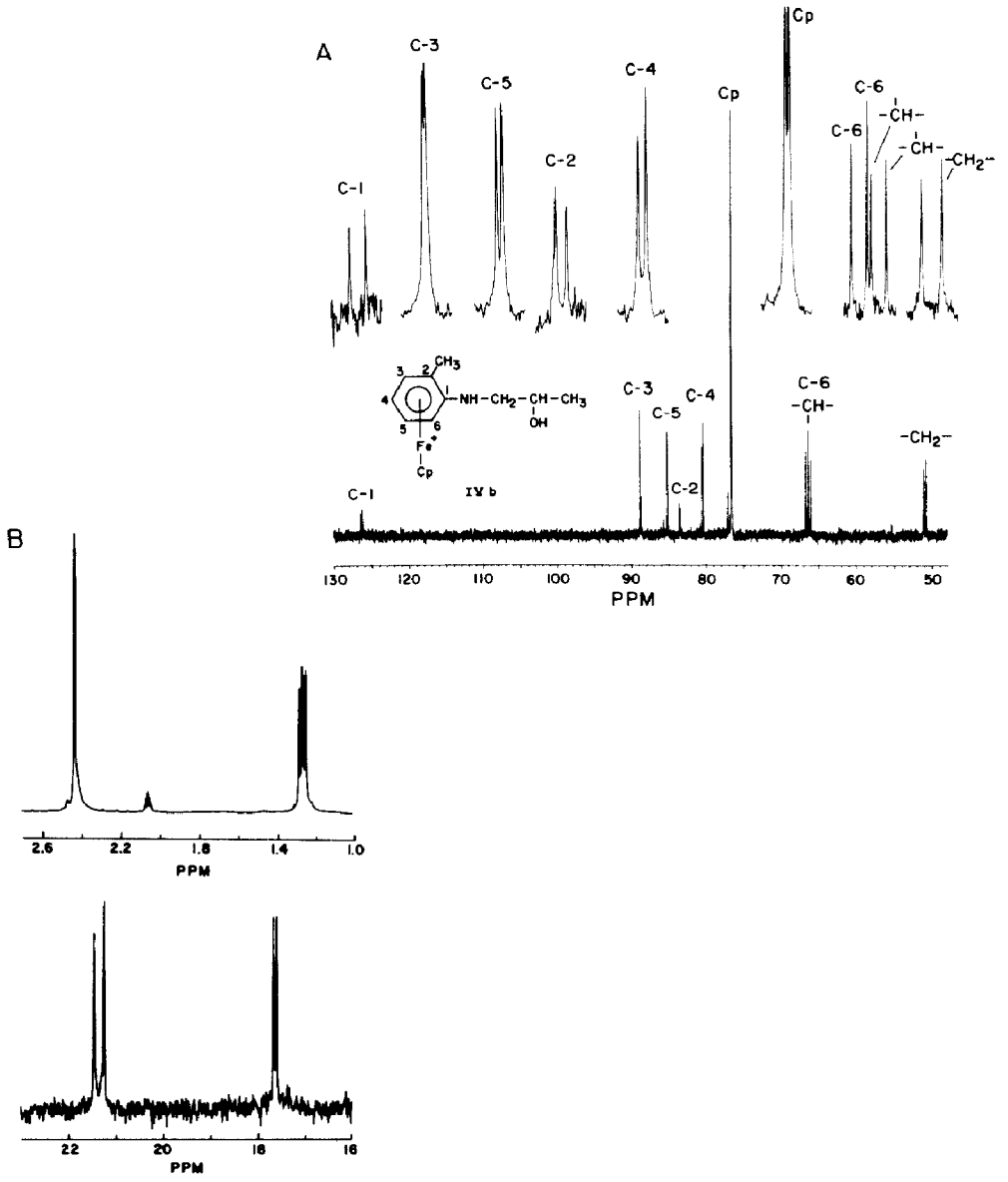


Fig. 1. A, ^{13}C NMR spectrum of η^6-*N*-(2-hydroxypropyl)-*o*-toluidine-η^5-cyclopentadienyliron hexafluorophosphate (IVbPF_6) with insets of expanded absorptions showing the presence of a pair of diastereomers; B, the expanded ^1H and ^{13}C NMR spectra for the methyl absorptions of IVbPF_6.

NMR data. For the η^6-*N*-(2-hydroxypropyl)-*o*-toluidine-η^5-cyclopentadienyliron cation IVb, besides the chiral C2 carbon of the propyl group, the unsymmetrically substituted CpFe complexed arene is also chiral, thus giving rise to a pair of (*R,S-S,R*)- and (*R,R-S,S*)-diastereomers showing two sets of ^1H and ^{13}C NMR absorptions. Besides the data summarized in Tables 2 and 3, Fig. 1A shows the ^{13}C NMR spectrum of IVb and some expanded absorptions clearly demonstrating the occurrence of two separate peaks for various C atoms, and Fig. 1B shows the expanded portions of the ^1H and ^{13}C absorptions for the methyl group attached to the aromatic ring and the methyl group of the 2-hydroxypropyl chain, again

demonstrating the presence of a pair of diastereomers. The early literature on the stereochemistry of the metallocenes has been reviewed [13] and some recent examples dealing with stereoselective syntheses have involved tricarbonylchromium complexed arenes [14–16]. In the case of CpFe complexed unsymmetrically substituted arenes, a recent study on the resolution of the oxime of η^6-α-tetralone-η^5-cyclopentadienyliron cation and some of its subsequent reactions has been reported [17]. The present observation that IVb exists as a pair of diastereomers thus constitutes a confirmation that the relatively simple CpFe complexed o-toluidine moiety of IVb is indeed chiral.

Experimental

CpFe complexed aminoarenes

The η^6-aniline-η^5-cyclopentadienyliron cation (Ia) [18], η^6-*p*- or *o*-toluidine-η^5-cyclopentadienyliron cation (IIIa or IVa, respectively) [8] and η^6-2,6-dimethylaniline-η^5-cyclopentadienyliron cation (Va) [19] were prepared as previously described from ligand exchange reactions and obtained as their hexafluorophosphates. The hexafluorophosphate of the η^6-*p*-chloroaniline-η^5-cyclopentadienyliron cation (VIa) was also obtained as previously described [20] from a nucleophilic substitution reaction between NH_3 and the CpFe complex of *p*-dichlorobenzene. The η^6-*p*-dimethylaminoaniline-η^5-cyclopentadienyliron cation (IIa) is a new complex and was prepared from VIa as described below.

A solution of 788 mg (2.0 mmol) ov $VIaPF_6$, 5.0 ml of a 25% aqueous solution of dimethylamine (1.25 g, 30 ml) and 1.0 ml of glacial acetic acid in 5.0 ml of *N*,*N*-dimethylformamide was stirred at room temperature for 3 days. The resulting material was concentrated to a small volume by a rotary evaporator and the residue was redissolved in CH_2Cl_2, washed with a 10% solution of $NaHCO_3$ and with H_2O. After drying over $MgSO_4$, most of the solvent was removed and the residual crude product was purified by passage through a short (5.0 cm) column packed with Fisher A-540 alumina that had been deactivated by exposure to air for 48 h. Impurities were first removed by elution with $CHCl_3$ and the desired product was then eluted with a 1/1 mixture of CH_2Cl_2/acetone. After removal of the solvent from the eluate, 579 mg (72%) of the yellow crystalline hexafluorophosphate of IIa was obtained, ^{1}H NMR: δ(acetone-d_6) 3.01 [s,6H,$(CH_3)_2N$], 4.85 (s, 5H, Cp), 5.28 (br.s, 2H, NH_2), 5.59 (d, $J = 7.0$, 2H), 5.68 (d, $J = 7.0$, 2H) ppm (Ph hydrogens); ^{13}C NMR: δ(acetone-d_6) 40.2 [$(CH_3)_2N$], 75.6 (Cp), 65.9 (2C), 68.6 (2C), 120.5 (quat.), 122.5 (quat.) ppm (Ph carbons). (Found for $IIaPF_6$: C, 39.05; H, 4.32; N, 6.87. $C_{13}H_{17}N_2FePF_6$ calcd.: C, 38.83; H, 4.26; N, 6.96%).

Reactions with propylene oxide

In a typical experiment, a mixture of 359 mg (1.0 mmol) of η^6-aniline-η^5-cyclopentadienyliron hexafluorophosphate ($IaPF_6$) and 224 mg (2.0 mmol) of t-BuOK in 10 or 30 ml of THF was stirred at room temperature for 4–5 min to give a deep red solution. Two ml (1.7 g, 29 mmol) of propylene oxide was then added and stirring was continued at room temperature for 48 h. The resulting material was filtered and the reaction flask was washed with CH_2Cl_2, the washing also being filtered. The combined filtrate was treated with a solution of 500 mg (3.0 mmol) of NH_4PF_6 in 10 ml of H_2O. The product was then recovered by extraction with CH_2Cl_2 (4×50 ml).

The combined extract was dried over $MgSO_4$, and after removal of the solvent, the residual crude product was purified by passage through a short column packed with alumina as described in the purification of IIa. Impurities including any unreacted aniline complex were first removed by elution with $CHCl_3$ and with 1/1 CH_2Cl_2/acetone. The yellow product, η^6-*N*-(2-hydroxypropyl)aniline-η^5-cyclopentadienyliron hexafluorophosphate ($IbPF_6$), was then eluted with 1/1 ethanol/acetone. The yield was 250 mg (60%) or 188 mg (45%), respectively, for the reaction carried out in 10 or 30 ml of THF. The ^1H and ^{13}C NMR data, obtained with a Bruker AM 300 spectrometer, are given in Tables 2 and 3. (Found for $IbPF_6$: C, 40.29; H, 4.32; N, 3.36. $C_{14}H_{18}ONFePF_6$ calcd.: C, 40.31; H, 4.35; N, 3.36%).

Reactions with 1.0 mmol of the hexafluorophosphates of IIa–VIa to give the hexafluorophosphates of IIb–VIb, respectively, were carried out in the same way except that in the chromatographic purification for IIb, Vb and VIb, after the removal of impurities and unreacted materials by elution with $CHCl_3$ and 1/1 CH_2Cl_2/acetone, the desired product was eluted with 1/1 acetone/CH_3CN instead of ethanol/acetone. All of these products gave satisfactory elemental analyses for C, H and N. The yields obtained are summarized in Table 1 and the ^1H and ^{13}C NMR data in support of their assigned structures are given in Tables 2 and 3.

η^6-N-(2-Mercaptopropyl)-p-toluidine-η^5-cyclopentadienyliron hexafluorophosphate ($VIIPF_6$)

A mixture of 373 mg (1.0 mmol) of η^6-*p*-toluidine-η^5-cyclopentadienyliron hexafluorophosphate ($IIIaPF_6$) and 224 mg (2.0 mmol) of t-BuOK in 10 or 30 ml of THF was stirred at room temperature for 4–5 min and then a solution of 2.0 ml of propylene sulfide (1.9 g, 26 mmol) in 5.0 ml of THF was added dropwise with stirring. Stirring at room temperature was continued for 48 h and the resulting material was worked up as described in the reactions with propylene oxide to give a sticky yellow oil. On purification by passage through the alumina column, impurities were first removed by elution with $CHCl_3$. The desired product, $VIIPF_6$, was then eluted with 3/1 $CHCl_3$/acetone as a yellow oil, the yield being 139 mg (31%) or 112 mg (25%), respectively, from reaction in 10 or 30 ml of THF. About 50–60% of unreacted $IIIaPF_6$ was also recovered as a third fraction from elution with 1/1 CH_2Cl_2/acetone. The ^1H and ^{13}C NMR data for $VIIPF_6$ are summarized in Tables 2 and 3. (Found for $VIIPF_6$: C, 40.15; H, 4.65; N, 3.02. $C_{15}H_{20}NSFePF_6$ calcd.: C, 40.28; H, 4.51; N, 3.13%).

η^6-N-(trans-2-Hydroxycyclohexyl)-p-toluidine-η^5-cyclopentadienyliron hexafluorophosphate ($VIIIPF_6$)

The reaction of 373 mg (1.0 mmol) of $IIIaPF_6$, 224 mg (2.0 mmol) of t-BuOK and 2.0 ml (1.9 g, 20 mmol) of cyclohexene oxide in 5.0 ml of THF was carried out at room temperature for 48 h as in the reaction with propylene oxide. After the usual work-up, the chromatographic purification included the removal of impurities and unreacted $IIIaPF_6$ by elution with $CHCl_3$ and with 1/1 CH_2Cl_2/acetone, while the desired product was finally eluted with ethanol to give 118 mg (25%) of $VIIIPF_6$ as a yellow solid. (Found for $VIIIPF_6$: C, 45.53; H, 5.01; N, 2.74. $C_{18}H_{24}ONFePF_6$ calcd.: C, 45.88; H, 5.13; N, 2.97%).

η^6-N-(threo- or erythro-3-Hydroxy-2-butyl)-p-toluidine-η^5-cyclopentadienyliron hexafluorophosphate (IXPF$_6$ or XPF$_6$)

The reaction of 373 mg (1.0 mmol) of IIIaPF$_6$, 224 mg (2.0 mmol) of t-BuOK and 1.44 g (20 mmol) of *cis*- or *trans*-2,3-butylene oxide in 5.0 ml of THF was carried out as described above for the reaction with cyclohexene oxide. In the chromatographic purification, following the removal of impurities and unreacted IIIaPF$_6$ by elution with $CHCl_3$ and with 1/1 CH_2Cl_2/acetone, the desired product was eluted with 1/2 ethanol/CH_3CN to give 112 mg (25%) of the *threo*-isomer IXPF$_6$ or 67 mg (15%) of the *erythro*-isomer XPF$_6$, respectively, from reaction with *cis*- or *trans*-2,3-butylene oxide. (Found for IXPF$_6$ and XPF$_6$, respectively: C, 43.15 and 43.25; H, 4.94 and 5.00; N, 3.18 and 3.20. $C_{16}H_{22}ONFePF_6$ calcd.: C, 43.16; H, 4.98; N, 3.14%).

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