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THE SYNTHESIS OF SOME η^6-KETOARENE-η^5-CYCLOPENTADIENYLIRON CATIONS AND THEIR REDUCTION WITH SODIUM BOROHYDRIDE

C.C. LEE*, K.J. DEMCHUK, U.S. GILL, and R.G. SUTHERLAND*

Department of Chemistry, University of Saskatchewan, Saskatoon, Sask., S7N OWO (Canada)

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Summary

η^6-Ketoarene-η^5-cyclopentadienyliron cations were prepared from $KMnO_4$ oxidation of the aqueous solution of the tetrachloroaluminate salts of η^6-arene-η^5-cyclopentadienyliron cations derived from ligand exchange reactions without the prior isolation of the product from the ligand exchange. Methylene groups α to the complexed aromatic ring were oxidized to carbonyl functions. The ketoarene complexes obtained include those with fluorenone, benzophenone and anthraquinone as the ketoarene ligand. Reduction of these complexed ketoarenes with $NaBH_4$ or $NaBD_4$ gave the corresponding complexed *endo*-alcohols derived from stereospecific *exo*-addition of the hydride or deuteride ion.

Introduction

The preparation of a large number of η^6-arene-η^5-cyclopentadienyliron cations via ligand exchange between an arene and ferrocene (FcH) in the presence of $AlCl_3$ has been reviewed [1]. No CpFe complexed ketoarene, however, was reported [1], and attempts in this laboratory to effect a direct ligand exchange between fluorenone or benzophenone with FcH have failed, presumably because the $AlCl_3$ interacts with the carbonyl group. Nesmeyanov et al. [2,3] have reported that permanganate oxidation of η^6-methyl substituted arene-η^5-cyclopentadienyliron tetrafluoroborate (arene = toluene and *m*- or *p*-chlorotoluene) gives the corresponding complexed benzoic acid in good yields. In the present work, $KMnO_4$ oxidation was utilized in converting the methylene groups α to the complexed aromatic ring to the corresponding carbonyl function. Reduction of such ketoarene complexes with $NaBH_4$ or $NaBD_4$ to give complexes containing the alcohol function was also studied.

Results and discussion

The cyclopentadienyliron complexes of fluorene, diphenylmethane and 9,10-dihydroanthracene were successfully converted to the corresponding ketoarene com-

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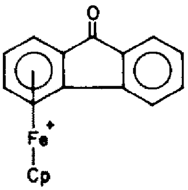
plexes by $KMnO_4$ oxidation. A major advantage of the procedure that was developed was that the oxidation could be carried out in situ on the water soluble tetrachloroaluminate salt of the arene-Fe-Cp^+ cation derived from the ligand exchange reaction without its prior isolation. In a typical preparation, the reactants, $FcH/AlCl_3/Al$/fluorene, in the ratio of approximately 1/5/1/1, were heated under reflux in decalin at 140 ± 2°C for 5 h. The mixture was then hydrolyzed with ice-water and the aqueous phase treated with 1.0 molar equivalent of $KMnO_4$ to give the η^6-fluorenone-η^5-cyclopentadienyliron cation (I), isolated as its hexafluorophosphate in 38–42% yields from several trials. Similar treatments starting with diphenylmethane or 9,10-dihydroanthracene gave the benzophenone complex II or the anthraquinone complex III.



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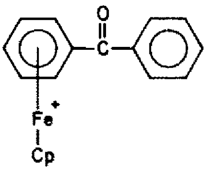

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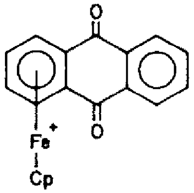
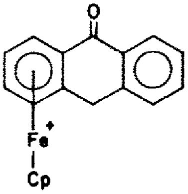


III

In the reaction starting with 9,10-dihydroanthracene, no anthrone complex IV was obtained, indicating that one methylene group could not be oxidized without the oxidation of the second methylene group in the 9,10-dihydroanthracene complex derived from the ligand exchange. When the η^6-fluorene-*trans*-bis-η^5-cyclopentadienyliron dication (V) [4] was prepared and oxidized in situ with $KMnO_4$, the corresponding fluorenone dication VI was also obtained. The yields and spectral data for the ketoarene complexes, I, II, III and VI are summarized in Tables 1 and 2.



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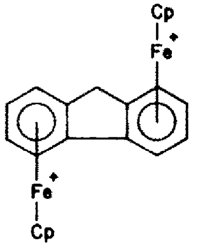
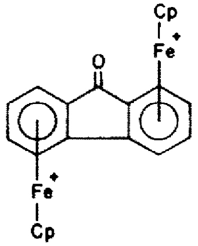


V



VI

Attempts were also made to carried out the in situ oxidation with $KMnO_4$ as described above on η^6-arene-η^5-cyclopentadienyliron cations with *o*-chlorotoluene, tetralin, acenaphthene or 9,10-dihydrophenanthrene as the arene ligand. In all of these cases, no isolable oxidation product was obtained and a small amount (10–20%) of the unreacted arene-Fe-Cp^+ cation was recovered as its hexafluorophosphate. Apparently, under the conditions used in the present work, only methylene groups bonded directly to two aromatic rings can be oxidized to the corresponding carbonyl function.

Both the ^{13}C and ^1H NMR spectral data, as recorded in Tables 1 and 2, were used in identifying the ketoarene complexes. The complexation of a benzene ring to

TABLE I

YIELDS, ^{1}H NMR CHEMICAL SHIFTS AND IR CARBONYL ABSORPTIONS OF THE HEXAFLUOROPHOSPHATE SALTS OF η^6-KETOARENE-η^5-CYCLOPENTADIENYLIRON CATIONS

Complex		Yield (%)	δ(CD_3CN) (ppm from TMS)			IR
			Cp	Complexed aromatic	Uncomplexed aromatic	ν(CO) (cm^{-1})
Fluorenone $FeCp^+$	(I)	38–42	4.9 (s,5H)	6.5–6.6 (m,2H) 6.7–6.9 (m,1H) 6.9–7.1 (m,1H)	7.6–8.0 (m,4H)	1715
Fluorenone $(FeCp)_2^{++}$	(VI)	42	5.2 (s,10H)	6.8–7.4 (m,8H)		1715
Benzophenone $FeCp^+$	(II)	18–20	5.1 (s,5H)	6.5–6.9 (m,5H)	7.6–8.1 (m,5H)	1680
9,10-Anthraquinone $FeCp^+$	(III)	30–40	5.0 (s,5H)	6.7–6.9 (m,2H) 7.1–7.3 (m,2H)	7.9–8.2 (m,2H) 8.3–8.5 (m,2H)	1680

TABLE 2

^{13}C NMR CHEMICAL SHIFTS FOR THE HEXAFLUOROPHOSPHATE SALTS OF η^6-KETOARENE-η^5-CYCLOPENTADIENYLIRON CATIONS AND FOR THE CORRESPONDING KETOARENES

Compound		$\delta(CD_3NO_2)$ (ppm from TMS)			
		Cp	Complexed aromatic [a]	Uncomplexed aromatic [a]	Carbonyl
Fluorenone [5]		–	–	121.1, 123.8, 129.4, 135.2, 133.2*, 143,9*	193.1
Fluorenone FeCp$^+$	(I)	79.0	82.2, 83.5, 86.8 [b], 88.3, 86.8*[b], 102.4*	122.2, 124.0, 131.1, 135.7, 133.0*, 140.1*	191.0
Fluorenone $(FeCp)_2^{++}$	(VI) [c]	80.3	85.3, 89.2, 89.9, 86.6*, 99.0*	–	191.7
Benzophenone [6]		–	–	128.1, 129.1, 132.4, 137.4*	196.2
Benzophenone FeCp$^+$	(II)	77.7	86.8, 88.1, 88.5 98.0*	128.1, 129.1, 133.6, 134.5*	193.1
9,10-Anthraquinone [7]		–	–	127.0, 134.0, 133.5*	183.0
9,10-Anthraquinone FeCp$^+$	(III)	79.4	85.9, 90.3, 88.7*	127.0, 135.0, 132.0*	182.6

[a] Asterisks denote quaternary carbons. [b] The peak at 86.8 ppm was split into two peaks at 87.4 and 87.7 ppm when the spectrum was recorded in DMSO-d_6. [c] The spectrum was recorded in DMSO-d_6.

a CpFe$^+$ unit results in a large upfield shift in the ^{13}C absorptions of about 40 ppm, making the complexed aromatic resonances easily identified. The H atoms attached to the complexed ring also show a similar upfield shift of about 0.5–1.0 ppm in the ^{1}H NMR spectra. The ^{13}C absorptions for the free ligands, fluorenone, benzophenone and 9,10-anthraquinone, obtained from the literature [5–7], are also recorded in Table 2 for comparison. All the ^{13}C and ^{1}H NMR chemical shifts are consistent with the structures assigned to the various ketoarene complexes. For example, the ^{13}C spectrum of cation I shows, besides the Cp and carbonyl absorptions at 79.0 and 191.0 ppm, respectively, peaks for all 12 carbon atoms, 6 being in the normal aromatic region and 6 in the complexed aromatic region. The presence of the carbonyl function is also supported by the characteristic IR absorptions as given in Table 1.

The base catalyzed oxidation by atmospheric oxygen (autoxidation) of relatively acidic hydrocarbons has been known for a long time [8]. More recently, Alneri et al. [9] have successfully carried out the autoxidation of aromatic substrates containing active methylene groups including fluorene and 9,10-dihydroanthracene. It was, therefore, of interest to investigate the possibility of obtaining the presently synthesized ketoarene complexes by autoxidation. When the hexafluorophosphate salt of η^6-fluorene-η^5-cyclopentadienyliron cation was treated with alcoholic KOH at room temperature in the presence of air, the fluorenone complex I was obtained in 87% yield. However, attempts to achieve a similar air oxidation of the cyclopen-

TABLE 3

YIELDS, ^{1}H NMR CHEMICAL SHIFTS AND IR HYDROXYL ABSORPTIONS FOR THE PRODUCTS FROM REACTIONS OF η^6-KETOARENE-η^5-CYCLOPENTADIENYLIRON CATIONS WITH $NaBH_4$ or $NaBD_4$

Ketoarene complex	Product		Yield (%)	$\delta(CD_3CN)$ (ppm from TMS)				IR
				Cp	Complexed aromatic	Uncomplexed aromatic	Others	ν(OH) (cm^{-1})
I	9H-Fluoren-9-ol-FeCp$^+$	(VIIa)	89	4.7 (s,5H)	6.1–6.4 (m,2H) 6.5–6.7 (m,1H) 6.8–6.9 (m,1H)	7.5–7.7 (m,3H) 7.8–8.0 (m,1H)	4.9 (d,1H,OH) 5.8 (d,1H,C*H*OH)	3574
	9D-Fluoren-9-ol-FeCp$^+$	(VIIb)	88	4.8 (s,5H)	6.2–6.5 (m,2H) 6.6–6.7 (m,1H) 6.8–6.9 (m,1H)	7.5–7.8 (m,3H) 7.8–8.0 (m,1H)	4.9 (s,1H,OH)	3576
III	*cis*-9,10-Dihydroxy-9,10-dihydroanthracene FeCp$^+$	(VIIIa)	55	4.3 (s,5H)	6.2–6.3 (m,2H) 6.4–6.7 (m,2H)	7.5–7.7 (m,2H) 7.8–7.9 (m,2H)	4.9 (d,1H,OH) 5.5 (d,1H,C*H*OH)	3437 3574
	cis-9,10-Dihydroxy-9,10-dideuterioanthracene-FeCp$^+$	(VIIIb)	52	4.3 (s,5H)	6.2–6.4 (m,2H) 6.5–6.7 (m,2H)	7.5–7.7 (m,2H) 7.7–7.9 (m,2H)	4.9 (s,1H,OH)	3430 3574
II	Diphenylmethanol-FeCp$^+$	(IXa)	60	5.0 (s,5H)	6.2(bs,3H) 6.4(bs,2H)	7.4 (bs,5H)	4.8 (s,1H,OH) 5.8 (s,1H,C*H*OH)	3598
	Deuteriodiphenylmethanol FeCp$^+$	(IXb)	54	5.0 (s,5H)	5.9–6.3(m,4H)	7.1–7.5 (m,5H)	4.8 (s,1H,OH)	3606

TABLE 4

^{13}C NMR CHEMICAL SHIFTS FOR THE PRODUCTS FROM REACTIONS OF η^6-KETOARENE-η^5-CYCLOPENTADIENYLIRON CATIONS WITH $NaBH_4$ or $NaBD_4$

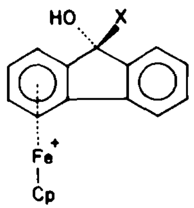
Product		δ(acetone-d_6) (ppm from TMS)			
		Cp	Complexed aromatic[a]	Uncomplexed aromatic[a]	Others
9H-Fluoren-9-ol-FeCp$^+$	(VIIa)	76.8	79.8, 83.2, 84.3, 86.1, 102.0*, 108.3*	121.4, 124.6, 128.6, 129.6, 135.2*, 147.3*	71.9 (CHOH)
9D-Fluoren-9-ol-FeCp$^+$	(VIIb)	76.8	79.7, 83.2, 84.3, 86.0, 102.1*, 108.2*	121.4, 124.6, 128.6, 129.6, 135.2*, 147.3*	70.1, 71.6, 73.0 (CDOH)
cis-9,10-Dihydroxy-9,10-dihydroanthracene-FeCp$^+$	(VIIIa)	75.1	81.7, 85.2, 105.1*	122.7, 126.8, 136.6*	63.9 (CHOH)
cis-9,10-Dihydroxy-9,10-dideuterioanthracene-FeCp$^+$	(VIIIb)[b]	75.7	82.3, 85.7, 105.2*	123.4, 127.6, 137.0*	63.0, 64.2, 65.7 (CDOH)
Diphenylmethanol-FeCp$^+$	(IXa)	75.2	81.9, 84.4, 85.6, 108.7*	124.4, 126.5, 126.9, 141.5*	71.2 (CHOH)
Deuteriodiphenylmethanol FeCp$^+$	(IXb)	76.0	82.8, 85.1, 86.4, 109.1*	125.4, 127.6, 128.1, 142.0*	70.1, 71.6, 73.2 (CDOH)

[a] Astericks denote quaternary carbons. [b] The spectrum was recorded in CD_3CN.

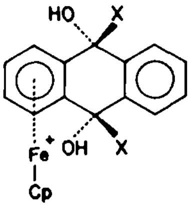
tadienyliron complex of diphenylmethane or 9,10-dihydroanthracene failed to give the ketoarene complex and led only to extensive decomposition. The reason for this failure is not clear.

The adddition of hydride ion from $NaBH_4$ to the cyclopentadienyliron complexes of various methyl, halogeno or methoxy substituted benzenes has been shown to take place at the arene ring to give the corresponding cyclohexadienyl derivatives [10–12]. Although reaction of a ketoarene complex with $NaBH_4$ might be attacked at the arene ring or at the carbonyl function, it was found that upon treatment with $NaBH_4$ or $NaBD_4$, only the carbonyl group was reduced to the secondary alcohol, and no hydride addition to the arene ring took place. From the fluorenone complex I, reaction with $NaBH_4$ or $NaBD_4$ gave the *endo*-alcohol VIIa or VIIb, respectively. The *endo*-configuration for the alcohol function was due to a stereospecific *exo*-attack by the hydride or deuteride ion, i.e. attack on the side opposite to the metal atom. Similarly, from the anthraquinone complex III, the reduction products were the complexed *endo*-diols VIIIa and VIIIb. With the benzophenone complex II, because of free rotations about single bonds, there would be no *endo*- or *exo*-configuration for the reduction products IXa and IXb. The yields and spectral data for these reduction products are given in Tables 3 and 4.

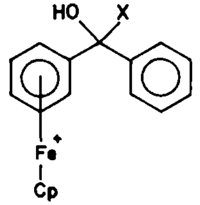
Addition of various nucleophiles to η^6-arene-η^5-cyclopentadienyliron cations are known to be stereospecifically *exo* [13]. As already indicated, such an *exo*-attack gave the complexed *endo*-alcohols VIIa, VIIb and VIIIa, VIIIb. Confirmation of the



VII a X=H
b X=D

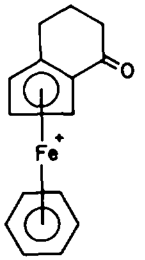


VIII a X=H
b X=D

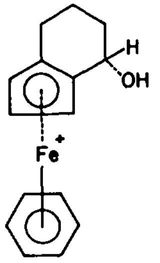


IX a X=H
b X=D

endo-structure is given by a sharp IR peak at 3574 cm^{-1} which may be attributed to O–H stretching of the hydroxyl group on the same side of, and hydrogen bonded to, the iron atom [4–16] *. Moreover, the NMR data given in Tables 3 and 4 are consistent with the assigned structures. For example, the ^1H NMR spectra of VIIa, VIIIa and IXa show two sets of doublets at 4.8–4.9 and 5.5–5.8 ppm, respectively, for the O*H* and C*H*OH resonances, while VIIb, VIIIb and IXb show only a singlet due to O*H* absorption at 4.8–4.9 ppm without splitting because of deuterium substitution. The present results from the borohydride reduction of ketoarene complexes I, II and III are thus similar to the recent finding of Astruc et al. [16] showing that the electroreduction, for example, of η^6-benzene-η^5-α-oxotetramethylenecyclopentadienyliron cation (X) gives stereospecifically the *endo*-alcohol XI.



X



XI

Experimental

η^6-Fluorenone-η^5-cyclopentadienyliron hexafluorophosphate (I-PF_6)

Fluorene (8.3 g, 50 mmol), FcH (9.3 g, 50 mmol), $AlCl_3$ (32.0 g, 240 mmol) and Al powder (1.8 g, 60 mmol) were heated under reflux in decalin (60 ml) at 140 ± 2°C for 5 h under a N_2 atmosphere. The reaction mixture was then hydrolyzed with ice cold water (about 300 ml). The aqueous phase was washed with ether (3 × 50 ml) and then poured into a potassium permanganate solution (8.0 g, 50 mmol in 120 ml of water). The reaction mixture was heated for 5 h at 55°C with vigorous stirring using a mercury sealed stirrer. The reaction was then allowed to continue for 10 h without further heating. The precipitated MnO_2 was removed by filtration through

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[*] For a number of methylferrocenylcarbinols with various methyl substituents in the ferrocenyl group, the IR absorption for the OH stretching range from 3561–3580 cm^{-1} for the *endo*-alcohols and from 3602–3610 for the *exo*-alcohols [15].

celite and the product was isolated as a yellow solid by addition of ammonium hexafluorophosphate (NH_4PF_6). Recrystallization from nitromethane/ether gave 9.37 g (42%) of η^6-fluorenone-η^5-cyclopentadienyliron hexafluorophosphate as a fine yellow powder.

(Found: C, 48.54; H, 2.94. $C_{18}H_{13}OFePF_6$ calcd.: C, 48.66; H, 3.18%.) The spectral data for this and other ketoarene complexes are summarized in Tables 1 and 2.

η^6-Fluorenone-trans-bis-η^5-cyclopentadienyliron dihexafluorophosphate ($VI(PF_6)_2$)

FcH (18.6 g, 100 mmol), $AlCl_3$ (32.0 g, 240 mmol), Al powder (0.8 g, 30 mmol) and fluorene (3.34 g, 20 mmol) were heated with stirring in decalin (65 ml) at 140 ± 2°C for 5 h. The resulting reaction mixture was cooled to about 50°C, hydrolyzed with cold water (about 300 ml) and then stirred for 15 min to disperse any pasty material. Any solid material that remained was removed by vacuum filtration. The aqueous layer was separated, washed with ether (3 × 50 ml) and then poured into a $KMnO_4$ solution (8.0 g, 50 mmol, in 100 ml H_2O). The reaction mixture was heated at 55°C for 10 h with vigorous stirring and then worked up using the procedure described in the preceding section. The crude yellow product was dissolved in nitromethane and then dried over anhydrous magnesium sulphate, filtered, concentrated and precipitated with ether to give a fine yellow powder. A yield of 6.84 (48%) of η^6-fluorenone-*trans*-bis-η^5-cyclopentadienyliron dihexafluorophosphate was obtained.

(Found: C, 39.02; H, 2.70. $C_{23}H_{18}OFe_2(PF_6)_2$ calcd.: C, 38.80; H, 2.55%.)

η^6-Benzophenone-η^5-cyclopentadienyliron hexafluorophosphate (II-PF_6)

FcH (9.3 g, 50 mmol), $AlCl_3$ (13.4 g, 100 mmol), Al powder (2.16 g, 80 mmol) and diphenylmethane (25.3 g, 150 mmol) were refluxed under N_2 in cyclohexane (60 ml) at 82°C for 10 h. The reaction mixture was worked-up as described above. The water soluble tetrachloroaluminate salt of the diphenylmethane complex was poured into a $KMnO_4$ (8.0 g, 50 mmol) solution in 100 ml of H_2O. The reaction mixture was then heated at 60°C with stirring for 10 h. After work-up and recrystallization from acetone/ether, 4.48 g (20%) of η^6-benzophenone-η^5-cyclopentadienyliron hexafluorophosphate was obtained.

(Found: C, 47.95; H, 3.25. $C_{18}H_{15}OFePF_6$ calcd.: C, 48.25; H, 3.37%.)

η^6-9,10-Anthraquinone-η^5-cyclopentadienyliron hexafluorophosphate (III-PF_6)

A mixture of FcH (9.3 g, 50 mmol), $AlCl_3$ (13.34 g, 100 mmol), Al powder (1.6 g, 60 mmol) and 9,10-dihydroanthracene (9.0 g, 50 mmol) was heated in decalin for 16 h at 140 ± 2°C. After cooling to 50°C, the reaction mixture was hydrolyzed with ice-water (about 250 ml) and then stirred for 10 min. The aqueous layer was separated, washed with ether (3 × 50 ml), poured into a $KMnO_4$ solution (8.0 g, 50 mmol, in 100 ml of water), and then heated at 45°C for 4 h. The usual work-up gave a crude product as a yellow solid, which was recrystallized from nitromethane. A yield of 9.0 g (38%) of η^6-9,10-anthraquinone-η^5-cyclopentadienyliron hexafluorophosphate was obtained.

(Found: C, 47.90; H, 2.80. $C_{19}H_{13}O_2FePF_6$ calcd.: C, 48.13; H, 2.76%.)

Autoxidation of η^6-fluorene-η^5-cyclopentadienyliron hexafluorophosphate

A suspension of 0.58 g (1.4 mmol) of η^6-fluorene-η^5-cyclopentadienyliron hexafluorophosphate in methanol/water (30/10 ml) was stirred at room temperature with KOH (0.20 g, 3.6 mmol) in air free from CO_2 and moisture (KOH guard tube). After 20 h, the reaction mixture was treated with 10% HCl and then with a concentrated solution of NH_4PF_6. The product was recovered the usual way by extraction with nitromethane, drying over $MgSO_4$, concentration and precipitation with ether to give 0.52 g (87%) of product I-PF_6 which was identical with that obtained by $KMnO_4$ oxidation.

η^6-9H-Fluoren-9-ol-η^5-cyclopentadienyliron hexafluorophosphate (VIIa-PF_6)

A suspension of the hexafluorophosphate salt of cation I (892 mg, 2.0 mmol) and $NaBH_4$ (38 mg, 1.0 mmol) in 30 ml of methylene chloride and about 1.0 ml of water was shaken in a 250 ml round-bottom flask. After 2–3 min, a clear brown solution was formed, but the shaking was continued for an additional 5 min. The reaction mixture was then treated with an aqueous solution of NH_4PF_6 and 10% hydrochloric acid. The mixture was extracted with methylene chloride to give a yellow extract which was dried over $MgSO_4$ and then evaporated to dryness.

After recrystallization from acetone/ether, 800 mg (89%) of η^6-9H-fluoren-9-ol-η^5-cyclopentadienyliron hexafluorophosphate was obtained as yellow plates.

(Found: C, 48.31; H, 3.42. $C_{18}H_{15}OFePF_6$ calcd.: C, 48.25; H, 3.37%.)

In a similar way, using 446 mg (1.0 mmol) of the hexafluorophosphate salt of cation I and 42 mg (1.0 mmol) of $NaBD_4$, the η^6-9D-fluoren-9-ol-η^5-cyclopentadienyliron hexafluorophosphate (VIIb-PF_6) was obtained as a yellow powder (394 mg, 88%). The spectral data for these and other borohydride reduction products are given in Tables 3 and 4.

η^6-cis-9,10-Dihydroxy-9,10-dihydroanthracene-η^5-cyclopentadienyliron hexafluorophosphate (VIIIa-PF_6)

A suspension of η^6-9,10-anthraquinone-η^5-cyclopentadienyliron hexafluorophosphate (III-PF_6) (474 mg, 1.0 mmol) and $NaBH_4$ (75 mg, 2 mmol) in 30 ml of methylene chloride and 1.0 ml of water was shaken in a 250 ml round-bottom flask. After 5 min, a greenish solution was formed. The shaking was continued for an additional 15 min. The reaction mixture was treated with aqueous NH_4PF_6 and 5 ml of 10% HCl. After diluting with 200 ml of methylene chloride, the mixture was filtered and the methylene chloride extract was dried over $MgSO_4$. Evaporation and recrystallization from acetone/ether gave 263 mg (55%) of VIIIa-PF_6 as a light yellow powder.

(Found: C, 48.02, H, 3.12. $C_{19}H_{17}O_2FePF_6$ calcd.: C, 47.73; H, 3.58%.)

With the same procedure but using $NaBD_4$ instead of $NaBH_4$, η^6-*cis*-9,10-dihydroxy-9,10-dideuterioanthracene-η^5-cyclopentadienyliron hexafluorophosphate (VIIIb-PF_6) was obtained in 52% yield.

η^6-Diphenylmethanol-η^5-cyclopentadienyliron hexafluorophosphate (IXa-PF_6)

The title compound, IXa-PF_6, and its deuterio analog, η^6-deuteriodiphenylmethanol-η^5-cyclopentadienyliron hexafluorophosphate (IXb-PF_6) were prepared by the $NaBH_4$ or $NaBD_4$ reduction of the hexafluorophosphate salt of cation II in the same way as described above for the reduction of cation I. The yields obtained were 60 and 54%, respectively, for IXa-PF_6 and IXb-PF_6.

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