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ZWITTERIONIC SPECIES FROM DEPROTONATION OF η^6-ARENE-η^5-CYCLOPENTADIENYLIRON CATIONS AND THEIR REACTIONS AS NUCLEOPHILES

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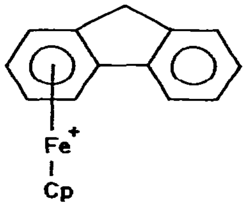
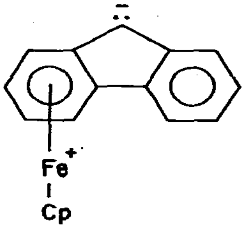
Summary

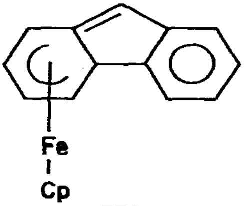
A variety of η^6-arene-η^5-cyclopentadienyliron cations in which the arene ligand has an α-carbon substituent containing one or more hydrogens can be deprotonated with base to give the corresponding neutral zwitterionic species. These zwitterions can react *in situ* as nucleophiles with different substrates such as CH_3I, other organic halides, CO_2 and CS_2 to give a wide range of synthetic applications.

Introduction

Recently, Johnson and Treichel [1] reported that the deprotonation of the η^6-fluorene-η^5-cyclopentadienyliron cation (I) with *t*-BuOK in benzene gave the neutral, zwitterionic η^6-9-fluorenyl-η^5-cyclopentadienyliron (II) which subsequently can react as a nucleophile with alkyl halides such as CH_3I. Similarly, Helling and Hendrickson [2] also obtained II from reaction of I with sodium bis(trimethylsilyl)amide in benzene, as well as the analogous neutral complexes from the treatment, with $NaNH_2$ in NH_3, of η^6-arene-η^5-cyclopentadienyliron cations in which the aromatic ligands were triphenylmethane, diphenylamine and carbazole. While the crystallographic studies of Treichel [1] indicated that II may be formulated with the zwitterionic structure IIa, Helling [2] also stressed the contribution from a π-cyclohexadienyliron complex with an exocyclic double bond, e.g. IIb, as is emphasized by their recent isolation of imino and other neutral complexes.


I


IIa


IIb

In conjunction with our studies on ligand exchange reactions between arene and ferrocene [3-7], we have also observed the formation of II from I, even under the relatively mild conditions of K_2CO_3 in dimethylformamide (DMF). We wish to report that the deprotonation to give zwitterionic species is not restricted to systems such as I but can occur in a variety of η^6-arene-η^5-cyclopentadienyliron cations (III) in which the arene ligand possesses one or more saturated α-hydrogens. The zwitterion can then react *in situ* as a nucleophile to provide a wide range of synthetic possibilities.

Results and Discussion

Nucleophilic substitution reactions

Various η^6-arene-η^5-cyclopentadienyliron cations (III) were prepared by ligand exchange between ferrocene and the arene, effected in the presence of $AlCl_3$-Al[4,5,8]. Deprotonation with *t*-BuOK in tetrahydrofuran (THF) followed by reaction with CH_3I gave a variety of methylated products as summarized in Table 1. It is of interest to note that such a reaction also occurs with heterocyclic ligands. Thus with xanthene and with phenothiazine as the aromatic ligand in the reactant, the products obtained were the η^6-9-methylxanthene-η^5-cyclopentadienyliron and η^6-10-methylphenothiazine-η^5-cyclopentadienyliron cations (IV and V).

Table 1. Reaction of zwitterionic species from deprotonation of η^6-arene-η^5-cyclopentadienyliron cations (III) with CH_3I at room temperature

			^1H NMR of product, δ(acetone-$\underline{d}_6$)ppm from TMS			
Arene ligand in reactant III	Arene ligand in product	Yield, %[a]	Uncomplexed aromatic	Complexed aromatic	Cp	Non-aromatic
CH_3Ph[b]	EtPh	60		6.4(s)	5.2(s)	1.3(t) CH_3, 2.9(q) CH_2
EtPh	i-PrPh	15		6.4(s)	5.2(s)	1.4(d) CH_3, 3.2 CH(weak)
o-$(CH_3)_2Ph$	*o*-$CH_3(Et)Ph$	60		6.3(s)	5.1(s)	1.3(m) $C\underline{H}_3CH_2$, 2.5(s) $C\underline{H}_3Ph$, 2.9(m) $CH_3C\underline{H}_2$
o-$Cl(CH_3)Ph$	*o*-Cl(Et)Ph	55		6.5(s)	5.2(s)	1.4(t) CH_3, 3.1(q) CH_2
1,3,5-$(CH_3)_3Ph$	1-Et-3,5-$(CH_3)_2Ph$	70		6.2(s)	5.2(s)	1.3(t) $C\underline{H}_3CH_2$, 2.5(s) $C\underline{H}_3Ph$ 2.9(q) $CH_3C\underline{H}_2$
Ph_2CH_2	Ph_2CHCH_3	70	7.4(broad s)	6.4(m)	5.1(s)	1.8(d) CH_3, 4.5(q) CH
	$Ph_2C(CH_3)_2$	10	7.4(broad s)	6.4(m)	5.2(s)	2.0(s) CH_3
Ph_3CH	Ph_3CCH_3	95	7.5(broad s)	6.6(m)	4.6(s)	3.1(s) CH_3
Tetralin[c]	α-Methyltetralin	80		6.2(m)	5.0(s)	1.3(d), 1.6(d) *exo* and *endo* CH_3 1.6(q) CH, 2.0(m), 2.9(m) CH_2
9,10-Dihydro-anthracene	9-Methyl-9,10-dihydroanthracene	7	7.4(m)	6.5(m)	4.6(s)	1.5(d) CH_3, 4.2(s) CH_2, 4.3(q) CH
	cis-9,10-Dimethyl-9,10-dihydro-anthracene	20	7.4(m)	6.5(m)	4.7(s)	1.6(d) CH_3, 4.4(q) CH
xanthene	9-methylxanthene	65	7.4(m)	6.5(m)	4.8(s) 4.9(s)	1.5(s), 1.6(d) *exo* and *endo* CH_3 4.5(q) CH
phenothiazine	10-methylpheno-thiazine	75	7.3(broad s)	6.4(m)	4.8(s)	3.5(s) CH_3

[a] These are relative yields obtained from NMR, with the values shown plus unreacted III totalling 100%; in the last two entries, pure products were isolated and their absolute yields are shown.

[b] Reaction with CH_3I carried out at -60°C.

[c] Reaction with CH_3I carried out at -20°C.

[d] 50% anthracene was also formed.

Table 2. Reaction of zwitterionic η^6-9-fluorenyl-η^5-cyclopentadienyliron (II) with different substrates

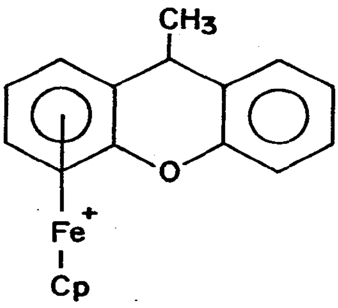
Substrate	Arene ligand in product [a]	Yield, %[d]	^1H NMR of product, δ(acetone-$\underline{d}_6$) ppm from TMS			
			Uncomplexed atomatic	Complexed atomatic	Cp	Non-aromatic
EtI	R-Et	60	7.5(m)	6.7(m)	4.9(s)	0.8(t) CH_3, 2.2(m) CH_2, 4.5(m) CH
	$R(Et)_2$	30	7.5(m)	6.7(m)	4.8(s)	0.2(t), 1.5(t) CH_3, 2.2(m) CH_2
$2,4-(NO_2)_2PhCl$	$2,4-(NO_2)_2Ph-R^-$ [b]	30	8.1(m)	6.0(m)	4.3(s)	
	$2,4-(NO_2)_2Ph-R$[c]	65	7.5(m)	6.5(m)	4.8(s)	CH (too weak)
$\underline{p}-Cl(CH_3)PhFeCp^+PF_6^-$	$R^--(\underline{p}-CH_3)PhFeCp^+PF_6^-$ [b]	40	8.0(m)	6.5(m)	4.2(s), 4.9(s)	2.6(s) CH_3
	$R-(\underline{p}-CH_3)PhFeCp^+PF_6^-$ [c]	65	8.0(m)	6.4(m)	5.0(s), 5.3(s)	2.5(s) CH_3, CH (too weak)

[a] R = 9-fluorenyl; e.g., the product with R-Et as the arene ligand is the η^6-9-ethylfluorene-η^5-cyclopentadienyliron cation.

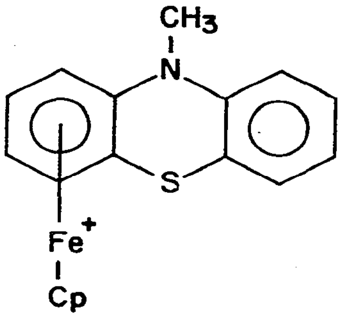
[b] Zwitterions from loss of the C-9 proton.

[c] Regenerated from treatment of the zwitterion with HCl.

[d] The values shown are absolute yields of isolated products except for the first entry for which relative yields are shown with 10% unreacted starting material, I, being also present.

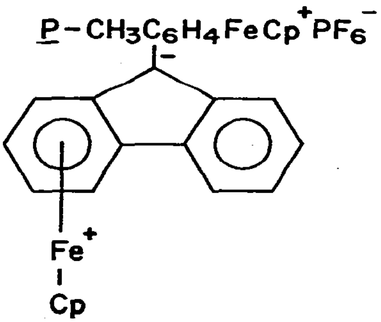


IV



V

To test the applicability of such nucleophilic substitution reactions with substrates other than CH_3I, the fluorene complex I was deprotonated with K_2CO_3 in DMF to give II and then treated with ethyl iodide, 2,4-dinitrochlorobenzene or η^6-p-chlorotoluene-η^5-cyclopentadienyliron hexafluorophosphate. The results are shown in Table 2. It may be pointed out that in the reaction of II with either of the latter two substrates, the reaction product readily loses its C-9 H to give the blue zwitterion, which has to be treated with HCl to regenerate the nucleophilic substitution product. For example, in the reaction with η^6-p-chlorotoluene-η^5-cyclopentadienyliron hexafluorophosphate as the substrate, VI and VII, respectively, are the structures of the zwitterion and the regenerated cationic product that were obtained.



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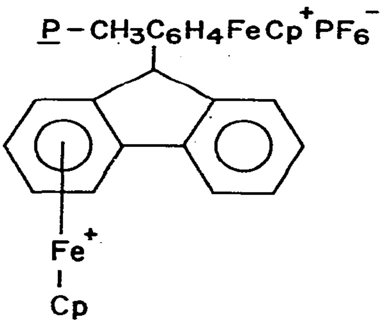


VII

Reactions with CO_2 or CS_2

To study further the synthetic utility of the zwitterions as nucleophiles, their reactions with CO_2 or CS_2 were investigated. Various zwitterions were

Table 3. Reaction of zwitterionic species from deprotonation of η^6-arene-η^5-cyclopentadienyliron cations (III) with CO_2 at room temperature followed by treatment with $(CH_3)_2SO_4$

Arene ligand in reactant III	Arene ligand in product	Yields, %[c]	^{1}H NMR of product, δ(acetone-$\underline{d}_6$)ppm from TMS		
			Complexed atomatic	Cp	Non-aromatic
$PhCH_3$ [a,b]	$PhCH_2COOH$	65	6.4(s)	5.1(s)	3.9(s) CH_2, 5.3(broad s) OH [d]
$PhCH_3$ [b]	$PhCH_2COOCH_3$	70	6.5(s)	5.2(s)	3.7(s) CH_2, 4.0(s) OCH_3
$PhCH_3$	$PhCH(CH_3)COOCH_3$	60	6.5(s)	5.2(s)	1.6(d) $CHC\underline{H}_3$, 3.8(s) OCH_3 4.1(q) $C\underline{H}CH_3$
$PhCH_2CH_3$	$PhCH(CH_3)COOCH_3$	50	6.5(s)	5.2(s)	1.6(d) $CHC\underline{H}_3$, 3.8(s) OCH_3 4.1(q) $C\underline{H}CH_3$
$PhCH(CH_3)_2$	$PhC(CH_3)_2COOCH_3$	85	6.5(s)	5.2(s)	1.7(s) CH_3, 3.8(s) OCH_3
$\underline{o}$-$ClPhCH_3$	$\underline{o}$-$ClPhCH_2COOCH_3$	50	6.6(m)	5.3(s)	3.7(s) OCH_3, 4.25(s), 4.28(s) CH_2

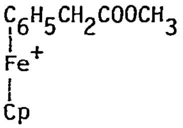
[a] The reaction mixture was treated with HCl instead of $(CH_3)_2SO_4$.

[b] The reaction was carried out at -50°C instead of at room temperature.

[c] Yields of isolated products.

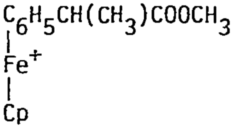
[d] Concentration and solvent dependent within range 4.5 to 7.0 ppm. Disappears on addition of D_2O.

generated as before from the deprotonation of cations III with t-BuOK. After reaction with CO_2 followed by treatment with $(CH_3)_2SO_4$, the ester function was introduced into the α-position of the original arene ligand. The results are shown in Table 3. It may be noted that with toluene as the arene ligand of the reactant, when the reaction with CO_2 and the subsequent treatment with $(CH_3)_2SO_4$ were carried out at -50°C, the expected product, the η^6-methyl phenylacetate-η^5-cyclopentadienyliron cation (VIII) was obtained. When these treatments were carried out at room temperature, however, a second deprotonation followed by methylation occurred at the α-position, giving rise to the η^6-methyl 2-phenylpropanoate-η^5-cyclopentadienyliron cation (IX), the same product as that obtained from using the η^6-ethylbenzene-η^5-cyclopentadienyliron cation as reactant.



$$\begin{array}{l} C_6H_5CH_2COOCH_3 \\ | \\ Fe^+ \\ | \\ Cp \end{array}$$

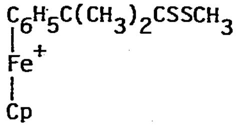
VIII



$$\begin{array}{l} C_6H_5CH(CH_3)COOCH_3 \\ | \\ Fe^+ \\ | \\ Cp \end{array}$$

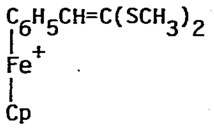
IX

The results from the reaction of zwitterionic species with CS_2 followed by treatment with $(CH_3)_2SO_4$ are summarized in Table 4. When the arene ligand in the reactant cation was isopropylbenzene which has only one α-H, the methyl dithioate function was introduced into the α-position of the arene ligand as expected, giving rise to the product cation X. When the arene ligand in the reactant has more than one α-H, under the basic conditions of the reaction, an enolization type of reaction took place and two methyl groups were incorporated. Thus with toluene or ethylbenzene as the arene ligand in the reactant, the product was XI or XII, respectively. The methyl dithioate product XIII was obtained when deprotonation of the η^6-ethylbenzene-η^5-cyclopentadienyliron cation was followed by treatment with a large excess of CS_2 before methylation with $(CH_3)_2SO_4$. Apparently, the large amount of CS_2 used up the excess base to form thiocarbonates, thus minimizing the enolization type of reaction.



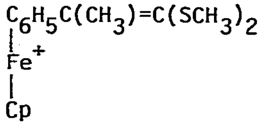
$$\begin{array}{l} C_6H_5C(CH_3)_2CSSCH_3 \\ | \\ Fe^+ \\ | \\ Cp \end{array}$$

X



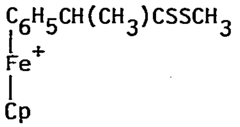
$$\begin{array}{l} C_6H_5CH{=}C(SCH_3)_2 \\ | \\ Fe^+ \\ | \\ Cp \end{array}$$

XI



$$\begin{array}{l} C_6H_5C(CH_3){=}C(SCH_3)_2 \\ | \\ Fe^+ \\ | \\ Cp \end{array}$$

XII



$$\begin{array}{l} C_6H_5CH(CH_3)CSSCH_3 \\ | \\ Fe^+ \\ | \\ Cp \end{array}$$

XIII

General discussion

The variety of reactions given in Tabels 1-4 illustrate the wide range of possible synthetic applications utilizing the zwitterionic species from deprotonation of η^6-arene-η^5-cyclopentadienyliron cations as nucleophiles. The ready formation of the zwitterions apparently arises from complexing the arene with the highly electron-withdrawing $CpFe^+$ group. Similar effects have been reported in the literature, and these include the greatly enhanced acidity of alkylcobalticinium salts [9] and the finding that π-complexation to transition metals activates the methyl groups of duroquinone toward both acid- and base-catalyzed reactions [10]. Closely related to the present study is the activation of the α-carbon in nucleophilic reactions by carbonylchronium groups in systems such as methyl arylacetate-chromium tricarbonyl and related compounds [11,12].

It is likely that other zwitterions besides those reported in Tables 1-4 may also be utilized as nucleophiles in reactions with many different substrates. These possibilities thus provide a general method for the alkylation and functionalization of η^6-arene-η^5-cyclopentadienyliron cations. Since we have already shown that the arene ligand in such cations may be regenerated as the arene itself either photolytically [4] or, in better yields, by pyrolytic sublimation under reduced pressure [6], the synthetic applications may be extended to include the preparation of substituted arenes. As an example from

Table 4. Reaction of zwitterionic species from deprotonation of η^6-arene-η^5-cyclopentadienyliron cations (III) with CS_2 at room temperature followed by treatment with $(CH_3)_2SO_4$

Arene ligand in reactant III	Arene ligand in product	Yield, %[c]	^1H NMR of product, δ(acetone-$\underline{d}_6$) ppm from TMS		
			Complexed atomatic	Cp	Non-aromatic
$PhCH_3$	$PhCH_2CS_2CH_3$ [a]		6.5(m)	5.3(s)	2.7(s) CH_3, 4.6(s) CH_2
	$PhCH{=}C(SCH_3)_2$	80	6.6(m)	5.2(s)	2.5(s), 2.6(s) CH_3, 6.6(s) CH
$PhCH_2CH_3$	$PhC(CH_3){=}C(SCH_3)_2$	40	6.5(s)	5.2(s)	2.2(s), 2.4(s), 2.7(s) CH_3
$PhCH_2CH_3$	$PhCH(CH_3)CS_2CH_3$ [b]	40	6.5(m)	5.3(s)	1.9(d) $CHC\underline{H}_3$, 2.7(s) SCH_3, 5.0(q) CH
$PhCH(CH_3)_2$	$PhC(CH_3)_2CS_2CH_3$	65	6.6(s)	5.3(s)	2.2(s) CCH_3, 2.6(s) SCH_3

[a] Observed by NMR as a side product, but not isolated.

[b] Obtained when the zwitterion was treated with a large excess of CS_2.

[c] Yields of isolated products.

the present work, 9-methylxanthene was recovered in about 90% yield from vacuum sublimation of the η6-9-methylxanthene-η5-cyclopentadienyliron cation (Table 1).

Experimental

As illustrations, some typical procedures for a number of preparations are described below.

η6-9-Methylxanthene-η5-cyclopentadienyliron hexafluorophosphate (XIV)

A suspension of 0.75 g (1.7 mmol) of η6-xanthene-η5-cyclopentadienyliron hexafluorophosphate in 40 ml of dry THF was treated under N_2 at room temperature with 0.19 g (1.7 mmol) of t-BuOK. A dark purple solution developed immediately. After the mixture was stirred for 5 min, an excess of CH_3I (about 2 ml) was added. A gradual color change occurred, giving rise to an orange suspension. Stirring was continued for 90 min, a concentrated aqueous solution of NH_4PF_6 was added, and the resulting mixture was extracted with CH_2Cl_2. The extract was dried over $MgSO_4$, concentrated in a rotary evaporator, and the product was precipitated as an oily solid by the addition of ether. Purification by passage through an alumina column (activated alumina F-20, Sargent-Welsh Scientific Co.) with elution by acetone gave a yellow solution. After concentration and addition of ether, 0.50 g (65%) of the pale yellow product XIV (the hexafluorophosphate salt of IV) was obtained. Its ^1H NMR data, as given in Table 1, showed that the product is a mixture with the CH_3 substituent exo and endo with respect to the $CpFe^+$ group. This conclusion is confirmed by its ^{13}C NMR spectrum: δ(acetone-d_6) in ppm, 149.1 (quaternary), 128.0, 125.1, 124.4, 116.1 (uncomplexed aromatic); 99.3, 93.7 (quaternary), 85.2, 84.2, 83.4, 80.9, 77,8, 77.0 (complexed aromatic); 76.0, 75.5 (Cp, exo and endo); 34.0 (CH); 32.8, 22.0 (CH_3, exo and endo).

The pyrolytic sublimation at 200°C of a 200-mg sample of XIV, using the procedure as described previously [6], gave a 90% yield of 9-methylxanthene, the ^1H NMR spectrum of which was essentially identical with that reported in the literature [13].

Table 5. Analytical and IR data for new η^6-arene-η^5-cyclopentadienyliron cations (III)

Arene ligand in	Analysis found (calcd.)(%)		IR data[a]
complex III	C	H	(cm^{-1})
$R-(\underline{p}-CH_3)PhFeCp^+PF_6^-$[b]	45.97 (45.72)	3.53 (3.33)	-
$PhCH_2CO_2H$	38.43 (38.84)	3.40 (3.26)	$\nu(C=O)$ 1720 s $\nu(O-H)$ 2600-3100 broad
$PhCH_2CO_2CH_3$	41.15 (40.41)	3.81 (3.63)	$\nu(C=O)$ 1730 s
$PhCH(CH_3)CO_2CH_3$	41.53 (41.89)	3.72 (3.98)	$\nu(C=O)$ 1730 s
$PhC(CH_3)_2CO_2CH_3$	43.41 (43.27)	3.96 (4.31)	$\nu(C=O)$ 1725 s
$PhCH=C(SCH_3)_2$	38.64 (38.97)	3.71 (3.71)	$\nu(C=C)$ 1565 ms
$PhC(CH_3)=C(SCH_3)_2$	40.79 (40.35)	3.89 (4.02)	$\nu(C=C)$ 1570 ms
$PhCH(CH_3)CSSCH_3$	38.44 (38.97)	3.76 (3.71)	$\nu(C=S)$[c] 1090w, 1165m
$PhC(CH_3)_2CSSCH_3$	39.80 (40.35)	4.07 (4.02)	$\nu(C=S)$[c] 1090m, 1160w

[a] Nujol Mull.

[b] R = O - fluorenyl. Satisfactory analysis for corresponding 2,4-dinitrophenyl derivative not obtained due to incomplete combustion.

[c] Tentative assignments.

η^6-9-(η^6-$\underline{p}$-Tolyl-η^5-cyclopentadienyliron)fluorene-η^5-cyclopentadienyliron dihexafluorophosphate (XV)

To a solution of 0.86 g (2.0 mmol) of η^6-fluorene-η^5-cyclopentadienyliron hexafluorophosphate in 10 ml of DMF 0.50 g (3.6 mmol) of K_2CO_3 was added. Solid η^6-$\underline{p}$-chlorotoluene-η^5-cyclopentadienyliron hexafluorophosphate (0.79 g, 2.0 mmol) was then introduced and the mixture was stirred at room temperature overnight. A deep blue suspension resulted and it was treated with a concentrated solution of NH_4PF_6 and with 10% HCl until a yellow solution was obtained. The product was extracted with CH_2Cl_2, dried over $MgSO_4$, concentrated and upon addition of ether, 1.02 g (65%) of XV (the hexafluorophosphate of cation VII) was precipitated. On passage through the alumina column, a deep blue component was formed, presumably arising from deprotonation on the column. Elution with acetone followed by concentration and precipitation with ether gave 0.52 g (40%) of the solid, deep blue zwitterionic species VI.

When a CH_2Cl_2 solution of this blue product was shaken with dilute HCl, a change in color occurred and the yellow organic layer was separated. After drying over $MgSO_4$, concentration and precipitation with ether, the regenerated substitution product XV was obtained. Its ^1H NMR data are given in Table 2. Its ^{13}C NMR spectrum is as follows: $\delta(CD_3NO_2)$ in ppm, 142.6, 136.6 (quaternary), 130.2, 129.2, 125.6, 121.9 (uncomplexed aromatic); 106.3, 104.4, 103.5, 102.7 (quaternary), 87.5, 87.1, 86.3, 85.0, 84.4, 84.0, 80.1 (complexed aromatic); 77.8, 76.7 (Cp); 50.0 (CH); 18.5 (CH_3).

η^6-Phenylacetic acid-η^5-cyclopentadienyliron hexafluorophosphate (XVI)

A suspension of 0.72 g (2.0 mmol) of η^6-toluene-η^5-cyclopentadienyliron hexafluorophosphate in 40 ml of THF under N_2 was cooled to -50°C by means of a 1-hexanol-liquid N_2 slush. An excess of t-BuOK (0.50 g, 4.5 mmol) was added with stirring and stirring was continued for 10 min. A deep red solution resulted and dried CO_2 gas was passed through the solution. An orange-yellow suspension was formed within about a min, but the CO_2 treatment was continued for 20 min. The reaction mixture was allowed to warm to about 10°C, ether was added and the pale yellow precipitate was collected by filtration. The precipitate was washed with ether and with CH_2Cl_2 and then dissolved in H_2O. The aqueous solution was treated with 10% HCl and with a concentrated solution of NH_4PF_6. The resulting material was extracted with CH_3NO_2. The extract was dried over $MgSO_4$, concentrated in a rotary evaporator and CH_2Cl_2 was added. A small amount of NH_4PF_6 that precipitated was filtered off, and upon addition of ether, 0.52 g (65%) of the orange-yellow product XVI was obtained. Its ^1H NMR data are given in Table 3. Its ^{13}C NMR showed the following absorptions: δ(acetone-d_6) in ppm, 169.8 (COOH); 98.7 (quaternary), 88.1, 87.0, 86.5 (complexed aromatic); 76.3 (Cp); 37.5 (CH_2). (Found: C, 38.43; H, 3.40. $C_{13}H_{13}O_2FePF_6$ calculated: C, 38.84; H, 3.26 %).

η^6-2-phenyl-1,1-bis(methylthio)ethene-η^5-cyclopentadienyliron hexafluorophosphate (XVII)

To a suspension of 0.72 g (2.0 mmol) of η^6-toluene-η^5-cyclopentadienyliron hexafluorophosphate in 40 ml of THF at room temperature and under N_2 was added with stirring 0.50 g (4.5 mmol) of t-BuOK. Stirring was continued for 5 min and the resulting dark red solution was treated with an excess of CS_2 (about 2 ml). A lighter brick red suspension was formed and the mixture was stirred at room temperature for 1.5 h. About 3 ml of $(CH_3)_2SO_4$ was then introduced and stirring was continued for an additional hour. Upon treatment with a concentrated solution of NH_4PF_6, an orange suspension resulted, and the product was recovered the usual way by extraction with CH_2Cl_2, drying over $MgSO_4$, concentration and precipitation with ether to give 0.74 g (80%) of the yellow product XVII (the hexafluorophosphate salt of XI). Its ^1H NMR data are given in Table 4. Its ^{13}C NMR spectrum showed the following absorptions: δ(acetone-d_6) in ppm, 145.5, 118.8 (C=C); 100.7 (quaternary), 86.7, 86.3, 85.5 (complexed aromatic); 76.9 (Cp); 15.6, 15.2 (CH_3). (Found: C, 38.64; H, 3.71. $C_{15}H_{17}S_2FePF_6$ calculated: C, 38.97; H, 3.71 %).

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