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MICHAEL ADDITION REACTIONS OF CYCLOHEXADIENYLIRON COMPLEXES BEARING EXOCYCLIC DOUBLE BONDS

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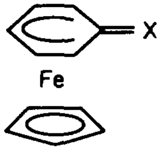
Summary

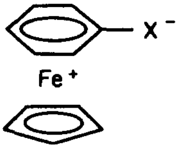
Neutral cyclohexadienyliron complexes with exocyclic C=C or C=N bonds react readily with Michael acceptors such as acrylonitrile and methyl acrylate to produce cationic adducts in 65–98% yields following protonation.

Introduction

Recently the isolation and characterization of several η^5-cyclohexadienyl-η^5-cyclopentadienyliron complexes (I) with exocyclic double bonds to C, N, O, or S has been reported [1–6]. An alternative zwitterionic representation (II) has been proposed for the fluorene derivative on the basis of X-ray diffraction studies [3]. Such complexes have been shown to react as nucleophiles toward a variety of species including alkyl halides, acyl halides, CO_2, CS_2, metal carbonyls, halogens, non-metal halides, and complex transition metal halides [7–11].



(I)



(II)

X = CH_2, CR_2, NH, NR, O, S, etc.

In our investigation of these species we have been interested in their behavior toward carbon–carbon multiple bonds since in principle several reaction paths might be possible. In this paper we wish to report some reactions with typical Michael acceptors such as acrylonitrile and methyl acrylate.

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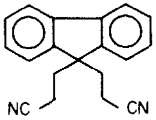
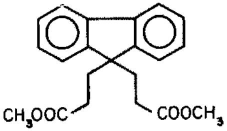
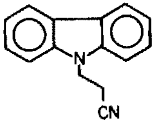
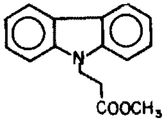
TABLE 1

^{1}H NMR SPECTRAL DATA (in acetone-d_6)

Compound	Arene ligand	δ (ppm from TMS)			
		Cp	Complexed aromatics	Uncomplexed aromatics	Others [c]
[Va]PF_6 [a]	$C_6H_5C(CH_3)_2(CH_2)_2CN$	5.16 (s,5H)	6.43 (s,5H)		1.62 (s,6H,CH_3) 1.96–2.33 (m,4H,CH_2)
[Vb]PF_6 [a]	$C_6H_5C(CH_3)_2(CH_2)_2COOCH_3$	5.20 (s,5H)	6.43 (s,5H)		1.60 (s,6H,CH_3) 1.85–2.33 (m,4H,CH_2) 3.60 (s,3H,OCH_3)
[VIa]PF_6	$C_6H_5NH(CH_2)_2CN$	5.10 (s,5H)	5.91–6.47 (m,5H)		2.95 (t,2H,CH_2,J 7) 3.72 (t,2H,CH_2, J 7)
[VIb]PF_6	$C_6H_5NH(CH_2)_2COOCH_3$	5.06 (s,5H)	5.80–6.38 (m,5H)		2.77 (t,2H,CH_2,J 7) 3.52 (t,2H,cH_2, J 7) 3.75 (s,3H,OCH_3)
[VIIa]PF_6 [b]		5.12 (s,5H)	6.58 (t,1H) 6.69 (t,1H) 6.97 (d,1H) 7.32 (d,1H)	7.66 (m,2H) 7.84 (d,1H) 8.18 (d,1H)	1.57–1.64 (m,2H) 2.61–2.69 (m,2H) 2.75–2.87 (m,2H) 3.28–3.35 (m,2H)

$[VIIb]PF_6$ [b]		5.10 (s,5H)	6.54 (t,1H) 6.67 (t,1H) 6.91 (d,1H) 7.30 (d,1H)	7.56–7.67 (m,2H) 7.74 (d,1H) 8.16 (d,1H)	1.38–1.47 (m,2H) 2.41–2.50 (m,2H) 2.61–2.68 (m,2H) 3.09–3.16 (m,2H) 3.37 (s,3H,OCH_3) 3.69 (s,3H,OCH_3)
$[VIIIa]PF_6$	$C_6H_5N(CH_3)(CH_2)_2CN$	5.12 (s,5H)	5.96–6.55 (m,5H)		3.00 (t,2H,CH_2,*J* 7) 3.96 (t,2H,CH_2,*J* 7) 3.26 (s,3H,CH_3)
$[VIIIb]PF_6$	$C_6H_5N(CH_3)(CH_2)_2COOCH_3$	5.10 (s,5H)	5.85–6.45 (m,5H)		2.85 (t,2H,CH_2,*J* 7) 3.75 (t,2H,CH_2,*J* 7) 3.20 (s,3H,CH_3) 3.75 (s,3H,OCH_3)
$[IXa]PF_6$		4.80 (s,5H)	6.30–6.50 (m,2H) 7.62–7.85 (m,1H) 7.97 (d,1H)	7.40–7.60 (m,2H) 7.62–7.85 (m,1H) 8.50 (d,1H)	3.32 (t,2H,CH_2,*J* 7) 5.00 (t,2H,CH_2,*J* 7)
$[IXb]PF_6$		4.75 (s,5H)	6.20–6.51 (m,2H) 7.26–7.75 (m,1H) 7.85 (d,1H)	7.26–7.75 (m,3H) 8.51 (d,1H)	3.15 (t,2H,CH_2,*J* 7) 4.86 (t,2H,CH_2,*J* 7) 3.64 (s,3H,OCH_3)

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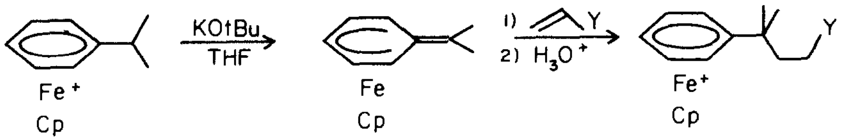
[a] Measured in CD_3NO_2. [b] Measured with a 300 MHz spectrometer. The other spectra were obtained using a 60 MHz spectrometer. [c] *J* in Hz.

Results and discussion

η^6-Arene-η^5-cyclopentadienyliron(II) cations III (arene = isopropylbenzene, IIIa; fluorene, IIIb; aniline, IIIc; or carbazole, IIId) were prepared by the $AlCl_3$-catalyzed ligand exchange reaction of ferrocene and the appropriate arene as previously described [1,2,12–14]. Hexafluorophosphate salts were isolated in yields of 30–40% in each case. An analogous complex of *N*-methylaniline IIIe was prepared by the reaction of methylamine and η^6-chlorobenzene-η^5-cyclopentadienyliron(II) hexafluorophosphate [15].

Deprotonation of the isopropylbenzene complex IIIa was readily effected with one equivalent of potassium t-butoxide in tetrahydrofuran (THF) at 25°C under nitrogen. A deep red solution of the neutral complex IV formed and was allowed to react with one equivalent of either acrylonitrile or methyl acrylate in THF (eq. 1). The solution turned orange during the reaction with acrylonitrile and reddish-brown during the reaction with methyl acrylate.



(1)

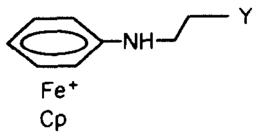
(IIIa)

(IV)

(Va) Y = CN
(Vb) Y = $COOCH_3$

The Michael additions were complete in 5–10 min. The zwitterionic intermediates were not isolated. After hydrolysis, which led to a yellow color, the cationic complexes Va and Vb were isolated as hexafluorophosphate salts which were fine yellow powders. ^1H NMR spectral data are presented in Table 1.

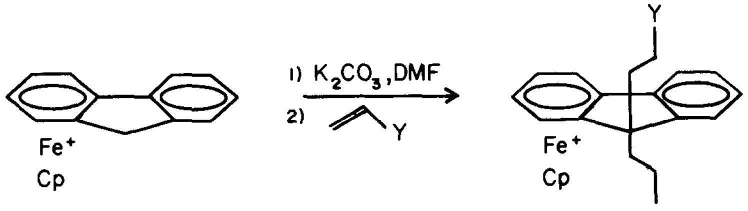
Analogous reactions proceed with the aniline complex IIIc to give the η^6-{*N*-(β-cyanoethyl)aniline} complex VIa and the η^6-{*N*-(β-carbomethoxyethyl)aniline} complex VIb in high yields.



(VIa) Y = CN
(VIb) Y = $COOCH_3$

Sutherland et al. [8] have found it convenient to use K_2CO_3 in DMF for deprotonation of relatively acidic cations. When the fluorene complex IIIb was reacted with K_2CO_3 in DMF and then treated with two equivalents of acrylonitrile or methyl acrylate, dialkylation occurred to give the Michael adducts VIIa or VIIb in yields of 70–80%.

Potassium carbonate in DMF was also used to deprotonate complexes IIIe and IIId derived from *N*-methylaniline and carbazole, respectively. Subsequent reactions with acrylonitrile or methyl acrylate gave good yields of Michael adducts. We were



(IIIb)

(VIIa) Y = CN
(VIIb) Y = COOCH$_3$

unable to obtain the product of the reaction of IIIe and methyl acrylate in a crystalline state although the ^{1}H NMR showed it was substantially pure.

The structures assigned to the products are supported by NMR, IR, and mass spectra as well as by elemental analyses. The ^{13}C NMR data for cations VIIa and VIIb are presented in Table 2 and analytical data are presented in Table 3. Assignment of chemical shifts for the *endo* and *exo* carbons was made by analogy to the ^{13}C spectra of η^6-*cis*-(*endo*-9,10-dihydro)-9,10-dimethylanthracene-η^5-cyclopentadienyliron(II) cation and the corresponding *exo* isomer which were reported by Sutherland and co-workers [16] with the assumption that the higher field absorption in a comparable pair of peaks belongs to the *endo* group.

While cyanoethylation of fluorene and carbazole occurs readily in the presence of benzyltrimethylammonium hydroxide to give good yields of Michael adducts [17], aniline reportedly gives no appreciable reaction with acrylonitrile in the presence of NaOCH$_3$ and poor yields after several hours at 150°C in $HC_2H_3O_2$ [18]. This is a marked contrast to the high reactivity of the deprotonated aniline complex.

Compounds [VIIa]PF$_6$ and [VIIb]PF$_6$ derived from fluorene were both found to undergo thermal decomposition when heated to 200° under vacuum. Good yields (82–85%) of the corresponding free, substituted aromatic ligand were obtained.

Michael reactions using complexes I should provide convenient routes to arene complexes with functionally-substituted aliphatic side-chains. The effect of complexes I on other unsaturated molecules is being studied.

Experimental

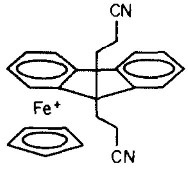
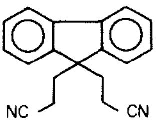
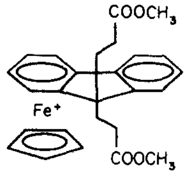
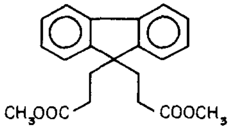
All reactions were performed under nitrogen. THF was dried and distilled under nitrogen from sodium benzophenone ketyl just before use. DMF was dried over molecular sieve 4A. η^6-Arene-η^5-cyclopentadienyliron(II) salts (arene = isopropylbenzene, fluorene, aniline, carbazole, *N*-methylaniline) were prepared using published procedures [1,2,12–15]. Acrylonitrile and methyl acrylate were distilled at 25°C under vacuum from molecular sieve 4A prior to use.

Spectral measurements were made with a Perkin–Elmer 283B infrared spectrometer, an AEI MS-30 mass spectrometer, a Varian EM 360L NMR spectrometer, a JEOL FX-100 NMR spectrometer, and a Nicolet NT-300 NMR spectrometer. Microanalyses were performed with a Carlo Erba Elemental Analyzer 1106.

Purification of products could be done by chromatography on Al_2O_3 or recrystallization from CH_2Cl_2/ether or acetone/ether.

TABLE 2

^{13}C NMR SPECTRAL DATA [a]

Particle	δ (ppm from TMS)			
	Cp	Complexed aromatic	Uncomplexed aromatic	Other
 (VIIa)	78.2	80.4, 85.9, 85.9, 87.4, 103.8[b], 115.1[b]	123.7, 125.4, 130.2, 132.0, 136.9[b], 148.8[c]	12.2, 33.3 (*endo* CH_2) 13.9, 35.7 (*exo* CH_2) 53.3[b] 119.2 (*endo* CN) 120.2 (*exo* CN)
			120.5, 122.6, 128.3 128.7, 141.0[b]. 144.5[b]	11.8, 35.0 (CH_2) 53.3[b] 119.0 (CN)
 (VIIb)	78.2	80.3, 85.8, 86.2, 87.1, 104.0[b], 116.8[b]	123.5, 125.3, 129.8, 131.8, 136.8[b], 150.9[b]	29.1, 33.0 (*endo* CH_2) 30.6, 35.8 (*exo* CH_2) 51.6 (*endo* OCH_3) 52.1 (*exo* OCH_3) 53.4[b] 172.8 (*endo* C=O) 173.8 (*exo* C=O)
			119.9, 122.9, 127.6, 127.6, 141.1[b], 147.4[b]	28.8, 34.6 (CH_2) 51.3 (OCH_3) 53.5[b] 173.7 (C=O)

[a] VIIa and VIIb were measured in acetone-d_6 and the free arenes were measured in $CDCl_3$. [b] Quaternary carbons.

$[\eta^5$-CpFe-η^6-$\{C_6H_5C(CH_3)_2(CH_2)_2CO_2Me\}]PF_6$ ($[Vb]PF_6$)

To a Schlenk tube containing THF (15 ml) were added $[\eta^5$-CpFe-η^6-$(C_6H_5CH(CH_3)_2)]PF_6$ (580 mg, 1.5 mmol) and potassium t-butoxide (180 mg, 1.6 mmol) at 25°C. The resulting deep red solution was magnetically stirred for 15 min. Then methyl acrylate (0.18 ml, 2.0 mmol) in THF (5 ml) was added dropwise during 5–7 min. The solution color faded. After an additional 5 min the mixture was treated with either 1% HCl (2 ml) or 5% aq. NH_4Cl (2 ml). After the yellow solution was taken to dryness using a rotary evaporator, the residue was dissolved in CH_2Cl_2 and dried over $MgSO_4$. Addition of ether to the solution after concentration produced yellow crystals of $[Vb]PF_6$ (0.388 g). Concentration of the mother liquor gave a residue which yielded [Vb]PF_6 (0.150 g, total yield 76%) after separation from starting material (0.050 g) by chromatography on Al_2O_3 using CH_2Cl_2 as an eluent.

[η^5-CpFe{η^6-$C_6H_5C(CH_3)_2(CH_2)_2CN$}]$PF_6$ ([Va]PF_6)

[Va]PF_6, a yellow crystalline salt, was prepared in 65% yield by the procedure described for [Vb]PF_6 but with acrylonitrile as the Michael acceptor. Microanalytical and spectral data are presented in Tables 1 and 2.

[η^5-CpFe{η^6-$C_6H_5NH(CH_2)_2CN$}]PF_6 ([VIa]PF_6)

The addition of potassium t-butoxide (150 mg, 1.30 mmol) to [η^5-CpFe{η^6-$C_6H_5NH_2$}]PF_6 (438 mg, 1.22 mmol) in THF (20 ml) at 25°C produced an immediate red solution which was stirred for 15 min before being treated with acrylonitrile (0.10 ml, 1.5 mmol). After 1.5 h the mixture was hydrolyzed with 10% HCl (2 ml), the volatile materials were removed in vacuo and the residue was extracted with CH_2Cl_2. The solution was dried over $MgSO_4$ and concentrated. Addition of ether gave a powder (0.493 g, 98%). Recrystallization produced yellow-orange crystals of [VIa]PF_6.

[η^5-CpFe{η^6-$C_6H_5NH(CH_2)_2COOCH_3$}]PF_6 ([VIb]PF_6)

[VIb]PF_6 was prepared as orange-brown crystals in 65–70% yield using the same procedure as that described for [VIa]PF_6 but with methyl acrylate as the Michael acceptor.

[η^5-CpFe{η^6-$C_6H_5N(CH_3)(CH_2)_2CN$}]PF_6 ([VIIIa]PF_6)

Dry DMF (5 ml) was added to a mixture of [η^5-CpFe-η^6-{$C_6H_5NHCH_3$}]PF_6 (457 mg, 1.20 mmol) and K_2CO_3 (345 mg, 2.50 mmol) at 25°C. A deep red solution formed. After 5 min of stirring, acrylonitrile (0.10 ml, 1.5 mmol) was added. The mixture was stirred for 20 h at 25°C and then filtered rapidly into a flask containing 5% aq. NH_4Cl (10 ml). The reaction vessel was washed with CH_2Cl_2. After H_2O and CH_2Cl_2 were removed with a rotary evaporator, the yellow DMF solution was treated with ether to give a brown precipitate. The solid was filtered, redissolved in CH_2Cl_2, and purified by chromatography on a short Al_2O_3 column using CH_2Cl_2/ether (8/1) as the eluent. After concentration of the solution and addition of ether, orange-brown crystals of [VIIIa]PF_6 were produced (0.406 g, 78%).

[η^5-CpFe-η^6-($C_{20}H_{17}N_2$)]PF_6 ([IXa]PF_6)

Dry DMF (5 ml) was added to a mixture of η^6-carbazole-η^5-cyclopentadienyliron(II) hexafluorophosphate (1.177 g, 2.72 mmol) and K_2CO_3 (1.126 g, 8.16 mmol). The resulting red solution was stirred for 5 min at 25°C and then treated with acrylonitrile (0.20 ml, 3.0 mmol). After 10 h of stirring, the reaction mixture was hydrolyzed and [IXa]PF_6 (1.122 g, 84%) was isolated as an orange-brown powder using the procedure described for [VIIIa]PF_6.

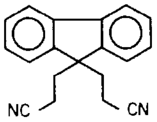
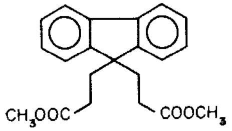
[η^5-CpFe-η^6-($C_{21}H_{20}NO_2$)]PF_6 ([IXb]PF_6)

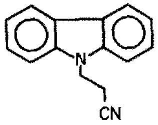
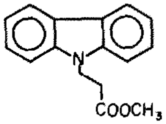
[IXb]PF_6, an orange-brown powder, was prepared in 73% yield by the procedure described for [IXa]PF_6 but with methyl acrylate as the Michael acceptor.

(Continued on p. 362)

TABLE 3

ANALYTICAL DATA

Compound	Arene ligand	Formula	Analyses (Calcd. (Found) (%))			M.p. (°C)	IR (cm^{-1})^{a}
			C	H	N		
[Va]PF_6	$C_6H_5C(CH_3)_2(CH_2)_2CN$	$C_{17}H_{20}NFePF_6$	46.49 (46.41)	4.59 (4.43)	3.19 (3.33)	156–158	ν(C≡N) 2240
[Vb]PF_6	$C_6H_5C(CH_3)_2(CH_2)_2COOCH_3$	$C_{18}H_{23}O_2FePF_6$	45.79 (45.58)	4.91 (4.92)		155–156	ν(C=O) 1735
[VIa]PF_6	$C_6H_5NH(CH_2)_2CN$	$C_{14}H_{15}N_2PF_6$	40.80 (40.78)	3.67 (3.59)	6.79 (6.76)	105–107	ν(C≡N) 2250 ν(NH) 1570, 3445
[VIb]PF_6	$C_6H_5NH(CH_2)_2COOCH_3$	$C_{15}H_{18}NO_2FePF_6$	40.47 (40.39)	4.08 (4.05)	3.15 (3.02)	81–82	ν(C=O) 1735 ν(NH) 1560, 3410
[VIIa]PF_6		$C_{24}H_{21}N_2FePF_6$	53.56 (54.10)	3.93 (4.50)	5.20 (4.68)	85–86	ν(C≡N)2245
[VIIb]PF_6		$C_{26}H_{27}O_4FePF_6$	51.68 (51.25)	4.50 (4.45)		163–166	ν(C=O) 1720, 1740

[VIIIa]PF_6	$C_6H_5N(CH_3)(CH_2)_2CN$	$C_{15}H_{17}N_2FePF_6$	42.28 (42.55)	4.02 (3.87)	6.57 (6.55)	145–147	ν(C≡N) 2260
[IXa]PF_6		$C_{20}H_{17}N_2FePF_6$	49.41 (49.52)	3.52 (3.59)	5.76 (5.58)	189–190	ν(C≡N) 2250
[IXb]PF_6		$C_{21}H_{20}NO_2FePF_6$	48.58 (48.91)	3.88 (4.00)	2.69 (2.58)	128–129	ν(C=O) 1740

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[a] [VIIa]PF_6 and [VIIb]PF_6 in KBr disc, others in Nujol mull.

[η^5-CpFe-η^6-($C_{26}H_{27}O_4$)]PF_6 ([VIIb]PF_6)

A mixture of η^6-fluorene-η^5-cyclopentadienyliron(II) hexafluorophosphate (0.432 g, 1.00 mmol), K_2CO_3 (0.414 g, 3.00 mmol) and DMF (5 ml) was stirred at 25°C and produced a deep blue solution. After 5 min methyl acrylate (0.20 ml, 2.2 mmol) was added. After being stirred for 10 h, the reaction mixture was hydrolyzed and [VIIb]PF_6 (0.476 g, 78%) was isolated as orange crystals using the procedure described for [VIIIa]PF_6.

[η^5-CpFe-η^6-($C_{24}H_{21}N_2$)]PF_6 ([VIIa]PF_6)

Golden crystals of [VIIa]PF_6 were prepared in 78% yield using the procedure described for [VIIb]PF_6 but with acrylonitrile as the Michael acceptor.

Thermolysis of [VIIb]PF_6

[VIIb]PF_6 (604 mg, 1 mmol) was placed in a vacuum sublimator, dissolved in a minimum amount of acetone, and dried to a thin film using a N_2 stream. It was heated under vacuum using an oil bath. Decomposition producing a sublimate on the Dry Ice-cooled cold finger appeared to begin at about 170°C and 0.5 mm. After 2 h of heating at 200°C, the sublimate was collected and chromatographed on Al_2O_3. Elution with ether gave 280 mg (82%) of dimethyl 9,9-fluorenedipropionate as a white, crystalline powder, m.p. 78–79°C (lit. [19] 78–79°C).

^{1}H NMR in $CDCl_3$, δ (ppm): 7.26–7.56 (m, 6H, aryl); 7.70–7.96 (m, 2H, aryl); 1.60 (t, 4H, CH_2); 2.43 (t, 4H, CH_2); 3.50 (s, 6H, CH_3).

Thermolysis of [VIIa]PF_6

[VIIa]PF_6 (538 mg, 1 mmol) was thermally decomposed by the same procedure described for [VIIb]PF_6 to give 230 mg (85% yield) of 9,9-fluorenedipropionitrile as a white, crystalline powder, m.p. 118–119°C (lit. [19] 120–121°C). Decomposition of [VIIa]PF_6 appeared to begin about 150°C.

^{1}H NMR in $CDCl_3$, δ (ppm): 7.32–7.68 (m, 6H, aryl); 7.68–8.00 (m, 2H, aryl); 1.50 (t, 4H, CH_2); 2.50 (t, 4H, CH_2)

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