

SYNTHETIC STUDIES WITH IRON CARBONYL COMPLEXES

REACTION OF CARBON NUCLEOPHILES WITH TRICARBONYL(CYCLOHEXADIENYL)IRON TETRAFLUOROBORATE: ADDITION OF THE ANION OF NITROMETHANE TO THE DIENYL CATION

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Summary

Reactions of carbon nucleophiles with tricarbonyl(cyclohexadienyl)iron tetrafluoroborate are described. Acetaldehyde formed traces of the addition product and methyl vinyl ketone gave several products, but not the expected tricarbonyl-5-*exo*-(2-oxobut-3-enyl)cyclohexa-1,3-dieneiron(0). The anion of nitromethane reacted with tricarbonyl(cyclohexadienyl)iron tetrafluoroborate to give tricarbonyl-5-*exo*-(nitromethyl)cyclohexa-1,3-dieneiron(0), which was reduced with zinc in acetic acid/hydrochloric acid to give tricarbonyl-5-*exo*-(aminomethyl)-cyclohexa-1,3-dieneiron(0).

Nucleophilic attack on tricarbonyl(dienyl)iron cations is currently of interest as a means of carbon-carbon bond formation [1]. Successful addition of acetone and butan-2-one [2] via the enol in refluxing ethanol, and of sodium anions of diketones and other stabilised enolates [3] in THF are well known. We report here the reactions of a variety of synthetically important carbon nucleophiles with tricarbonyl(cyclohexadienyl)iron tetrafluoroborate.

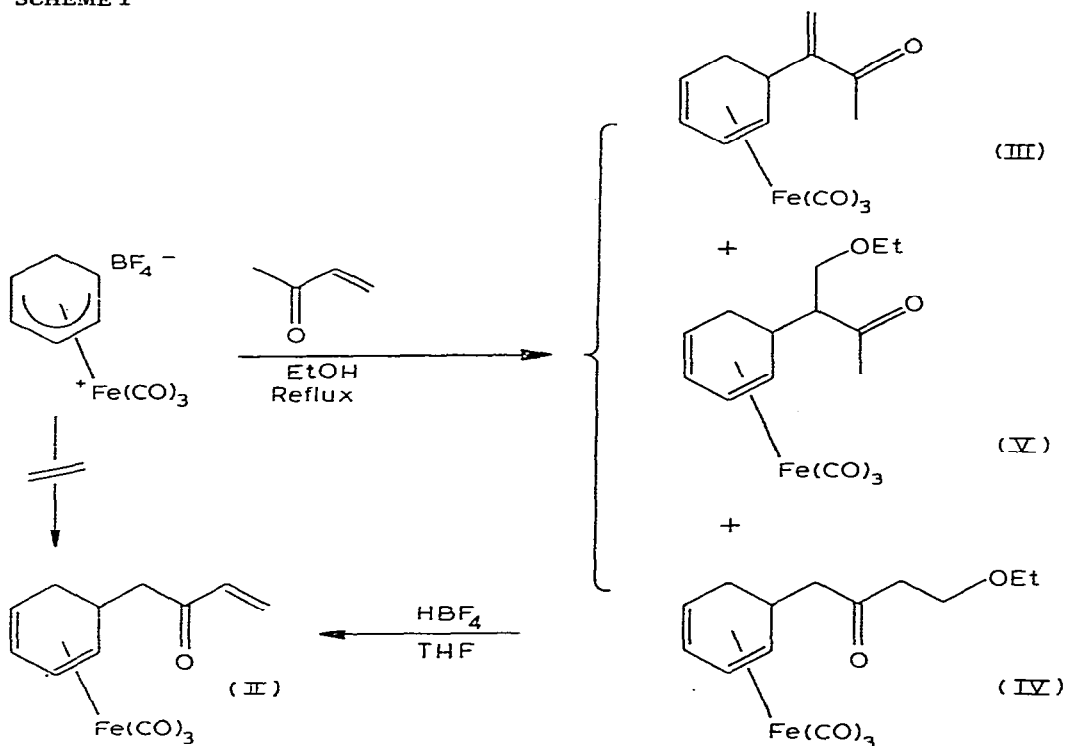
Ethyl acetate and acetonitrile have a higher pK_a than acetone and failed to react with tricarbonyl(cyclohexadienyl)iron tetrafluoroborate in refluxing ethanol. Attempted addition of acetophenone was also unsuccessful, the only product from these reactions being tricarbonyl-5-*exo*-ethoxy(cyclohexa-1,3-diene)iron(0), formed by solvolysis of the dienyl cation. With acetaldehyde

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traces of the desired addition product, tricarbonyl-3-*exo*-(2-oxoethyl)cyclohexa-1,3-dieneiron(0) (I), were isolated. Since methyl vinyl ketone can enolise in only one direction, it was hoped that its addition would provide a good route to tricarbonyl-5-*exo*-(2-oxobut-3-enyl)cyclohexa-1,3-dieneiron(0) (II). In the event, none of the complex was isolated when tricarbonyl(cyclohexadienyl)iron tetrafluoroborate was heated with methyl vinyl ketone under reflux in ethanol, though its isomer, tricarbonyl-5-*exo*-(1-acetylethenyl)cyclohexa-1,3-diene-iron(0) (III) was obtained in 14% yield. The nature of this complex was confirmed unambiguously by its ^{13}C NMR spectrum (see Table 1). Overall recovery of diene complexes from this reaction is high and tricarbonyl-5-*exo*-(2-oxo-4-ethoxybutyl)cyclohexa-1,3-dieneiron(0) (IV) (23%) and tricarbonyl-5-*exo*-(1-acetyl-2-ethoxyethyl)cyclohexa-1,3-dieneiron(0) (V) (20%) were also produced (Scheme 1).

SCHEME 1



Addition of ethanol across the double bond of the methyl vinyl ketone followed by preferential enolisation toward the more substituted carbon atom accounts for the formation of products with branched sidechains. Reaction conditions avoiding the use of ethanol were tried without success. However, II was produced slowly from IV by treatment with HBF_4 in THF.

When lithium acetylide, stabilised by ethylenediamine, was added to a suspension of tricarbonyl(cyclohexadienyl)iron tetrafluoroborate in ether, the only complexes obtained appeared to be addition products of ethylenediamine to the dienyl cation. These were not characterised. The considerably less basic anion of

TABLE I
 IR, ^1H AND ^{13}C NMR SPECTRA (in CDCl_3) OF COMPOUNDS I—VII

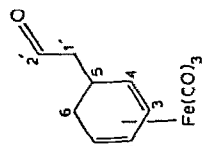
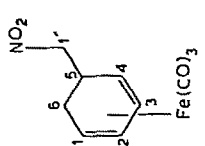
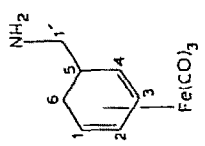
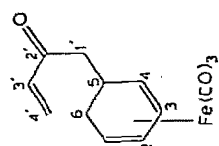
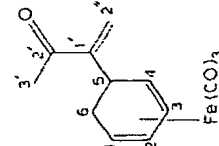
Complex	Proton	Chemical shift (τ) ppm	Intensity	Multiplicity	IR (cm^{-1})
 (I)	H(2')	0.40	1	t ^a	cyclohexane
	H(2), H(3)	4.70	2	m	
	H(1), H(4)	6.90	2	m	2047
	H(1')	7.6	2	d ^a	1980
	H(5)	8.4	3		1730
	H(5), H(6)	8.68 8.89			
 (I)	H(2), H(3)	4.61	2	m	cyclohexane
	H(1')	5.92	1	d ^a	
	H(1), H(4)	7.05	2	m	2054
	H(5)	7.3	1	(observed) ^b	1987
	H(6)	7.89		t of d	1987
	H(6)	8.63	1	d	1982
					liquid film 1540 1375
 (VII)	H(2), H(3)	4.7	2	m	cyclohexane
	H(1), H(4)	6.8	2	m	
	H(5)	7.95	?	t	2046
	NH ₂	8.1	2	v, broad	1975
	H(6)	8.72	1	t	liquid film
	H(6)	8.9	1	d	3200 (broad) 1575

TABLE 1 (continued)

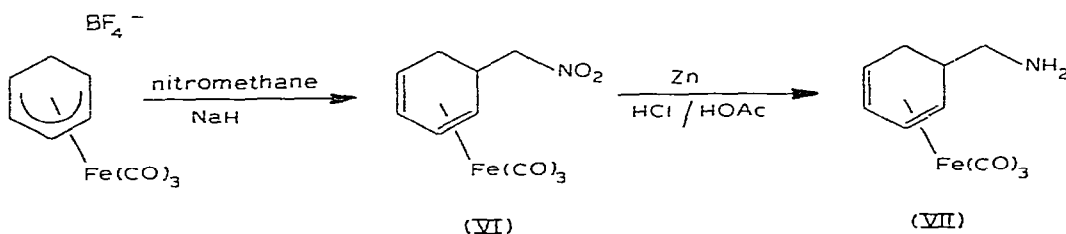
Complex	Proton	Chemical shift (τ) ppm	Intensity	Multiplicity	Carbon	Chemical shift	Multiplicity	$J(\text{CH})(\text{Hz})$	IR (cm^{-1})	
 (II)									cyclohexane	
		PMR spectrum not recorded								
		Characterisation based on comparison of ^{13}C NMR with spectra of III, IV, V								
					C(1)	59.6				
					C(2)	84.1				2048
					C(3)	85.9				1980
 (III)										

^a Small coupling demonstrated by decoupling experiment. ^b Coupling demonstrated by decoupling experiment to indicate approximate position of H5'. ^c Sharp singlet.

phenylacetylene was prepared in situ in dioxane with lithium amide. No iron complexes were obtained from the reaction of this salt with tricarbonyl(cyclohexadienyl)iron tetrafluoroborate, though 1,4-diphenylbuta-1,3-diyne [5] was isolated in 35% yield. The salt is, however, reported to react successfully with the tricarbonyl(cycloheptatrienyl)chromium cation [6]. The problem with its application to the tricarbonyl(cyclohexadienyl)iron system lies most probably in the basicity of the nucleophile, since the cyclohexadienyl ring, unlike tricarbonyl(tropylium)metal complexes, has a hydrogen which may be readily removed, producing benzene with spontaneous destruction of the complex.

Nitromethane has a very low pK_a (similar to keto esters) and its anion added successfully to tricarbonyl(cyclohexadienyl)iron tetrafluoroborate (Scheme 2).

SCHEME 2



Sodium hydride (50% dispersion in oil) was washed with pentane and added cautiously and in small portions to a vast excess of dry nitromethane, which also served as solvent for the reaction, cooled in ice under a stream of nitrogen and with vigorous stirring*. Subsequent addition of the dienyl cation yielded tricarbonyl-5-*exo*-(nitromethyl)cyclohexa-1,3-dieneiron(0); VI was obtained in 87% yield after chromatography. Reduction with a large excess of zinc in a 2/1 mixture of glacial acetic acid and concentrated hydrochloric acid over 24 h gave tricarbonyl-5-*exo*-(aminomethyl)cyclohexa-1,3-dieneiron(0) (VII), a useful result since attempts to prepare this complex by reduction of tricarbonyl-5-*exo*-cyano(cyclohexa-1,3-diene)iron(0) with a number of hydride-reducing agents has met with no success.

As in other reports [1,2,3] nucleophilic addition in these reactions occurs to the *N-exo* face of the ligand. The complexes were characterised by their spectroscopic properties (see Table 1) and satisfactory elemental analysis.

Experimental

^{13}C NMR spectra were recorded on a Varian Associates XL 100 spectrometer operating in the Fourier Transfer mode at 25.2 MHz. All ^{13}C NMR spectra were 1H decoupled. Chemical shifts are relative to TMS. 1H NMR spectra were recorded on a Varian Associates CFT 20 spectrometer operating in the Fourier Transform mode at 80 MHz, or on a Varian R24 60 MHz. Mass spectral data were recorded on an AEI MS 12 spectrometer, and infrared data on a Perkin-Elmer 257 spectrophotometer.

* Over-rapid addition is indicated by small explosions within the vessel; for this reason it is advisable to perform the reaction only on a small scale.

Tricarbonyl(cyclohexadienyl)iron tetrafluoroborate was prepared according to a literature procedure [1].

Tricarbonyl-5-exo-(2-oxoethyl)cyclohexa-1,3-dieneiron(0) (I). Acetaldehyde (10 ml) was heated with tricarbonyl(cyclohexadienyl)iron tetrafluoroborate (1 g, 3.36 mmol) in ethanol (60 ml) under reflux for 4 h. More acetaldehyde (10 ml) was added and the heating continued for a further 4 h before pouring into water (100 ml) and extracting with ether (3 × 50 ml). The combined extracts were washed with water and dried over magnesium sulphate, filtered and the solvent removed in vacuo. Column chromatography followed by TLC eluting with 1/1 hexane/diethyl ether gave the product (0.02 g, 0.1 mmol, 2%) as a golden oil. *m/e* 262, -3 CO, -H₂.

Reaction with methyl vinyl ketone

Tricarbonyl(cyclohexadienyl)iron tetrafluoroborate (0.600 g, 1.96 mmol) was heated with methyl vinyl ketone (5 ml) under reflux in ethanol (25 ml) for 15 h. The resulting yellow solution was poured into water (150 ml) and extracted with diethyl ether (3 × 50 ml) and the combined extracts were washed thoroughly with water (4 × 40 ml), dried over magnesium sulphate and filtered, and the solvent was removed in vacuo. A small amount of tricarbonyl-5-exo-(ethoxy)cyclohexadieneiron(0) was separated from two other bands by preparative TLC, eluting with 1/1 hexane/diethyl ether.

The slowest moving band was extracted to give tricarbonyl-5-exo-(2-oxo-4-ethoxybutanyl)cyclohexa-1,3-dieneiron(0) (IV, 0.152 g, 0.46 mmols, 23%), a yellow oil. Analysis: Found: C, 54.9; H, 5.64. C₁₅H₁₈O₅Fe calcd.: C, 53.9; H, 5.42%. *m/e* 334, -3 CO, -H₂: 334, -46, -3 CO, -H₂.

The faster band was further separated by TLC, eluting this time with benzene; the faster moving compound was tricarbonyl-5-exo-(1-acetylenyl)cyclohexa-1,3-dieneiron(0) (III), a pale yellow waxy solid (0.078 g, 0.219 mmol, 14%). Analysis: Found: C, 53.2; H, 4.33. C₁₃H₁₂O₄Fe calcd.: C, 54.2; H, 4.20%. *m/e* 288, -3 CO, 158, 148, 134, 105, 103.

The other compound obtained from the reaction was tricarbonyl(1-acetyl-2-ethoxyethyl)cyclohexa-1,3-dieneiron(0) (V), a mixture of diastereoisomers (0.152 g, 0.321 mmol, 20%). Analysis: Found: C, 55.1; H, 5.61. C₁₅H₁₈O₅Fe calcd.: C, 53.9; H, 5.42%. *m/e* 334, -3 CO, 220, 204, 202, 172, 163, 148, 134.

Tricarbonyl-5-exo-(2-oxobut-3-enyl)cyclohexa-1,3-dieneiron(0) (II). Tricarbonyl-5-exo-(2-oxo-4-ethoxybutanyl)cyclohexa-1,3-dieneiron(0) (IV 0.152 g, 0.46 mmol) was dissolved in THF (30 ml). 50% aqueous tetrafluoroboric acid (3 ml) was added and the mixture stirred at room temperature for 20 h, and then poured into distilled water (150 ml) and extracted with ether (3 × 40 ml) and dried over magnesium sulphate. The product (0.024 g, 0.09 mmol, 20%) was separated from unchanged starting material (0.064 g, 0.19 mmol, 41%) by TLC, eluting with 1/1 hexane/diethyl ether. *m/e* 288, -3 CO, -H₂, 174, 148, 134, 126, 91, 85, 83.

Tricarbonyl-5-exo-(nitromethyl)cyclohexa-1,3-dieneiron(0) (VI). Sodium hydride (0.5 g, 50% dispersion in oil, 10 mmol) was washed twice with dry nitromethane (150 ml) cooled in ice with vigorous stirring. Over-rapid addition causes small explosions in the vessel, so great care should be taken at this stage. After 1 h tricarbonyl(cyclohexadienyl)iron tetrafluoroborate (2.0 g, 6.55 mmol)

is added in portions, and after stirring at 0°C for 5 min the dark reaction mixture is filtered under suction through a column of alumina and the solvent removed to leave a brown gum. Chromatography on silica, eluting with 1/1 hexane/diethyl ether gives VI as a golden oil (1.6 g, 5.74 mmol, 87%). Analysis: Found: ⁸C, 43.8; H, 3.39; N, 5.11. C₁₀H₉NO₅Fe calcd.: C, 43.1; H, 3.25; N, 5.02%. *m/e* 279, -3 CO, 151, 135, 134, 112, 91.

Tricarbonyl-5-exo-(aminomethyl)cyclohexa-1,3-dieniron(0), (VII). *Tricarbonyl-5-exo-(nitromethyl)cyclohexa-1,3-dieneiron(0)* (VI) (0.206 g, 0.74 mmol) was dissolved in glacial acetic acid (5 ml). Concentrated hydrochloric acid (2.5 ml) was added and the mixture was stirred for 24 h with slow addition of zinc turnings (2.19 g, 33 mmol) over the first 6 h. A green scum developed on the surface. The mixture was poured into iced 10% potassium hydroxide solution (200 ml) and extracted with ether (3 × 50 ml). The combined extracts were dried over sodium carbonate to give VII (0.15 g, 0.60 mmol, 81%) as a golden oil. *m/e* 249, -3 CO, -H₂, 148, 134 (base peak), 106, 91.

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