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Note

Electronic properties of the trimethylenemethaneiron tricarbonyl group

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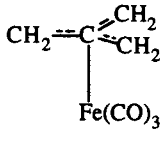
Abstract

The substituent electronic effects of trimethylenemethaneiron tricarbonyl [TMMFe(CO)$_3$] have been studied, with σ values reported. Determination of these values was accomplished through three different techniques: a study of acidity relative to benzoic acid with TMMFe(CO)$_3$ acting as a substituent of benzoic acid; ^{19}F-nuclear magnetic resonance (NMR) shielding analysis of *m*-fluorophenylTMMFe(CO)$_3$; and ^{13}C-NMR shielding analysis of phenylTMMFe(CO)$_3$. The TMMFe(CO)$_3$ group behaves in much the same manner as a phenyl group (i.e. weakly electron releasing by resonance and weakly electron attracting by induction). The syntheses of the substituted phenyltrimethyleneiron tricarbonyl compounds are described. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Trimethylenemethane; Iron; Complexes; Spectroscopy

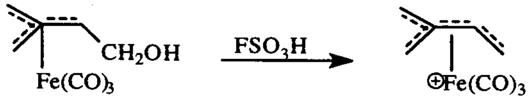
1. Introduction

As part of our continuing studies of highly reactive C$_4$-hydrocarbons bonded to metal carbonyl systems [1,2], we have examined the electronic behavior of trimethylenemethaneiron tricarbonyl (I, TMMFe(CO)$_3$) when it is present as a substituent on a benzene ring. Some organometallic systems have been shown to be very electron rich.



I

For example, ferrocene undergoes electrophilic aromatic substitution reactions rapidly and stabilizes adjacent carbocations to a greater extent than does benzene [3]. On the other hand, electrophilic aromatic substitution reactions with TMMFe(CO)$_3$ are only marginally successful [4] and attempts to generate a carbocation at a position adjacent to I, lead to the formation of (cross-conjugated pentadienyl)iron tricarbonyl cations, III [5,6]. These cross-conjugated metal-stabilized cations have been employed in a variety of organic syntheses [7,8].



II III

It has been suggested [9] that the diminished reactivity of I in Friedel–Crafts reactions may result because it is too electron poor. On the basis of photoelectron [10] and ESCA data [11] it has been shown that 1,3-butadiene, cyclobutadiene, and trimethylenemethane possess very similar ligand donor-acceptor properties. However, it has been observed that the iron tricarbonyl complexes of 1,3-butadiene and cyclobutadiene undergo electrophilic substitution reactions readily. Therefore, in an attempt to explore the electronic character of I as a substitutent, we have examined its effect on the acidity of benzoic acids, as well as its effects on the ^{19}F chemical shift in fluorobenzenes and the ^{13}C chemical shifts of carbon atoms in benzene.

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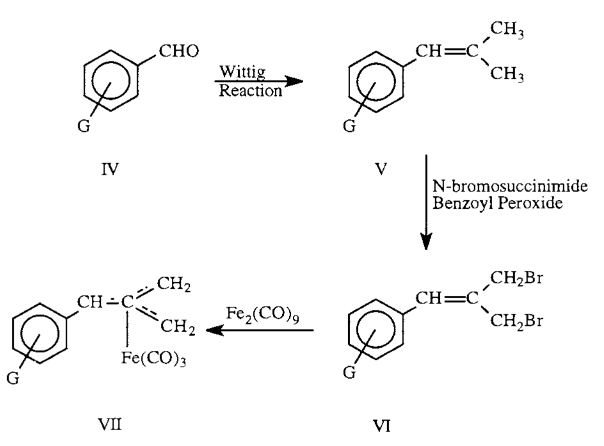


a = H
b = m-F
c = p-F
d = m-CO_2CH_3
e = p-CO_2CH_3

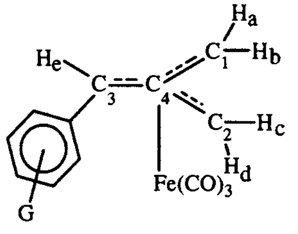
Scheme 1. Pathway for synthesis of substituted aryl trimethylenemethaneiron tricarbonyl complexes. a, H; b, m-F; c, p-F; d, m-CO_2CH_3; e, p-CO_2CH_3.

2. Results and discussion

The compounds required for this study were prepared by a modification of the procedure Ehrlich and Emerson employed to synthesize phenyltrimethylenemethaneiron tricarbonyl [4]. Overall yields for this three-step process (Scheme 1) range from 20–35%. Alkaline hydrolysis of the esters (VIId, e) produces the corresponding benzoic acids (VIIf, g). Proton (Table 1) and carbon NMR (Table 2) chemical shifts are similar for all of these compounds.

The electronic character of organometallic systems is often probed by measuring their ability to stabilize adjacent carbocations. This technique depends on establishing an equilibrium between an alcohol and its related carbocation in acidic solutions. Since the TMM-$Fe(CO)_3$-substituted alcohols rearrange to cross-conjugated pentadienyl cations in acid solution [5], we have been unable to utilize this approach. However, a number of important relationships between substituent groups and chemical properties have been established. The Hammett equation is one of the most widely applied of these relationships. When pK_a values for

Table 1
Proton chemical shifts in substituted trimethylenemethaneiron tricarbonyl complexes ($CDCl_3$ solvent)



Compound	Substituent	H_a [a]	H_b [c]	H_c [b]	H_d [a]	H_e [b]	Aryl
VIIa	H	1.90	1.92	2.37	2.91	4.22	7.1–7.4
VIIb	m-F	1.83	1.82	2.27	2.80	4.12	6.7–7.2
VIIc	p-F	1.89	1.91	2.36	2.83	4.28	6.8–7.3
VIIf	m-COOH	1.90	1.88	2.33	2.82	4.21	7.3–7.9
VIIg	p-COOH	1.91	1.88	2.31	2.82	4.18	7.2–7.9

[a] Doublet, $J_{ad} = 4.2$–4.5 Hz.
[b] Doublet, $J_{ce} = 2.1$–2.5 Hz.
[c] Singlet.

Table 2
Carbon chemical shifts in substituted trimethylenemethaneiron tricarbonyl complexes

Compound	Substituent	C_1	C_2	C_3	C_4	Aryl	Metal–CO	COOH
VIIa [a]	H	51.5	54.8	79.1	103.2	126.8, 128.5, 129.5, 139.0	212.2, 211.7, 210.0	–
VIIb [a]	m-F	51.7	54.7	77.2	103.3	113.7, 115.9, 125.1, 129.9, 130.1, 141.7	211.7, 211.3, 210.0	–
VIIc [a]	p-F	51.5	54.6	77.9	103.3	115.2, 115.5, 131.0, 134.5	211.9, 211.5, 210.0	–
VIIf [b]	m-COOH	52.7	55.3	78.8	104.2	128.5, 129.4, 130.8, 131.7, 134.3, 140.4	212.6, 212.4, 211.1	167.7
VIIg [b]	p-COOH	52.6	55.2	78.2	103.9	129.3, 129.5, 130.3, 145.2	212.2, 212.1, 210.7	167.4

[a] $CDCl_3$ solution.
[b] d_6-Acetone solution.

Table 3
Acidity constants in 50% aqueous ethanol

Compound	pK_a values
p-Nitrobenzoic acid	4.40
p-Chlorobenzoic acid	5.12
VIIf	5.47
VIIg	5.52
p-Methylbenzoic acid	5.77
p-Methoxybenzoic acid	5.89

Table 4
Comparison of substitutent constant values [16]

Substituent	σ_{meta}	σ_{para}	σ_I	$\sigma_{R°}$
TMMFe(CO)$_3$	0.03	−0.01	0.12	−0.13
Phenyl	0.06	−0.01	0.10	−0.11

meta- and *para*-substituted benzoic acids (measured in water) are plotted versus Hammett substituent constants (σ_{meta}, σ_{para}), linear graphs are obtained. [12]. Since the TMMFe(CO)$_3$-substituted benzoic acids are water insoluble, the titrimetric determination of pK_a was conducted in 50% aqueous ethanol solution. Acidity constants (i.e. pK_a) for several substituted benzoic acids, as well as VIIf, g, were determined in 50% aqueous ethanol (Table 3) and plotted versus Hammett substituent values. From this standard graph, the following σ values were obtained for the TMMFe(CO)$_3$ substituent: $\sigma_{meta} = 0.03$, $\sigma_{para} = -0.01$. The σ_{meta} constants are considered to be measures of the inductive effect of a group; whereas, σ_{para} values are combinations of inductive and resonance effects. Therefore, this data indicates that the TMMFe(CO)$_3$ group is slightly electron withdrawing by induction.

Another constant, σ_I, has been proposed by Taft [13] as a measure of the polar (i.e. inductive) effect of a substituent. It has been shown that fluorine NMR shielding parameters for *meta*-substituted fluorobenzenes can be correlated with σ_I [14]. Thus the ^{19}F chemical shift of the m-fluorophenylTMMFe(CO)$_3$ complex was determined in both CDCl$_3$ and d$_6$-benzene solutions. In order to determine the fluorine chemical shift difference between fluorobenzene and m-fluorophenylTMMFe(CO)$_3$ a spectrum was obtained of a dilute solution of a mixture of VIIb and fluorobenzene in CDCl$_3$. The difference was small (0.33 ppm) with the signal of VIIb being further upfield from the internal standard (CFCl$_3$). Using Taft's equations, the σ_I value of the TMMFe(CO)$_3$ group is calculated to be $+0.12$. This supports the earlier conclusion that the TMMFe(CO)$_3$ group is weakly electron withdrawing by induction.

Resonance effects, measured by the constant $\sigma_{R°}$, can also be calculated from the fluorine spectra; however, an improved method [15] has been developed based on ^{13}C-NMR analysis of the *para*-carbon chemical shifts of monosubstituted benzenes. Analysis of the ^{13}C-spectrum of phenylTMMFe(CO)$_3$ in CDCl$_3$ solution provides a chemical shift of 126.83 ppm for the *para*-carbon atom of the complex compared to 128.39 ppm for the carbon atoms in benzene. Using this method, a $\sigma_{R°}$ value of -0.13 is calculated for the TMMFe(CO)$_3$ substituent; therefore, TMMFe(CO)$_3$ is shown to be weakly electron releasing by resonance.

An examination of various tables of constants reveals that the TMMFe(CO)$_3$ group most closely approximates the behavior of a phenyl substituent group in a variety of chemical reactions. A comparison is shown in Table 4. These results do not explain the observed sluggish behavior of TMMFe(CO)$_3$ complexes in electrophilic aromatic substitution reactions. Instead they suggest that the reaction intermediates may be too unstable for the reaction to proceed normally.

3. Experimental

3.1. Analytical services

NMR spectra were obtained on Varian Gemini 200 MHz and Unity 300 MHz FT-NMR instruments utilizing either CDCl$_3$, d_6-acetone, or d_6-benzene as solvents. Tetramethylsilane (TMS) was employed as an internal standard for the proton and carbon spectra while CFCl$_3$ was used as the standard for the fluorine spectra. The IR spectra were obtained on a Perkin–Elmer 1600 FT-IR. Elemental analyses were performed by Chemalytics, Inc., Tempe, Arizona. Pertinent analytical and infrared spectral data for all new compounds are included in Table 5.

3.2. Chemicals

The *m*- and *p*-carbomethoxybenzaldehydes were synthesized according to literature procedures [17]. All other reagents were purchased from Aldrich Chemical Company and used as received.

3.3. pK_a measurements

All pK_a measurements were conducted in 50% (by weight) aqueous ethanol solutions by titrimetric methods at 20 ± 1°C. Standardization was accomplished by the use of an aqueous ethanol buffer [18]. During the titration, equal weights of dilute base and ethanol were added to maintain the percent composition of the solution. The pH values thus obtained were used to calculate the pK_a values by the method of Albert and Serjeant [19].

3.4. Synthesis of the substituted trimethylenemethaneiron tricarbonyl compounds

3.4.1. Phenyltrimethylenemethaneiron tricarbonyl (VIIa)

This compound was prepared as described by Emerson [4].

3.4.2. Preparation of (3-Fluorophenyl)trimethylenemethaneiron Tricarbonyl (VIIb)

A dry 250 ml three-necked flask was equipped with a stir bar and a condenser fitted with a nitrogen inlet/outlet tube. After the flask was flushed with nitrogen gas for 10 min, isopropyl triphenylphosphonium iodide (10.38 g, 0.024 mol) and 60 ml of anhydrous ethyl ether were added and the necks sealed with a glass stopper and a rubber septum. Fifteen milliliters of a 1.6 M solution of butyllithium in hexanes (0.024 mol) were added by syringe over a 1 h period, and the mixture was allowed to stir at room temperature for 4 h. A solution of 2.23 g (0.018 mol) of 3-fluorobenzaldehyde in 10 ml anhydrous tetrahydrofuran (THF) was added over a period of 1 h, and the mixture stirred at room temperature overnight. The mixture was filtered through a celite pad, and the pad was washed with 50 ml of petroleum ether. The filtrate was washed with water and dried over magnesium sulfate. After removal of the solvent, 2.18 g (81%) of the crude product remained as a yellow oil which was purified by distillation, bp 76–80°C, 28 mm Hg.

In a 250 ml round-bottom flask was placed 1.11 g (0.0074 mol) of the purified alkene (from above), 2.90 g (0.016 mol) *N*-bromosuccinimide and 30 ml of CCl_4. Nitrogen gas was bubbled through the solution for 15 min, 0.25 g of dibenzoyl peroxide was added and the flask was fitted with a condenser topped with a N_2 inlet/outlet tube. The mixture was refluxed for 4.5 h. After cooling to room temperature, the succinimide was removed by filtration and the solvent removed under reduced pressure to yield the crude dibromo compound as a yellow oil (2.19 g). The oil was dissolved in 100 ml hexanes and transferred to a 250 ml round-bottom flask where N_2 gas was bubbled through the solution for 10 min. Diiron nonacarbonyl (5.11 g, 0.014 mol) was added, and the solution was allowed to stir at room temperature for two days. At the end of this time, the mixture was filtered through a celite pad. After the solvent was removed, the product was purified by elution from an alumina column with a 25% ethyl ether/75% hexanes solution. The product was obtained as a pale yellow solid (1.19 g, 58% — based on amount of alkene used), mp 39–41°C. Fluorine-NMR chemical shifts for VIIb were measured as -113.18 ppm (d_6-benzene solvent) and -113.79 ppm ($CDCl_3$ solvent) utilizing $CFCl_3$ as the internal standard.

The *para*-fluoro compound (VIIc) was prepared by the same pathway. Fluorine-NMR chemical shifts were measured as -114.95 ppm (d_6-benzene solvent) and -115.55 ppm ($CDCl_3$ solvent) utilizing $CFCl_3$ as the internal standard.

The syntheses of the other compounds were virtually identical except that the crude dibromo derivatives of the 1-(carbomethoxyphenyl)-2-methylpropenes were reacted with diiron noncarbonyl in benzene solution instead of hexanes.

3.4.3. Preparation of (3-carboxyphenyl)-trimethylenemethaneiron tricarbonyl (VIIf)

In a 100 ml round-bottom flask was placed 30 ml methanol which was purged with N_2 gas for 10 min. To the stirred methanol was added 0.88 g (2.7 mmol) of (3-carbomethoxyphenyl)trimethylenemethaneiron tricarbonyl, 0.56 g (9.3 mmol) of potassium hydroxide and 0.8 ml water. The mixture was stirred for two days at room temperature under a N_2 atmosphere. At the end of this period, the mixture was poured into water and extracted with diethyl ether. The aqueous solution was acidified with concentrated hydrochloric acid; whereupon a precipitate formed. The product was isolated by filtration, washed with water and dried under vacuum to yield 0.74 g (88%) of the desired product as a pale yellow solid, mp 172–174°C. The *para*-substituted benzoic acid (VIIg) was obtained in a similar manner.

Table 5
Physical properties and IR spectral data

Compound	Substituent	mp (°C)	Analysis, found (calcd.) (%)		IR metal carbonyl (cm^{-1})
			C	H	
VIIb	*m*-F	39–41	54.40 (54.21)	3.12 (3.15)	2039, 1990 [a]
VIIc	*p*-F	58–60	54.46 (54.21)	3.08 (3.15)	2037, 1989 [a]
VIIf	*m*-COOH	172–174	53.37 (53.54)	3.07 (3.21)	2060, 2002, 1972 [b]
VIIg	*p*-COOH	207–209	53.70 (53.54)	3.29 (3.21)	2068, 2002, 1980 [b]

[a] CS_2 solution.

[b] Nujol mull.

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