Substituent Effects in the Tricarbonylcyclobutadieneiron System

By **Paul L. Pruitt, Edward R. Biehl,** and **Perry C. Reeves,*** Department of Chemistry, Southern Methodist University, Dallas, Texas 75275, U.S.A.

Proton n.m.r. spectra of twenty-one substituted tricarbonylcyclobutadieneiron complexes in deuteriochloroform reveal that a substituent modifies electron density at the ring positions adjacent to it in much the same fashion as a substituent in the benzene system. A substituent has a significant influence on electron density at the carbon atom directly across the ring.

THERE has been considerable interest in the study of substituent effects in organometallic systems.[1] Attention has been focused primarily on the ferrocene, benzenetricarbonylchromium, and tricarbonylcyclopentadienylmanganese systems. Since each displays aromatic properties similar to those of benzene, the effect of a substituent on electron density at various ring positions has been examined in order that comparisons of substituent effects with those in purely organic aromatic compounds can be made. The major techniques applied to this study have been measurements of chemical reactivities (such as relative site reactivities and deuterium exchange rates) and spectroscopy (n.m.r., u.v., and i.r.). Fitzpatrick [2] found that in the Friedel–Crafts acetylation of tricarbonylmethylcyclobutadieneiron, 2-acetyl-1-methyl- and 3-acetyl-1-methylcyclobutadienetricarbonyliron were produced in the ratio 1 : 2. This corresponds to a relative site reactivity of 1 : 4 for C-2 and -4 as opposed to C-3. Relative site reactivities of 1 : 4 for the isopropyl complex,[3] 1 : 5 for the ethyl complex,[4] and 1 : 10 for the t-butyl complex [3] have also been reported. Because of problems in synthesising other substrates, this technique has been applied successfully only in cases where the substituent is an alkyl group. By use of the isotopic exchange technique Broussard [5] found that tricarbonylmethoxycyclobutadieneiron reacted with trifluoroacetic [^{2}H]acid to incorporate deuterium exclusively at the 3-position. Under identical conditions all ring protons of tricarbonylcyclobutadieneiron were exchanged. No detailed study of substituent effects in this system has been reported.

^{1}H N.m.r. chemical shifts can be partially correlated with electron densities at the adjacent carbon atoms, and have been used in the present study. Even though the anisotropy of neighbouring groups may complicate the observations, the method can be applied satisfactorily in the presence of many types of group.

RESULTS

Many substituted tricarbonylcyclobutadieneiron complexes have been prepared and their ^{1}H n.m.r. spectra recorded in the literature. Unfortunately, many different concentrations and solvents were used, making direct comparisons uninformative. In this study all spectra were determined for 10% (w/w) solutions in [^{2}H]chloroform (see Table). In all cases the ring protons appeared as two sharp singlets in integral ratio 2 : 1. H-2 and -4 are always equivalent and $J_{2,3}$ is zero. Almost all the substituents, especially those containing a carbonyl group, cause deshielding of the ring protons relative to the unsubstituted complex. Of all substituents studied, only the methoxy and amino groups cause considerable shielding of the ring protons and, in both cases, maximum shielding occurs at H-3.

In attempting to understand the manner in which substituents affect the chemical shifts of H-2 and -4 correlations were attempted with several substituent constants derived from Hammett and modified-Hammett linear free energy equations. Tolerable correlations were obtained with Traynham's [6] Hammett-like constant, σ_0^-, and with Schaefer's Q constants [7,8] (Figures 1 and 2), but not with other σ constants. These results

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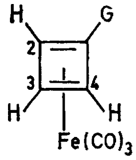
suggest that substituents influence changes in electron density at the adjacent position of the tricarbonylcyclobutadieneiron system in much the same manner as in other aromatic systems. No similar correlation was found for the chemical shifts of H-3; thus factors other than inductive and resonance effects must be operating to influence the electron density at C-3. One possible explanation involves 1,3-interactions through space. Studies of tricarbonylcyclobutadieneiron [9] and its methyl derivatives [10] reveal that a long-range coupling of *ca.* 9 Hz exists between one ring proton and a proton directly opposite on the ring, whereas coupling is too small to be observed or zero between protons on adjacent carbon atoms. This may be rationalized in terms of overlap of the small orbital lobes across the centre of the ring as has been postulated for similar long-range coupling (W effect) in other systems.[11-13]

Chemical shifts of ring protons of monosubstituted tricarbonylcyclobutadieneiron derivatives



Class	Substituent (G)	τ Values ($CDCl_3$) H-2, -4	H-3	Ref.[a]
Alkyl/ alkenyl	H	6.09 (0.0) [b]	6.09 (0.0)	3
	Me	6.07 (−0.02)	6.20 (+0.11)	2
	Et	6.03 (−0.06)	6.06 (−0.03)	
	Pr^i	6.05 (−0.04)	5.97 (−0.12)	3
	$CMe{:}CH_2$	5.78 (−0.31)	5.93 (−0.16)	3
Acyl	CHO	5.35 (−0.74)	5.50 (−0.59)	2
	Ac	5.44 (−0.65)	5.57 (−0.52)	14
	Bz	5.42 (−0.67)	5.62 (−0.47)	14
Carboxylic	CO_2H	5.45 (−0.64)	5.65 (−0.44)	15
	CO_2Me_3	5.54 (−0.55)	5.78 (−0.31)	
	$CO{\cdot}NH_2$	5.32 (−0.77)	5.52 (−0.57)	
	CN	5.50 (−0.59)	5.73 (−0.36)	
Alcohols	$CH_2{\cdot}OH$	5.90 (−0.19)	6.03 (−0.06)	2
	$-CHMe{\cdot}OH$	6.01 (−0.08)	5.95 (−0.14)	2
	$-CHPh{\cdot}OH$	5.95 (−0.14)	5.85 (−0.24)	14
Other	CH_2Cl	5.84 (−0.25)	6.10 (+0.01)	2
	I	5.76 (−0.33)	5.61 (−0.48)	16
	Br	5.82 (−0.27)	5.87 (−0.22)	17
	Ph	5.64 (−0.45)	5.72 (−0.37)	5
	OMe_3	6.19 (+0.10)	6.65 (+0.56)	5
	NH_2	6.33 (+0.24)	6.50 (+0.41)	16
	HgCl	6.07 (−0.02)	5.60 (−0.49)	2

[a] To preparation. [b] Values in parentheses are chemical shift differences from the unsubstituted complex; a negative value indicates deshielding relative to the reference.

In summary, the effect of the substituent in modifying electron density at the adjacent position of the tricarbonylcyclobutadieneiron system parallels, to a first approximation, the substituent effect in the benzene system. In addition, it appears that this system may be useful for the study of ' non-bonded ' 1,3-interactions.

EXPERIMENTAL

N.m.r. spectra were measured with a Perkin-Elmer R12B spectrometer, with tetramethylsilane as internal standard and $CDCl_3$ as solvent; all solutions were 10% (w/w). In one case (carboxamide), [$^2H_6$]acetone was used as solvent.

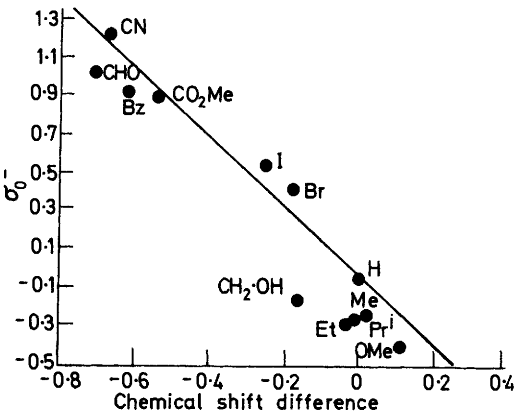


FIGURE 1 Plot of σ_0^- values *vs.* chemical shift differences

Many of the compounds were prepared according to literature procedures [2,3,14-17] (see Table); however, alternative syntheses were developed for the compounds specified. Elemental analyses were performed by Chemalytics, Inc., Tempe, Arizona.

Tricarbonyl(cyclobutadienecarboxamide)iron.—Tricarbonyl(cyclobutadienecarboxylic acid)iron (0.31 g, 1.3 mmol) was dissolved in anhydrous benzene (25 ml). Oxalyl chloride (4 ml) was added dropwise over 10 min under nitrogen. After the initial evolution of gas had subsided, the solution was refluxed for 1.5 h. The benzene was then removed *in vacuo* and the resultant red oil dissolved in ether (50 ml) which had been saturated with ammonia. Ammonia was bubbled through the solution for 10 min. Evaporation left a yellow crystalline solid (0.25 g, 67%). A *sample* repeatedly recrystallized from chloroform had m.p. 123—

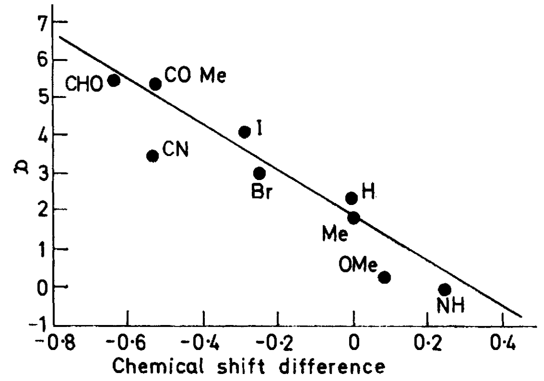


FIGURE 2 Plot of Q values *vs.* chemical shift differences

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124° (Found: C, 40.5; H, 2.15. $C_8H_5FeNO_4$ requires C, 40.8; H, 2.1%).

Tricarbonyl(methyl cyclobutadienecarboxylate)iron.—To the acid chloride (0.17 g, 0.7 mmol) of the corresponding carboxylic acid (from the acid and oxalyl chloride in benzene) was added anhydrous methanol (20 ml). The mixture was refluxed for 2 h and poured into water (250 ml). The mixture was extracted with ether and the extracts washed (5% $NaHCO_3$), dried ($MgSO_4$), and concentrated to yield the methyl ester (0.12 g, 75%), with properties identical with those reported.[18]

Tricarbonyl(cyclobutadienecarbonitrile)iron.—Tricarbonyl-(cyclobutadienecarbaldehyde)iron (1.2 g, 5.4 mmol), hydroxylamine hydrochloride (3.5 g, 50 mmol), and sodium acetate (7.3 g, 90 mmol) were dissolved in 80% ethanol. The solution was refluxed for 0.5 h and then poured into water. The yellow precipitate was extracted with ether. The extracts were treated with charcoal, dried ($MgSO_4$), filtered, and concentrated, leaving the crude oxime (0.9 g). This was dissolved in acetic anhydride (10 ml) and the solution refluxed for 0.5 h in nitrogen, poured into water, and extracted with chloroform. The extracts were washed with several portions of aqueous 5% sodium hydroxide. Concentration of the chloroform layer yielded a brown solid which was chromatographed on alumina with ether as eluant. A yellow liquid (0.4 g, 34%) was obtained which solidified on cooling. The purified compound had a m.p. 36° (lit.,[5] 39°).

Tricarbonyl(ethylcyclobutadiene)iron.—To a stirred slurry of lithium aluminium hydride (0.25 g, 6.6 mol), anhydrous aluminium chloride (0.75 g, 5.6 mmol), and anhydrous ether (25 ml) was added a solution of (acetylcyclobutadiene)tricarbonyliron (0.41 g, 1.7 mmol) in anhydrous ether (20 ml). Stirring was continued for 15 min and water (20 ml) was added to hydrolyse the unchanged reagents. The organic phase was separated, washed (5% $NaHCO_3$), dried ($MgSO_4$), and concentrated. The resultant orange oil was chromatographed over an alumina column (pentane) to yield a pale yellow oil (0.21 g, 60%), b.p. 58—60° at 2.5 mmHg, identical with that obtained [4] *via* a different route.

We thank the Robert A. Welch Foundation for financial support.

[6/1760 *Received, 17th September,* 1976]

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