A Correlaton between Infrared Stretching Frequencies and Carbon-13 Chemical Shifts for Some π-Cyclopentadienyliron Carbonyls

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Abstract: Carbon-13 nmr spectra of 18 monomeric derivatives of the π-cyclopentadienyliron dicarbonyl dimer have been determined. Each compound of general formula π-CpFe(CO)$_2$X exhibits one carbonyl and one cyclopentadienyl resonance. Carbonyl chemical shift parameters are observed to be linearly dependent on the Taft σ_I values of the X substituent and on measured carbonyl stretching frequencies. These relationships are satisfactorily explained by considering variation in δ_{CO} to be principally determined by changes in the paramagnetic screening term.

Recently, ^{1}H, ^{13}C, and ^{31}P chemical shifts have been measured to investigate structure and bonding in organometallic compounds.[1-3] One proton magnetic resonance (pmr) study obtained and compared chemical shift data of alkyl-substituted π-cyclopentadienyl (π-Cp) carbonyls with those of alkyl halides.[4] Other workers noted a relationship between aromatic pmr shifts and metal carbonyl infrared (ν_{CO}) frequencies for compounds of general formula π-Cp-Fe(CO)$_2$X.[5] The objective of these two studies was to examine the relative σ, π character of metal–carbonyl bonds. Carbon-13 nuclear magnetic resonance (cmr) would seem to be a more direct method with which to investigate this problem.

The only cmr study of cyclopentadienyl and carbonyl derivatives thus far reported attempts solely to relate ^{13}C and ^{1}H cyclopentadienyl shifts for a series of derivatives of different transition metals, though some carbonyl chemical shifts were detected.[6] We wish to present evidence that iron-bonded CO screening constants can be correlated with metal–carbon–oxygen π bonding for π-C$_5$H$_5$Fe(CO)$_2$X compounds. This study reports carbon and proton nmr measurements of 18 derivatives for which substituents, X, were chosen either to have widely varying σ_I and σ_R parameters or to have elements of varying electronegativities bonded to iron.

Carbonyl stretching frequencies, force constants, and bond intensities have been described as being related to either the σ or π character of the metal carbonyl bond or to both.[7-13] Nesmeyanov,[14] *et al.*, found that for π-CpFe(CO)$_2$X a linear relation exists between Hammett σ parameters and carbonyl stretching frequencies for molecules with an iron–carbon Fe–X bond. It was inferred that only the σ_I electron-withdrawing character of the X ligand influenced variation in the CO force constant. Our carbonyl chemical shift studies of molecules with metal–carbon M–X bonds support this conclusion. However, when X is a group IV element other than carbon, more complex π-bonding effects are observed.

Experimental Section

All cmr spectra were observed on a Brüker Model HFX-90 spectrometer. The proton nmr spectra were measured on a Varian Model A-56/60. TMS served as both a proton and carbon nmr internal standard. The infrared spectra were measured using a Beckman IR-20 spectrometer. No measurable concentration dependences of chemical shifts were detected.

Reagent dichloromethane was distilled under nitrogen from P$_4$O$_{10}$ before use. All solutions were prepared on vacuum line. The concentration of complex was ~0.5 *M*. Samples were degassed twice before sealing into 10-mm sample tubes.

All preparations were carried out under oxygen-free nitrogen. Known methods were used where possible.[15-21] Preparations for new compounds are reported below.

Similar preparative methods were used to synthesize [(CH$_3$)$_3$Ge]-Fe(CO)$_2$(π-C$_5$H$_5$), [(C$_6$H$_5$)$_3$Si]Fe(CO)(π-C$_5$H$_5$), and [(CH$_3$)$_3$Sn]Fe(CO)$_2$(π-C$_5$H$_5$). Sodium dicarbonyl-π-cyclopentadienyliron (2.5 mmol) was prepared from (π-C$_5$H$_5$)$_2$Fe$_2$(CO)$_4$ by reaction with sodium amalgam in 60 ml of tetrahydrofuran (THF) solution. To this was added 2.5 mmol of (CH$_3$)$_3$GeI, (C$_6$H$_5$)$_3$SiCl, or (CH$_3$)$_3$SnCl in 30 ml of THF. The mixture was mechanically stirred for ~24 hr. After evaporation of THF under vacuum, the residue was extracted with two 20-ml portions of CH$_2$Cl$_2$, which was subsequently removed by vacuum distillation. Sublimation of residues yielded the triethylgermyl, *p*-chlorobenzoyl, and triphenylsilyl derivatives. The orange liquid trimethylstannyl compound was purified by vacuum distillation. *Anal.* Calcd for [(CH$_3$)$_3$GeFe(CO)$_2$(π-C$_5$H$_5$)]: C, 40.7; H, 4.8. Found: C, 40.5; H, 4.6. Calcd for [(CH$_3$)$_3$SnFe(CO)$_2$(π-C$_5$H$_5$)]: C, 35.3; H, 4.1. Found: C, 35.0; H, 4.2. Calcd for (C$_6$H$_5$)$_3$SiFe(CO)$_2$(π-C$_5$H$_5$): C, 68.6; H, 4.6. Found: C, 68.9; H, 4.5.

The *p*-ClC$_6$H$_4$Fe(CO)$_2$(π-C$_5$H$_5$) was prepared by photolysis of dicarbonyl-*p*-chlorobenzoyl-π-cyclopentadienyliron. After 5 hr of

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Table I. Carbonyl Stretching Frequencies and Force Constants, Chemical Shift Values for Compounds of General Formula π-$C_5H_5Fe(CO)_2X$, and Taft Inductive (σ_I) Parameters for X Substituents[a]

X	$\delta_{^{13}C}$ CO	$\delta_{^{13}C}$ π-C_5H_5	ν_s	ν_a	k	k_i	$\delta_{^1H}$ π-C_5H_5	σ_I
CN	−211.4	−82.3	2055	2009	16.68	0.377	5.11	0.58
Cl	−213.3	−85.9	2050	2002	16.58	0.393	4.98	0.47
Br	−213.5	−85.9	2045	1999	16.51	0.376	5.05	0.45
I	−213.6	−84.7	2038	1998	16.45	0.326	5.07	0.38
C_6H_5	−214.6	−86.0	2035	1987	16.42	0.334	4.97	
C_6H_5CO	−215.1	−87.1	2018	1968	16.03	0.402	4.88	
CH_3CO	−215.4	−87.1	2015	1963	16.01	0.386	4.75	0.28
p-ClC_6H_4	−216.8	−86.7	2014	1968	16.01	0.370	4.84	
C_6H_5	−217.1	−86.3	2011	1965	15.96	0.369	4.81	0.10
$C_6H_5CH_2$	−217.9	−86.7	2000	1952	15.77	0.383	4.63	0.04
CH_3	−218.3	−85.7	2003	1949	15.77	0.431	4.70	−0.05
CH_3CH_2	−218.6	−86.3	1997	1944	15.68	0.422	4.7	−0.08
$(CH_3)_3Sn$	−215.7	−81.4	1987	1932	15.51	0.435	4.75	
$(C_6H_5)_3Sn$	−215.7	−83.3	1997	1935	15.61	0.49	4.77	
$(CH_3)_3Ge$	−213.2	−87.7	1990	1935	15.56	0.436	4.71	
$(C_6H_5)_3Ge$	−216.3	−84.7	1997	1940	15.65	0.453	4.69	
$(CH_3)_3Si$	−216.5	−84.2	1995	1936	15.60	0.468	4.72	
$(C_6H_5)_3Si$	−216.5	−85.5	1997	1938	15.64	0.469	4.64	

[a] Chemical shifts relative to internal TMS.

irradiation with a 400-W Hg arc, a benzene solution of 5 mmol of starting material was reduced under vacuum to 10-ml volume and chromatographed on alumina using benzene as eluent. The bright yellow fraction was collected and evaporated to dryness and the oily residue dissolved in pentane, from which yellow crystals of product were isolated. *Anal.* Calcd for $ClC_6H_4Fe(CO)_2(\pi$-$C_5H_5)$: C, 54.1; H, 3.1. Found: C, 53.9; H, 2.9.

Results

Carbon-13 and proton chemical shifts of 18 derivatives of the π-cyclopentadienyliron carbonyl dimer with general formula π-$C_5H_5Fe(CO)_2X$ are collected in Table I together with carbonyl infrared stretching frequencies and calculated force constants.

Each compound studied supplies one proton resonance for cyclopentadiene, one nmr signal for the two identical carbonyl groups, and, under conditions of proton decoupling, one cyclopentadienyl cmr resonance. Measured intensities of cyclopentadiene *vs.* carbonyl carbon were well in excess of the simple 5:2 ratio, indicating substantial Overhauser enhancement of the proton-bonded carbon signals.

The infrared spectra in the C–O stretching region are characterized by two intense absorptions corresponding to symmetric and antisymmetric stretching modes. Frequencies recorded in the table were used to calculate approximate force constants by a suitably modified Cotton–Kraihanzel approach.[8] The secular equations used were: $\lambda_2 = \mu(k + k_i)$, $\lambda_2 = \mu(k - k_i)$. Values of k and k_i refer, respectively, to the stretching force constant of the two carbonyls and to the stretch–stretch interaction constant.[5] This infrared study was undertaken specifically to eliminate any possible solvent effect on correlations of nmr and infrared data.

The inductive (σ_I) and resonance (σ_R) reactivity parameters and polarographic reduction potentials given in the table were taken from the literature.

Discussion

Since carbon-13 nmr promises to be a most important tool in organometallic chemistry, it is of interest to discern from our experimental data some of the electronic and molecular parameters important to determining cmr shifts of carbonyls or at least to deduce empirical correlations of chemical shifts with bonding parameters. The familiar[22] picture of bonding in metal carbonyls in which the metal–carbon bond is thought to have both σ and π character serves a a framework within which to discuss our results. A σ bond may be formed by overlap of filled ligand orbitals. Filled metal d orbitals may overlap with empty π-antibonding (π^*CO) carbonyl orbitals. Population of this π^* orbital reduces the CO bond order to between 2 and 3.

It is usual to approximate the total shielding (σ_N) for the carbon-13 nucleus by the sum of a diamagnetic screening (Lamb) terms (σ_d), a term representing anisotropy contributions and other nonlocalized effects(σ'), and a paramagnetic screening constant (δ_p), the latter of which $\sigma_N = \sigma_d + \sigma' + \sigma_p$ is thought to dominate cmr shifts.[23–26] Contributions from diamagnetic screening are small. In the absence of large anisotropic effects, the differential shieldings observed in the present series of carbonyls are dominated by variations of the local paramagnetic screening constant which has been approximated by Pople[24,26,27] as

$$\sigma_p = \frac{e^2h^2}{2m^2c^2(\Delta E)}\langle r_{2p}^{-3}\rangle Q_{AA} + \sum_{B \neq A} Q_{AB}$$

where Q_{AA} and Q_{AB} are terms which, being dependent solely on the bond order and charge density matrix of the ground-state molecule, would reflect changes in the π-bond order for the series of carbonyls under study, r_{2p} is the radius of the carbon 2p orbital, and ΔE is an average excitation energy between the ground state and lowest lying paramagnetic state of the molecule. Variations in screening may be considered qualitatively upon examination of certain trends in the cmr data.[25]

We first discuss carbonyl shifts of molecules with an iron–carbon Fe–X bond. A graph, shown in Figure 1, of the Taft σ_I parameter *vs.* cmr shift of the carbonyl resonances of all complexes with an Fe–X iron–carbon bond is linear. The presence of strongly electron-with-

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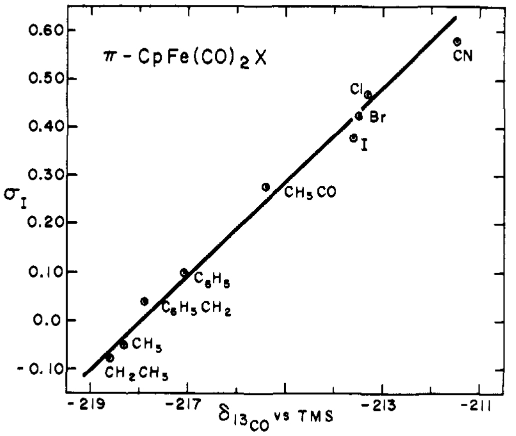

Figure 1. Carbonyl chemical shifts *vs.* Taft inductive (σ_I) parameters.

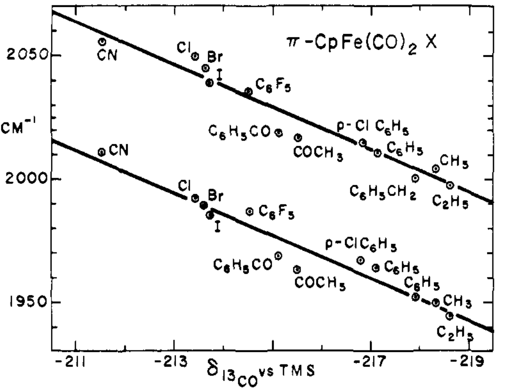

Figure 2. Carbonyl chemical shifts *vs.* carbonyl stretching frequencies.

drawing ligands results in carbonyl resonances being detected at higher magnetic fields, indicating enhanced paramagnetic screening. If only diamagnetic considerations were considered, *deshielding* would result. Additionally, a plot of calculated carbonyl stretching frequencies *vs.* cmr carbonyl shifts is linear (Figure 2), with force constants increasing as ligands bonded to iron become more electronegative. A better correlation is obtained by plotting k_{CO} values.

It appears that upon withdrawal of electrons from iron, d orbitals contract. The effect of this is to reduce overlap between d and the π^*(CO) orbitals. The net result is a stronger CO bond (higher k_{CO}) and an increased paramagnetic screening (greater local carbon π-bond order). Synergistic with this would be a contraction of the carbonyl carbon 2p orbital, which could also contribute to the observed chemical shift.

A further examination of this formulation of bonding is provided by the linear graph cmr carbonyl shifts *vs.* polarographic $E_{1/2}$ values for addition of electrons to a molecule[14] (Figure 3). Clearly, ligands with strong electron-withdrawing characteristics remove electron density from iron, facilitating the reduction reaction. This serves to support the likely expectation that iron d orbitals would be contracted by strongly electron-withdrawing ligands. If one assumes the usual[24–26] approximation of an average energy (ΔE) between ground and paramagnetic excited states on the carbonyl carbon,[29] this leaves variations in M–CO π bonding as being principally responsible for observed variations in carbonyl chemical shifts. We recognize that this formulation has the hidden assumption that no large changes in bond anisotropies are observed, but we do note that our interpretation parallels cmr studies by Maciel of bonding in organic carbonyl compounds.[27] There, variations between CO bond orders of 1–2 were reflected in δ_{CO} values. This study demonstrates the same effect for changes in the bond order range 2–3.

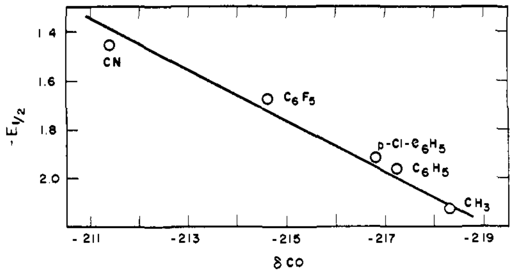

Figure 3. Carbonyl chemical shifts *vs.* reductive half-wave potentials for π-$C_5H_5Fe(CO)_2X$ complexes. $E_{1/2}$ values are from ref 14.

Proton and carbon chemical shifts for cyclopentadienyl ligands are also recorded in Table I. A relatively small variation of chemical shifts is observed. No good correlation between Taft parameters is detected; however, it can be said that the trend of both proton and cmr resonances is to high field with increased electron withdrawal from iron. Only small variations of cmr shifts are reasonable when one considers that their principal iron–carbon bonding is between *filled* orbitals originating on cyclopentadiene and *empty* iron orbitals.[5] σ-Bonded ligands influence most strongly *filled* iron orbitals. The cmr shifts vary little because retrodative bonding from iron to cyclopentadiene is less important.

Recently, King has reported[5] a relationship between π-cyclopentadienyl proton resonances and metal carbonyl infrared stretching frequencies for molecules similar to those studied here. We report that in the present study, this correlation is acceptable, with variations from the linear correlation being less than 0.15 ppm. An attempt to similarly correlate k_{CO} and π-C_5H_5 cmr shifts gives no useful information.

Chemical shifts, carbonyl stretching frequencies, and force constants for molecules with iron to silicon, germanium, or tin bonds are recorded in Table I. Little variation in carbonyl chemical shifts is detected between molecules with methyl and phenyl substituents of the same group IV atom. Similar to the trends observed for similar molecules with iron–carbon Fe–X bonds, the more electronegative Ge substituents give rise to carbonyl chemical shifts downfield from Si or Sn. The availability of d orbitals for retrodative Fe–X bonding differentiates these molecules from those with Fe–C bonds. No clear interpretation of those factors influencing the carbonyl shift seems possible now.

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