^{13}C Nuclear Magnetic Resonance Study of Cyclopentadienyl Iron Acyls

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^{13}C chemical shifts for terminal CO's in transition metal carbonyls and organometallic complexes have been studied by several groups [1]. In particular, Gansow, *et al.* [1a] noted a linear correlation between δ^{13}CO and carbonyl stretching frequencies for a series of compounds $CpFe(CO)_2X$ ($C_p = \eta^5\text{-}C_5H_5$; X = halide, pseudo-halide, alkyl, SiR_3, GeR_3, SnR_3, acetyl and benzoyl). Their interpretation of these interesting results in terms of electronic structures was, however, marred by neglect of a minus sign [1d]. Whereas the average value of the C≡O stretching frequency in this series spans from 60 cm^{-1}, the range of δ^{13}C is only some 7 ppm.

We have now investigated the ^{13}C nmr spectra of a series of compounds $CpFe(CO)(L)C(O)R$ (L = CO, phosphine, phosphite, CH_3NC; R = CH_3, $p\text{-}C_6H_4$-OCH_3). Resonances due both to terminal and to acyl carbonyls were observed. Remarkably, the acyl carbonyl chemical shift shows much greater sensitivity to the nature of L than does the terminal. Over our series δ^{13}C for acyl CO's spans a range of some 25 ppm while for terminal CO's the range is only ~6 ppm. Table I presents pertinent results.

In the absence of large anisotropic shifts, the carbonyl chemical shifts are thought to be dominated by the paramagnetic screening term [2–4] which has been approximated by Pople as

$$\sigma_p = -\frac{e^2h^2}{2m^2c^2}\left(\frac{1}{\Delta E}\right)\langle r^{-3}\rangle_{2p}[Q_{AA} + \sum_{A \neq B} Q_{AB}]$$

where $\langle r^{-3}\rangle_{2p}$ is the expectation value of the reciprocal of the 2p orbital, Q_{AA} and Q_{AB} depend solely on the charge density and bond order matrices, respectively, of the ground state molecule and ΔE is the average excitation energy between ground state and the lowest lying paramagnetic state of the molecule.

We propose that the greatly enhanced sensitivity of acyl carbon chemical shifts to the nature of L is

due to contributions of the $Q_{AB} = Q_{FeC}$ terms to the shielding. These terms would be expected to be small for the cylindrically symmetric iron-terminal carbonyl bond just as Q_{AB} averages to zero in acetylenes [1d]. Because the acyl CO is not in a cylindrically symmetric environment, Q_{Fe-C} is unlikely to average to zero. This feature attests to the importance of resonance structures depicting π bonding between Fe and the acyl carbon. If the effect of replacing CO by more basic L (thus increasing the negative charge on Fe) were merely to diminish the strength of the Fe–C(O)R σ bond, Q_{Fe-C} would be lowered and upfield chemical shifts would be anticipated contrary to observation. Furthermore, we have observed a linear correlation between $(\Delta E)^{-1}$ and chemical shift for both terminal and acyl carbonyl δ^{13}C. ΔE has been taken as the energy of the lowest uv transition involving charge transfer from the metal to the π^* carbonyl molecular orbital (intended to approximate the singlet → triplet excitation energy). Since the π^* state of CO is stabilized by metal pi backbonding, ΔE is expected to decrease as L becomes more electron-donating. This would result in a larger negative value of σ_p and so a lower chemical shift for C as observed. Both Sheline, *et al.* [5] and Braterman, *et al.* [1d] have observed similar correlations. On the other hand, Gansow, *et al.* [1a] assumed ΔE to be constant in their interpretation of results on similar Fe complexes. Our observations cast doubt on the validity of this assumption. Although both terminal and acyl chemical shifts parallel $(\Delta E)^{-1}$, the greatly enhanced sensitively of the acyl chemical shift to L is due to the added contribution of Q_{Fe-C} (which should also parallel ΔE).

That the other terms in the expression for σ_p do not dominate can be seen readily from the following discussion.

Employing the notion that decreasing values of the infrared carbonyl stretching frequency mean increasing pi back donation to the remaining carbonyl [1a], ligand substitution by the less effective pi acids should result in an increase in the electron density on carbonyl carbon atoms with a concomitant decrease in C–O bond order, a decrease in $\langle r^{-3}\rangle_{2p}$ and thus would be predicted to give upfield shifts in disagreement with the downfield shifts that are observed. Likewise, the more negative Q_{CC} accompanying this effect would be expected to result in upfield shifts which are not observed. For many compounds, the Q_{AA} term in thought to remain essentially constant [6].

It is worth inquiring why the sensitivity of δ^{13}C for the acyl carbonyl to L is not correlated with large changes in acyl stretch frequency. Indeed, the variation in the stretching frequency is only about half that for terminal CO over the series. The reason

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TABLE I. Spectral Data for CpFe(CO)(L)C(O)R.

L	CO Stretching Frequency (cm^{-1})		^{13}C Chemical Shifts[a]					Lowest Metal–Ligand Charge Transfer (cm^{-1})
	Terminal	Acyl	CO	O CR	C$_p$	R	L	
R = CH$_3$								
CO	2015, 1936	1655	215.0	253.3	86.7	52.1		30,950
P(OPh)$_3$	1950	1608	217.5	264.5	84.6	52.2	151.9, 129.8 122.7, 125.2	30,350
P(OBu)$_3$	1932	1598	218.1	268.4	84.7	51.4	65.1, 32.9 19.8, 14.6	30,300
CNCH$_3$	1938	1600	218.6	267.5	85.2	51.8	127.3, 30.9	–
PPh$_3$	1920	1595	220.3	274.8	85.5	52.3	137.4, 133.9 128.6, 130.4	29,600
PBu$_3$	1916	1590	220.6	276.8	83.9	52.8	29.1, 28.2 26.4, 14.1	29,500
R = CF$_3$								
CO	2046, 1995	1654	212.1	243.6	86.8	114.6		
PPh$_3$	1946	1626	219.1	262.9	85.7	–		
R = p-C$_6$H$_4$OCH$_3$								
CO	2017, 1958	1608	214.1	250.0	86.4	144.1, 130.0 133.4, 161.7, 55.4		
PPh$_3$	1910	1575	220.7	270.2	85.7	146.6, 129.1 112.8, 160.5, 55.2		

[a]Resonances reported (±0.3 ppm) downfield to internal TMS = 0 ppm in CDCl$_3$.

is most likely the far superior ability of terminal CO's to act as π-acids causing large changes in the iron-terminal CO bond order which are not reflected in $\delta^{13}C$ because of the cylindrical symmetry. On the other hand, relatively modest changes in Q_{Fe-C} for the acyl carbon contribute their full magnitude to the shielding parameter.

The chemical shift of the acyl carbon is somewhat dependent on the nature of R such that $\nu_{C=O}$ decreases in the order $CF_3 > C_6H_4OCH_3 > CH_3$. This is the same order as σ_I effects that Maciel [7] found in his study on the carbonyl shifts of ketones. The fact that the iron acyl carbonyl is not as sensitive to changes in R as are ketones is understandable in view of the increased number of resonance structures that can be written involving the iron center.

Compounds of Mn and Mo are currently under study.

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