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## Fourier Transform Carbon-13 Nuclear Magnetic Resonance Study of Transition Metal Carbonyl Complexes

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A correlation has been observed between the  $^{13}\text{C}$  nmr carbonyl chemical shifts and the carbonyl stretching frequencies for a series of ( $\pi$ -arene)tricarbonylchromium complexes. From the sign of this correlation it is postulated that changes in the carbonyl chemical shift with varying substituents on the arene ring may be explained in terms of changes in the extent of transition metal  $\rightarrow$  carbonyl  $\pi$  back-donation. This hypothesis has been extended to the analysis of  $\pi$  back-donation in  $\text{LCr}(\text{CO})_5$  and  $\text{L}_2\text{Cr}(\text{CO})_4$  derivatives where a linear correlation has been observed between the carbonyl chemical shifts and the metal-carbon bond lengths and to a series of isoelectronic ( $\pi\text{-C}_5\text{H}_5$ ) $\text{M}(\text{CO})_3$  complexes,  $\text{M} = \text{Cr}^-$ ,  $\text{Mn}^0$ , and  $\text{Fe}^+$ .

### Introduction

Although limited during the early rise in popularity of  $^{13}\text{C}$  nmr spectroscopy by their low sensitivity,<sup>1-4</sup> studies of the  $^{13}\text{C}$  nmr spectra of transition metal carbonyl complexes have been revived by the recent advent of Fourier transform pulsed nmr techniques. Gansow, *et al.*, studied the  $^{13}\text{C}$  nmr spectra of  $\text{LW}(\text{CO})_5$  and  $\pi\text{-(C}_5\text{H}_5\text{)Fe}(\text{CO})_2\text{X}^6$  derivatives and found a linear correlation between the carbonyl chemical shifts and the carbonyl stretching force constants. Vergamini and Matwiyoff<sup>7</sup> have reported similar results for a series of rhodium-carbonyl complexes. We have observed an analogous correlation for the carbonyl chemical shifts in pentacarbonylchromium- and pentacarbonylchromium-carbene complexes.<sup>8</sup>

In order to obtain a more complete understanding of the implications of this correlation on studies of the nature of the transition metal-carbonyl bond we have investigated the  $^{13}\text{C}$  nmr spectra of a series of complexes of the general formulas ( $\pi\text{-C}_6\text{H}_5\text{X})\text{Cr}(\text{CO})_3$ ,  $\text{L}_n\text{Cr}(\text{CO})_{6-n}$ , and ( $\pi\text{-C}_5\text{H}_5$ ) $\text{M}(\text{CO})_3$ , where  $\text{M} = \text{Cr}^-$ ,  $\text{Mn}^0$ , and  $\text{Fe}^+$ .

### Experimental Section

**Materials.**  $\text{Cr}(\text{CO})_6$ ,  $\text{NaV}(\text{CO})_6$ ,  $\text{Mn}_2(\text{CO})_{10}$ , and  $[\pi\text{-(C}_5\text{H}_5\text{)Fe}(\text{CO})_2]_2$  were purchased from the Pressure Chemical Co. A sample of (methyl benzoate)tricarbonylchromium was purchased from the Strem Chemical Co. ( $\pi\text{-C}_5\text{H}_5$ ) $\text{Mn}(\text{CO})_3$  was generously provided by the Ethyl Corp.

The synthesis and characterization of the ( $\pi\text{-C}_6\text{H}_5\text{X})\text{Cr}(\text{CO})_3$  complexes have been reported elsewhere.<sup>9</sup>  $\text{LCr}(\text{CO})_5$  and  $\text{L}_2\text{Cr}(\text{CO})_4$  complexes,  $\text{L} = \text{PPh}_3$  and  $\text{P(OPh)}_3$ , were prepared by the method of Wotiz, *et al.*,<sup>10</sup> and characterized *via* a combination of melting points, infrared spectroscopy, and mass spectroscopy.

$(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{PF}_6$  was synthesized by oxidation of  $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$  with  $\text{NOPF}_6$  in acetonitrile solution<sup>11</sup> and characterized

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**Table I.**  $^{13}\text{C}$  Nmr Chemical Shifts of the Carbonyl Resonance in ( $\pi\text{-C}_6\text{H}_5\text{X})\text{Cr}(\text{CO})_3$  Derivatives

X	$\delta^a$	X	$\delta^a$	X	$\delta^a$
$\text{N}(\text{CH}_3)_2$	-235.05	$\text{OCH}_3$	-233.53	Cl	-231.99
$\text{NH}_2$	-234.62	H	-233.34	$\text{CO}_2\text{CH}_3$	-231.23
$\text{CH}_3$	-233.64	F	-232.05		

<sup>a</sup> Chemical shifts were measured in dichloromethane solution relative to the internal  $\text{CH}_2\text{Cl}_2$  solvent resonance and are reported in ppm *downfield* from TMS using the conversion  $\delta_{\text{TMS}} = \delta_{\text{CH}_2\text{Cl}_2} - 53.89 (\pm 0.06)$  ppm.

by microanalytical data and infrared spectroscopy.

$(\pi\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_3\text{Na}$  was prepared *via* the reaction of  $\text{Cr}(\text{CO})_6$  and  $\text{NaC}_5\text{H}_5$  in THF solution<sup>12</sup> and characterized by infrared spectroscopy.

**Instrumentation.**  $^{13}\text{C}$  nmr spectra were obtained in dichloromethane, acetone, chloroform, and tetrahydrofuran solution with a Fourier transform pulsed nmr spectrometer operating at 15.08 MHz as described previously<sup>13</sup> and with a Varian Associates XL-100-FT spectrometer operating at 25.1 MHz. The  $^{13}\text{C}$  nmr chemical shifts were measured relative to the internal solvent resonance and are reported in ppm *downfield* from TMS using the following conversions:  $\delta_{\text{TMS}} = \delta_{\text{CH}_2\text{Cl}_2} - 53.89$  ppm;  $\delta_{\text{TMS}} = \delta_{\text{CHCl}_3} - 77.18$  ppm;  $\delta_{\text{TMS}} = \delta_{\text{THF}[\text{C}(2,5)]} = 68.05$  ppm;  $\delta_{\text{TMS}} = \delta_{(\text{CH}_3)_2\text{CO}} - 30.43$  ppm. All chemical shifts were found to be reproducible to within  $\pm 0.06$  ppm.

### Results

The  $^{13}\text{C}$  nmr spectra of ( $\pi$ -arene)tricarbonylchromium complexes exhibit a low-field carbonyl resonance and a pattern of arene resonances analogous to those of the free arene but displaced approximately 30 ppm upfield.<sup>9</sup> The  $^{13}\text{C}$  nmr chemical shifts of the carbonyl resonances for a series of ( $\pi\text{-C}_6\text{H}_5\text{X})\text{Cr}(\text{CO})_3$  derivatives are given in Table I. These data are the result of at least two independent measurements on each sample with a precision of approximately  $\pm 0.06$  ppm.

The results of an analysis of the  $^{13}\text{C}$  nmr spectra of a series of  $\text{L}_n\text{Cr}(\text{CO})_{6-n}$  complexes are presented in Table II along with a tabulation of the transition metal-ligand bond lengths as determined by X-ray crystallography.<sup>14-17</sup>

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Table II.  $^{13}\text{C}$  Nmr Chemical Shifts and Cr-C and Cr-P Bond Lengths in  $\text{L}_n\text{Cr}(\text{CO})_{6-n}$  Derivatives

Complex	$\delta^a$		Length, Å		
	Trans CO	Cis CO	Cr-C <sup>trans</sup>	Cr-C <sup>cis</sup>	Cr-P
$\text{Cr}(\text{CO})_6$		-211.18		1.909 (3) <sup>b</sup>	
$\text{Ph}_3\text{PCr}(\text{CO})_5$	-221.34	-216.53	1.844 (4)	1.880 (4)	2.422 (1) <sup>c</sup>
$(\text{PhO})_3\text{PCr}(\text{CO})_5$	-217.57	-213.87	1.861 (4)	1.896 (4)	2.309 (1) <sup>c</sup>
<i>trans</i> - $[(\text{PhO})_3\text{P}]_2\text{Cr}(\text{CO})_4$		-216.67		1.878 (6)	2.252 (1) <sup>d</sup>

<sup>a</sup>  $^{13}\text{C}$  nmr chemical shifts of the carbonyl resonance, in ppm, downfield from TMS in chloroform solution. <sup>b</sup> See ref 17. <sup>c</sup> See ref 16. <sup>d</sup> See ref 15.

Table III.  $^{13}\text{C}$  Nmr Chemical Shifts of the Carbonyl Resonance in  $\text{M}(\text{CO})_6$  and  $(\pi\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3$  Derivatives

Complex	$\delta^a$	Solvent	Complex	$\delta^a$	Solvent
$\text{V}(\text{CO})_6^-$	-225.71	THF	$(\pi\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_3^-$	-246.75	THF
$\text{Cr}(\text{CO})_6$	-212.5 <sup>b</sup>	THF	$(\pi\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3$	-225.1 <sup>c</sup>	$\text{CHCl}_3$
$\text{Cr}(\text{CO})_6$	-211.28	$\text{CHCl}_3$	$(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_3^+$	-202.98	$(\text{CH}_3)_2\text{CO}$

<sup>a</sup> Chemical shifts in ppm downfield from TMS,  $\pm 0.06$  ppm. <sup>b</sup> Only marginally soluble in THF. <sup>c</sup> Width at half-height is approximately 20 Hz due to coupling with the quadrupolar  $^{55}\text{Mn}$  nucleus;  $I = 5/2$ .

The  $^{13}\text{C}$  nmr chemical shifts of a series of  $\text{M}(\text{CO})_6$  and  $(\pi\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3$  complexes are presented in Table III. The spectrum of  $\text{V}(\text{CO})_6^-$  exhibits an eight-line pattern due to coupling with the  $^{51}\text{V}$  nucleus,  $^1J_{^{51}\text{V}^{13}\text{C}} = 116$  Hz, as reported by Lauterbur and King<sup>3</sup> from a study of the  $^{51}\text{V}$  nmr of this complex.

## Discussion

Numerous authors have attempted to use infrared spectroscopy to interpret the nature of the transition metal-carbonyl bond. Cotton and Kraihanzel<sup>18</sup> established a simple model for the calculation of force constants from carbonyl stretching frequencies by assuming that a carbonyl factored force field could be solved, neglecting all other stretching modes, to yield meaningful force constants. Although this approximation has been criticized,<sup>19-21</sup> it has been shown to yield good relative force constants for a series of closely related derivatives.<sup>20-22</sup>

Cotton<sup>18,23</sup> originally proposed that changes in the magnitude of the force constants were directly proportional to changes in the extent of metal-to-carbon  $\pi$  donation. Darensbourg and Brown<sup>24,25</sup> have subsequently shown that changes in the  $\sigma$ -donor ability of the carbonyl may also lead to changes in the magnitude of the force constants. Graham<sup>26</sup> and Brown and Dobson<sup>27</sup> have attempted to isolate the relative contributions from  $\sigma$  and  $\pi$  effects using differing approximations. Darensbourg and Darensbourg<sup>28</sup> have recently concluded that while a separation of  $\sigma$  and  $\pi$  effects is contentious, *the magnitude of the stretching force constant is directly proportional to the positive character of the carbonyl carbon*. Their conclusion rests upon two distinct lines of argument. First, Brown and Darensbourg<sup>24</sup> had previously shown that the carbonyl force constant increases with an increase in the carbonyl  $\sigma$ -donor ability. This postulate has been substantiated by a series

of molecular orbital calculations by Fenske and coworkers<sup>29-31</sup> in which the carbonyl  $5\sigma$  orbital involved in dative bonding to the transition metal is shown to have a negative overlap population such that donation of electron density from this orbital strengthens the C-O  $\sigma$  bond. Second, as the extent of transition metal  $\rightarrow$  carbonyl  $\pi$  back-donation decreases, the electron density placed into the carbonyl  $\pi^*$  orbital also decreases. Since this molecular orbital is predominantly carbon in character, this leads to a decrease in the electron density on the carbon atom with a concomitant increase in the C-O bond strength.

The conclusions of the Darensbourgs are consistent with several experimental observations: (1) within a given complex, RLi reagents attack at the carbonyl with the largest force constant,<sup>28</sup> (2) when the force constant is less than approximately 15.3 mdyn/Å, RLi reagents will not attack the carbonyl,<sup>28</sup> and (3) the relative rates of attack by  $\text{CH}_3\text{Li}$  on  $\text{LW}(\text{CO})_5$  derivatives increase with increasing force constants.<sup>32</sup> If this postulate is correct and the  $^{13}\text{C}$  nmr carbonyl chemical shifts are dominated by a dependence upon electron density at the carbonyl carbon, one would observe a net deshielding of the carbonyl resonance with increasing stretching force constants within a series of closely related derivatives.

Figure 1 shows a plot of the  $^{13}\text{C}$  nmr chemical shifts for the carbonyl resonances of a series of  $(\pi\text{-C}_5\text{H}_5\text{X})\text{Cr}(\text{CO})_3$  complexes vs. the infrared stretching frequencies for the two carbonyl modes.<sup>33,34</sup> There is indeed a linear correlation between the carbonyl chemical shifts and the infrared stretching frequencies, but the sign of this correlation is the opposite of what was to be expected on the basis of the arguments presented above. For these complexes, and for all others studied to date, the carbonyl resonances are shielded with an increase in the carbonyl stretching force constants.

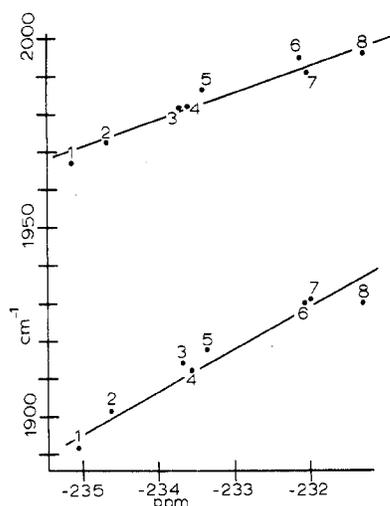
## Theory of $^{13}\text{C}$ Nmr Chemical Shifts

The  $^{13}\text{C}$  nmr screening tensor for nucleus A can be divided into five contributing terms<sup>35-39</sup>

$$\sigma^A = \sigma_d^A + \sigma_p^A + \sum_{B \neq A} \sigma^{AB} + \sigma^{\text{ring}} + \sigma^{\text{ED}} \quad (1)$$

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**Figure 1.** Plot of the  $^{13}\text{C}$  nmr chemical shifts in ppm for the carbonyl resonances in  $(\pi\text{-C}_6\text{H}_5\text{X})\text{Cr}(\text{CO})_3$  derivatives vs. the infrared stretching frequencies for the two carbonyl modes (correlation coefficients 96.4 and 97.6%). X: 1,  $\text{N}(\text{CH}_3)_2$ ; 2,  $\text{NH}_2$ ; 3,  $\text{CH}_3$ ; 4,  $\text{OCH}_3$ ; 5, H; 6, F; 7, Cl; 8,  $\text{CO}_2\text{CH}_3$ . Increasingly negative values of the chemical shift imply carbonyl resonances which are increasingly deshielded relative to TMS.

where  $\sigma_d$  represents the contribution from diamagnetic electron currents on atom A,<sup>40</sup>  $\sigma_p$  is a paramagnetic term arising from the field-induced mixing of ground and excited electronic states,  $\Sigma\sigma^{AB}$  is the contribution from the anisotropy in the diamagnetic susceptibilities of neighboring atoms,<sup>41,42</sup>  $\sigma^{\text{ring}}$  arises from electronic currents which cannot be localized on an individual atom, and  $\sigma^{\text{ED}}$  is the contribution due to the electric field at atom A arising from polar substituents on the molecular framework.<sup>43</sup>

For the  $(\pi\text{-C}_6\text{H}_5\text{X})\text{Cr}(\text{CO})_3$  derivatives studied herein where we are interested in the carbonyl chemical shifts relative to the carbonyl resonances in the  $(\pi\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$  complex, rather than the absolute magnitude of the chemical shift, this equation can be greatly simplified. The contribution due to molecular ring currents, while of importance in determining the  $^{13}\text{C}$  nmr chemical shifts of the arene resonances,<sup>9,44,45</sup> will be negligible at the carbonyls. The excellent correlation of the carbonyl resonance chemical shifts with substituent constants such as those of Swain and Lupton<sup>9,46</sup> obviates the  $\sigma^{\text{ED}}$  term which could be operant in only a few of these derivatives. The contribution to the chemical shift from neighboring anisotropy can be neglected since its magnitude is proportional solely to the magnitude of the anisotropy in the diamagnetic susceptibilities and the geometry of the molecule, neither of which will be variant at the carbonyl.

Of the two remaining terms in the chemical shift screen-

ing tensor, the  $\sigma_p$  term has been assumed to be dominant for  $^{13}\text{C}$  nmr.<sup>37</sup> While this assumption has been questioned by Mason,<sup>47</sup> we can see from the expression for the diamagnetic screening tensor<sup>40</sup>

$$\sigma_d = (e^2/3mc^2)\Sigma\langle r_i^{-1} \rangle \quad (2)$$

where  $\langle r^{-1} \rangle$  is the mean inverse distance of electron  $i$  from the nucleus and the summation is over all electrons on the atom, that if this term made a significant contribution to the chemical shift, an increase in the carbonyl stretching force constant would lead to a deshielding of the carbonyl resonance, as opposed to the trend observed in Figure 1.

The expression for the paramagnetic screening tensor derived by Karplus and Pople<sup>37</sup> has the form

$$\sigma_p = -[e^2\hbar^2/2m^2c^2(\Delta E)]\langle r^{-3} \rangle_{2p} [Q_{AA} + \Sigma_{B \neq A} Q_{AB}] \quad (3)$$

where  $\Delta E$  involves the replacement of all electronic excitation energies with a mean value,  $\langle r^{-3} \rangle$  is the mean inverse cube expectation value for the distance from the nucleus for a carbon 2p atomic orbital, and  $\Sigma Q_{AB}$  is a complex term involving the anisotropy of the p-orbital occupations which is directly proportional<sup>38</sup> to the  $\pi$  mobile bond order for aromatic systems.

If the orbital expansion term  $\langle r^{-3} \rangle$ , which is proportional to the local charge density, dominates the  $\sigma_p$  screening tensor, we should expect the carbonyl resonances of the  $(\pi\text{-C}_6\text{H}_5\text{NH}_2)\text{Cr}(\text{CO})_3$  and  $(\pi\text{-C}_6\text{H}_5\text{CO}_2\text{CH}_3)\text{Cr}(\text{CO})_3$  derivatives to be the most shielded and deshielded, respectively, the opposite of what is observed. Gansow, *et al.*,<sup>6</sup> have assumed that  $\Delta E$  is effectively constant within a series of closely related derivatives<sup>48</sup> and that the carbonyl resonance is deshielded with an increase in the transition metal  $\rightarrow$  carbonyl  $\pi$  back-donation due to the concomitant decrease in the C-O  $\pi$  bond order contribution to  $\Sigma Q_{AB}$ . Unfortunately these authors neglected the negative sign of the  $\sigma_p$  screening tensor which implies that a reduction in the C-O  $\pi$  bond order leads to a net *shielding* of the carbonyl resonance.<sup>49</sup> Braterman and Randall, *et al.*,<sup>49</sup> have argued that the contribution from the  $\Sigma Q_{AB}$  term will be small due to the cylindrical symmetry of the MCO group. These authors observed a correlation between the carbonyl chemical shift and the frequency of the lowest energy uv transition which involves a charge transfer from the metal to the carbonyl  $\pi^*$  molecular orbital. As carbonyl ligands are replaced with either phosphine or phosphite ligands,  $\Delta E$  decreases and the magnitude of the  $\sigma_p$  screening tensor increases as expected. Braterman and Randall argued that the observed order of increasing carbonyl chemical shift for  $\text{LM}(\text{CO})_3$  derivatives,  $\text{L} = \text{CO} < \text{P}(\text{OR})_3 < \text{PR}_3 < \text{amine} < \text{carbene}$ , is consistent with an increase in the charge donor ability of these ligands. We would like to point out that this sequence is also consistent with a decrease in the  $\pi$ -acceptor abilities of these ligands. In either case it is immediately apparent that *the carbonyl resonance is deshielded with increasing electron density at the transition metal.*

We have shown previously that there is a net donation of electron density from the arene ring to the  $\text{Cr}(\text{CO})_3$  moiety in  $(\pi\text{-C}_6\text{H}_5\text{X})\text{Cr}(\text{CO})_3$  complexes.<sup>9</sup> The extent of this charge transfer will increase for electron-donating X substituents and will decrease for electron-withdrawing

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X substituents. We observe (Figure 1) that the carbonyl resonance is deshielded with increasing electron density on the  $\text{Cr}(\text{CO})_3$  fragment. We expect that the extent of transition metal  $\rightarrow$  carbonyl  $\pi$  back-donation will increase as the electron density on the  $\text{Cr}(\text{CO})_3$  fragment increases. These data imply that the carbonyl chemical shift within a series of closely related derivatives might be a linear measure of the extent of transition metal  $\rightarrow$  carbonyl  $\pi$  back-donation.

Additional evidence in support of this contention can be obtained from a study of the  $^{13}\text{C}$  nmr spectra of a series of  $\text{LCr}(\text{CO})_5$  and  $\text{L}_2\text{Cr}(\text{CO})_4$  derivatives (see Table II) for which X-ray crystallographic data are available. Grim and coworkers<sup>14-16</sup> have argued that the replacement of CO in  $\text{Cr}(\text{CO})_6$  with a weaker  $\pi$  acceptor such as  $\text{PPh}_3$  or  $\text{P}(\text{O}Ph)_3$  will lead to an increase in the extent of transition metal  $\rightarrow$  carbonyl  $\pi$  back-donation to the five remaining carbonyls. Since  $\text{P}(\text{O}Ph)_3$  is a better  $\pi$  acceptor than  $\text{PPh}_3$  we would expect the  $\pi$  back-donation to the carbonyls will decrease in the order  $\text{Ph}_3\text{PCr}(\text{CO})_5 > (\text{PhO})_3\text{PCr}(\text{CO})_5 > \text{Cr}(\text{CO})_6$ . Data presented above suggest that the carbonyl resonance is deshielded with increasing  $\pi$  back-donation. We would therefore expect that the carbonyl chemical shift should decrease in the order  $\text{Ph}_3\text{PCr}(\text{CO})_5 > (\text{PhO})_3\text{PCr}(\text{CO})_5 > \text{Cr}(\text{CO})_6$ , in agreement with observed trends (Table II). The replacement of a second carbonyl with  $(\text{PhO})_3\text{P}$  would lead the cis carbonyl resonance for the *trans*- $[(\text{PhO})_3\text{P}]_2\text{Cr}(\text{CO})_4$  complex to be deshielded relative to the cis carbonyl resonance of the  $(\text{PhO})_3\text{PCr}(\text{CO})_5$  complex. The fortuitous agreement between both the  $\text{Cr}-\text{C}^{\text{cis}}$  bond lengths and the  $^{13}\text{C}$  nmr chemical shifts for the *trans*- $[(\text{PhO})_3\text{P}]_2\text{Cr}(\text{CO})_4$  and  $\text{Ph}_3\text{PCr}(\text{CO})_5$  complexes led us to investigate this correlation further, as shown in Figures 2 and 3. As the transition metal  $\rightarrow$  carbonyl  $\pi$  back-donation increases, the  $\text{Cr}-\text{C}$  bond length decreases and the  $^{13}\text{C}$  nmr chemical shift is deshielded.

Molecular orbital calculations on the isoelectronic series  $\text{M}(\text{CO})_6$ , where  $\text{M} = \text{V}^-$ ,  $\text{Cr}^0$ , and  $\text{Mn}^+$ , have shown a significant increase in the transition metal  $\rightarrow$  carbonyl  $\pi$  back-donation with increasing negative charge on the complex.<sup>29</sup> The chemical shifts of the  $\text{V}(\text{CO})_6^-$  and  $\text{Cr}(\text{CO})_6$  derivatives are shown in Table III. Several attempts have been made to extend this correlation to the isoelectronic  $\text{Mn}(\text{CO})_6^+\text{X}^-$  complex. These have met with little success due to the low solubility of derivatives characterized to date. We have therefore characterized complexes of the type  $\pi\text{-}(\text{C}_5\text{H}_5)\text{M}(\text{CO})_3$ , where  $\text{M} = \text{Cr}^-$ ,  $\text{Mn}^0$ , and  $\text{Fe}^+$ , and these data are included in Table III. The large difference between the carbonyl chemical shifts within this series and the observed deshielding of the carbonyl resonance with increasing  $\pi$  back-donation are consistent with arguments cited above.

### Conclusions

The data discussed within are consistent with a model in which the  $^{13}\text{C}$  nmr carbonyl chemical shifts for a series of closely related derivatives are a linear measure of the extent of transition metal  $\rightarrow$  carbonyl  $\pi$  back-donation. Additional evidence in support of this contention and a theoretical treatment of the possible mechanism for this dependence will be the subject of succeeding papers in this series.

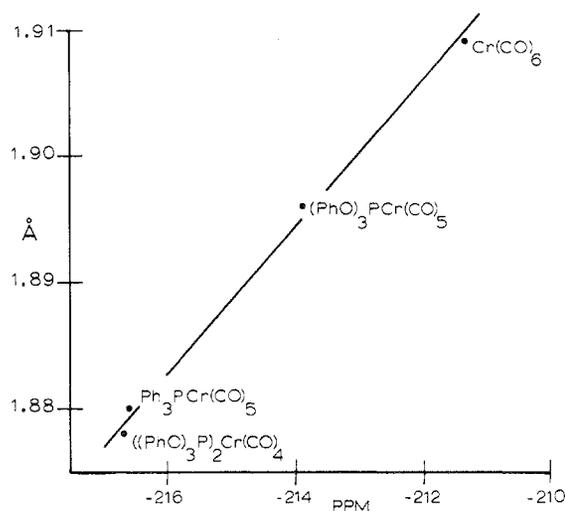


Figure 2. Plot of the  $^{13}\text{C}$  nmr chemical shifts for the cis carbonyls vs.  $\text{Cr}-\text{C}^{\text{cis}}$  bond lengths for  $\text{Cr}(\text{CO})_6$ ,  $\text{LCr}(\text{CO})_5$ , and  $\text{L}_2\text{Cr}(\text{CO})_4$  complexes.

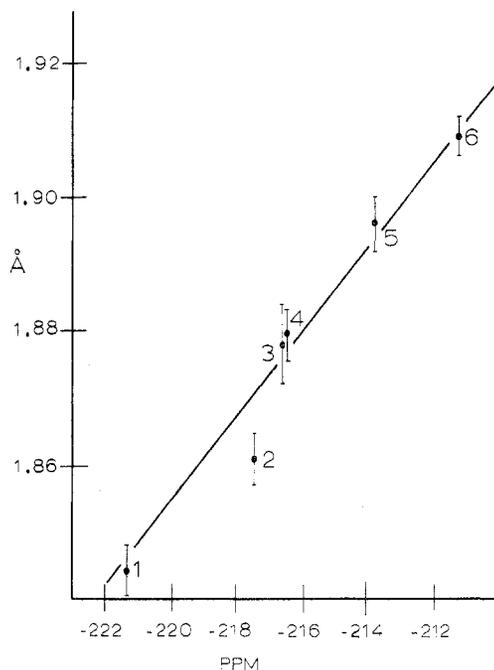


Figure 3. Plot of the  $^{13}\text{C}$  nmr chemical shifts vs. the  $\text{Cr}-\text{C}$  bond lengths: 1, *trans* CO in  $\text{Ph}_3\text{PCr}(\text{CO})_5$ ; 2, *trans* CO in  $(\text{PhO})_3\text{PCr}(\text{CO})_5$ ; 3, *cis* CO in  $[(\text{PhO})_3\text{P}]_2\text{Cr}(\text{CO})_4$ ; 4, *cis* CO in  $\text{Ph}_3\text{PCr}(\text{CO})_5$ ; 5, *cis* CO in  $(\text{PhO})_3\text{PCr}(\text{CO})_5$ ; 6,  $\text{Cr}(\text{CO})_6$ .

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**Registry No.**  $[\pi\text{-C}_6\text{H}_5\text{N}(\text{CH}_3)_2]\text{Cr}(\text{CO})_3$ , 12109-10-3;  $(\pi\text{-C}_6\text{H}_5\text{-NH}_2)\text{Cr}(\text{CO})_3$ , 12108-11-1;  $(\pi\text{-C}_6\text{H}_5\text{CH}_3)\text{Cr}(\text{CO})_3$ , 12083-24-8;  $(\pi\text{-C}_6\text{H}_5\text{OCH}_3)\text{Cr}(\text{CO})_3$ , 12116-44-8;  $(\pi\text{-C}_6\text{H}_5)\text{Cr}(\text{CO})_3$ , 12082-08-5;  $(\pi\text{-C}_6\text{H}_5\text{F})\text{Cr}(\text{CO})_3$ , 12082-05-2;  $(\pi\text{-C}_6\text{H}_5\text{Cl})\text{Cr}(\text{CO})_3$ , 12082-03-0;  $(\pi\text{-C}_6\text{H}_5\text{CO}_2\text{CH}_3)\text{Cr}(\text{CO})_3$ , 12125-87-0;  $\text{Cr}(\text{CO})_6$ , 13007-92-6;  $\text{Ph}_3\text{PCr}(\text{CO})_5$ , 14917-12-5;  $(\text{PhO})_3\text{PCr}(\text{CO})_5$ , 18461-39-7; *trans*- $[(\text{PhO})_3\text{P}]_2\text{Cr}(\text{CO})_4$ , 35039-06-6;  $\text{NaV}(\text{CO})_6$ , 15602-41-2;  $(\pi\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_3\text{-PF}_6$ , 51108-59-9;  $(\pi\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3$ , 12079-65-1;  $(\pi\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_3\text{-Na}$ , 12203-12-2;  $^{13}\text{C}$ , 14762-74-4.