A Fourier-Transform Carbon-13 Nuclear Magnetic Resonance Study of (Arene)tricarbonylchromium Complexes

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13C nmr spectroscopy was employed to study the perturbations in bonding for monosubstituted benzene derivatives upon complexation with Cr(CO)3. An analysis of the C(4) 13C nmr chemical shifts of both free and complexed arenes implies that there is no significant change in the transmission of resonance substituent effects upon complexation. A similar analysis of the C(1) 13C nmr chemical shifts and the 1J(13C,1H) coupling constants indicates a net withdrawal of electron density by the Cr(CO)3 fragment from the 6 framework of the arene ring.

Introduction

The chemical reactivity of arenes has been found to be greatly altered by complexation in (arene)tricarbonylchromium complexes. (Chlorobenzene)tricarbonylchromium undergoes rapid nucleophilic substitution to yield (anisole)tricarbonylchromium,1 and (benzene)tricarbonylchromium has been found to undergo both acid-3 and base-catalyzed deuterium exchange under conditions where the free arenes will not react. Other studies have shown that both benzoic acid and phenol are weaker acids than (benzoic acid)tricarbonylchromium2,3 and (phenol)tricarbonylchromium4 and that aniline is a stronger base than (aniline)tricarbonylchromium5. These data are consistent with, but do not necessarily imply, an electron-withdrawing character for the Cr(CO)3 moiety in the ground state. For example, Kursanov, et al.,6 have shown that under conditions analogous to those in the solvolysis of (benzyl chloride)tricarbonylchromium7 and the hydrolysis of (benzyl alcohol)tricarbonylchromium8 both have been found to occur at a rate 105 times faster than the free arenes. These data may be interpreted in terms of a net donation of electron density from the Cr(CO)3 moiety, but unfortunately these data may depend upon a number of factors other than changes in the ground-state electronic distribution upon complexation.

More conclusive evidence for the electron-withdrawing nature of the Cr(CO)3 moiety can be found in the semiempirical molecular orbital calculations by Caroll and McGlynn9 and by Brown and Rawlinson,10 which have shown a net positive charge on the arene ring, and in the very substantial dipole moment (5.08 D) found for (benzene)tricarbonylchromium.11 Studies of the pmr spectra of (arene)tricarbonylchromium complexes have been interpreted in terms of an electron-withdrawing character for the Cr(CO)3 group,12-14 and similar arguments have been made by Khandkarova and Gubin from studies of the polarographic reductions of free and complexed (acetophenone)tricarbonylchromium,15 the polarographic oxidation of ferrocenyl-substituted (arene)-tricarbonylchromium derivatives,16 and the 19F nmr chemical shifts of Cr(CO)3 complexes of fluorinated dibenzylnaphtalene.17

In a somewhat contradictory fashion, studies of the transmission of substituent effects in complexed arenes by Reeves, et al.,18 and by Brown and coworkers19-21 have shown no significant reduction in the transmission of π-substituent effects in arenes upon complexation with Cr(CO)3. Preliminary 13C nmr data for (benzene)tricarbonylchromium have been reported by Farnell, Randall, and Rosenberg,22 while a study of the 13C nmr spectra of a series of LM(CO)3 complexes with L = mesitylene and durene and M = Cr, Mo, and W has been reported by Mann.23 In order to obtain a better understanding of the perturbations in bonding of arenes caused by complexation with Cr(CO)3, we have undertaken a systematic study of the 13C nmr spectra of a series of derivatives of the type π(C6H4XCr(CO)3) [X = H, F, Cl, CH3, OCH3, O-CH2-CH2-OH, CO2CH3, NH2, N(CH3)2] and have compared these results obtained from a study of monosubstituted benzene derivatives.

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Experimental Section

Materials. Cr(CO)₅ was purchased from the Pressure Chemical Co. and a sample of (methyl benzoate)tricarbonylchromium was purchased from the Aremco Chemical Co. Arenes were stored over 4A molecular sieves and then used without further purification.

Complexes of the type \((\text{H}_5X)\text{Cr(CO)}_3 \) \((X = H, F, Cl, CH_3, OCH_3, \text{O-n-Bu}, \text{NH}_2, N(CH_3)_2)\) were prepared by the method of Rausch, et al., by refluxing the respective arene with \((\text{NH}_3)_2\text{-Cr(CO)}_5\) in dioxane under an inert atmosphere for 4-12 hr.

All complexes were characterized by a combination of melting points, infrared spectroscopy, mass spectroscopy, and microanalytical data. The fact that these complexes could be recovered subsequent to recording the \(^{13}C\) nmr spectra either by sublimation or by recrystallization demonstrates the chemical integrity of these samples during the 2-6 hr required to record the spectrum.

Instrumentation. The \(^{13}C\) nmr spectra were obtained in either dichloromethane or carbon tetrachloride solution with a Fourier-transform pulsed nmr spectrometer operating at 15.08 MHz as described previously. The \(^{13}C\) nmr chemical shifts were measured relative to the internal solvent resonance and are reported in ppm downfield from TMS using the following conversions: \(\delta_{\text{TMS}} = \delta_{\text{CHCl}_3} - 53.89 \text{ ppm}; \delta_{\text{CCl}_4} = \delta_{\text{CH}_2} - 95.99 \text{ ppm}.\) All chemical shifts were found to be reproducible within ±0.06 ppm.

Results and Discussion

Arene Ring \(^{13}C\) Nmr Chemical Shifts. The proton-decoupled Fourier-transform \(^{13}C\) nmr studies of (arene)tricarbonylchromium complexes in dichloromethane solution exhibit well-resolved spectra (see Figure 1). The low-field resonance can be readily assigned to the carbonyl carbon by analogy with other group VIb transition metal carbonyl derivatives studied. The assignment of the \(C(1)\) and \(C(4)\) carbon resonances of the arene ring is simplified by the absence of a nuclear Overhauser effect for the quaternary \(C(1)\) carbon atoms. The assignment of the \(C(2,6)\) and \(C(3,5)\) carbon resonances follows the original work of Spieesecke and Schneider and Nelson, Levy, and Cargioli for the monosubstituted benzenes.

The \(^{13}C\) nmr chemical shifts for the \(C(4)\) carbon resonance in \((	ext{C}_6\text{H}_5\text{X})\text{Cr(CO)}_3\) derivatives [\(X = \text{H, F, Cl, CH}_3, \text{OCH}_3, \text{O-n-Bu}, \text{CO}_2\text{CH}_3, \text{NH}_2, N(CH_3)_2\)] are given in Tables I and II, respectively.

The \(C(4)\) carbon chemical shifts in monosubstituted benzenes have been assumed to be indicative of changes in the \(\pi\)-electron density with varying substituent groups. To determine the validity of this hypothesis we have calculated an optimal fit for the experimental \(^{13}C\) nmr chemical shifts using the equation

\[ f_{\text{H}}\text{x}C(4) = fF_X + nR_X \]  

where \(f_{\text{H}}\text{x}C(4)\) is the change in the \(^{13}C\) nmr chemical shift of the \(C(4)\) carbon resonance upon substitution of \(H\) for \(X\).

![Figure 1. The \(^1H\)-decoupled Fourier-transform pulsed \(^{13}C\) nmr spectrum of \((\text{C}_6\text{H}_5\text{CH}_3)\text{Cr(CO)}_3\), in methylene chloride solution; 512 scans, 10-sec pulse delay, 200-ppm window.](https://example.com/figure1.png)

<table>
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<th>(X)</th>
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\(^{13}C\) nmr spectra were recorded in carbon tetrachloride solution, 20% by weight. Chemical shifts were measured relative to the internal CO solvent resonance and are reported relative to an internal TMS standard, using the conversion \(\delta_{\text{TMS}} = \delta_{\text{CHCl}_3} - 95.99 \text{ ppm}.\) The C(1) carbon resonance was identified by the absence of an NOE upon \(^1H\) irradiation. The assignment of the \(C(2,6)\) vs. \(C(3,5)\) carbon resonances follows the work of Spieesecke and Schneider and Nelson, Levy, and Cargioli.

At \(C(1)\) \(F_X\) is the inductive (or field) and \(R_X\) is the resonance parameter for substituent \(X\) as tabulated by Swain and Lupton, and \(f\) and \(r\) are the relative contributions to the \(^{13}C\) nmr chemical shift from inductive and resonance effects, respectively. Optimal values of \(f\) and \(r\) are calculated by a minimization of the difference between the experimental chemical shifts and the chemical shifts calculated on the basis of eq 1.22

Analysis of the \(^{13}C\) nmr chemical shift data for the \(C(4)\) carbon resonance in \((\text{C}_6\text{H}_5\text{X})\text{Cr(CO)}_3\) derivatives via eq 1 yields values of \(f\) and \(r\) of 10 and 90%, respectively. The high linear correlation coefficient, \(r = 99.2\%\), between the experimental and calculated \(C(4)\) chemical shifts is gratifying and the predominance of resonance substituent effects is easily understood. A similar analysis of the \(C(4)\) carbon resonance chemical shifts for the \(\pi(\text{C}_6\text{H}_5\text{X})\text{Cr(CO)}_3\) complexes yields values of \(f\) and \(r\) which are 11 and 89%, respectively, \(r = 97.9\%\). Both the high linear correlation coefficient and the continued predominance of resonance substituent effects are of interest.

Maciel and Natterstadt postulated that the contributions to the \(^{13}C\) nmr chemical shift from inductive and ring current effects should be approximately the same at both the \(C(3,5)\) and \(C(2,6)\) carbon resonances. The high linear correlation coefficient and the continued predominance of resonance substituent effects are of interest.
where \( S_x \) and inductive and resonance effects (see Figure 3). We have attribution from these two effects to the \( C(1) \) chemical shift in the transmission of inductive substituent effects upon complexation. The substantially larger range of \( C(1) \) chemical shifts for the complexed arenes than for the free arenes and, therefore, a plot of the \( C(1) \) resonances of \( (C_6H_5-X)\) vs. the free and complexed arenes which are upfield of the corrected chemical shift for \( (C_6H_5-H) \) and \( (C_6H_5-X)Cr(CO)_3 \), respectively.

\[
\delta' = \delta_{C(4)} - \delta_{C(3,5)} \quad (2)
\]

An analysis of the corrected chemical shifts, \( \delta' \), via eq 1, yields values of \( f \) and \( r \) of 3% and 97% for the free arenes and 1% and 99% for the \( Cr(CO)_3 \) complexes. These data are in complete agreement with the postulate of Maciel and Natterstad and imply that \( \delta' \) is a direct measure of perturbations in the transmission of resonance substituent effects. A plot of \( \delta' \) for free vs. complexed arenes is shown in Figure 2. The excellent agreement between the corrected chemical shifts would argue against any substantial perturbations in the transmission of resonance substituent effects upon complexation.

The \( ^{13}C \) nmr chemical shifts of the \( C(1) \) carbon resonance, although most likely dominated by inductive effects, should not be analyzed via eq 1, but instead with an expanded expression

\[
J_{X \cdot C(1)} = J_{F \cdot X} + r_{R \cdot X} + s_{S \cdot X} + a_{A \cdot X} \quad (3)
\]

where \( S_X \) and \( A_X \) are parameters accounting for the steric and anisotropic contributions to the chemical shifts, and \( s \) and \( a \) are the relative sensitivities to these effects. The contribution from these two effects to the \( C(1) \) chemical shift will be approximately the same for both free and complexed arenes, and therefore a plot of the \( C(1) \) resonances of \( (C_6H_5-X) \) vs. the \( C(1) \) resonances of \( n(C_6H_5-X)Cr(CO)_3 \) derivatives can be interpreted in terms of changes in the transmission of inductive and resonance effects (see Figure 3). We have argued above that there is no significant change in the transmission of resonance substituent effects to \( C(4) \). We can therefore conclude that the substantial deviation of the correlation in Figure 3 from unit slope implies a distinct alteration in the transmission of inductive substituent effects upon complexation. The substantially larger range of \( C(1) \) chemical shifts for the complexed arenes than for the free arenes suggests an increased sensitivity to inductive substituent effects due to the net withdrawal of electron density from the \( \sigma \) framework of the arene ring.

Changes in the \( J_{CH} \) Coupling Constant upon Complexation. Emanuel and Randall noted changes in the directly bound \( 1J_{C=H} \) nuclear spin-spin coupling constants of arenes upon complexation with \( Cr(CO)_3 \) in a study of the pmr spectra of these complexes. These authors used an approxi-
Figure 3. Plot of the C(1) chemical shifts, in ppm, for the C,H,X derivatives vs. the C(1) chemical shifts for \( n-(C,H,X)\text{Cr(CO)}_3 \) derivatives. The theoretical line of slope equal to unity is also shown. Negative values of the chemical shift for free and complexed arenes imply carbon resonances which are downfield of C,H, and \( n-(C,H,X)\text{Cr(CO)}_3 \), respectively.

Metal complexes that there is a significant overlap of transition metal hybrid orbitals with the \( \sigma \) framework of the arene ring. This overlap would be expected to lead to a net reduction in the amount of \( s \) character available for the C-H bond, and one would expect the coupling constant to decrease upon complexation. Emanuel and Randall argued that the removal of electron density from the \( \pi \) framework would explain an increase in the effective nuclear charge of the ring carbons upon complexation. This second mechanism is consistent with the results discussed above.

**Carbonyl Resonance \( ^{13}C \) Nmr Chemical Shifts.** We have investigated the transmission of substituent effects from the arene ring to the Cr(CO)_3 moiety \( ^{13}C \) nmr analysis of the \( ^{13}C \) nmr chemical shifts of the carbonyl resonance with eq 1. The predominance of inductive effects \((f = 54\%\) and \( r = 46\%\)) is in accord with our postulate of extensive overlap of the metal hybrid orbitals with the \( \sigma \) framework of the arene ring, and the excellent agreement between calculated and experimental chemical shifts, \( f = 98.7\%\), allows us to ignore perturbations caused by changes in electric dipole and neighboring anisotropy or ring current effects and to interpret the observed chemical shifts in terms of changes in the nature of the transition metal-carbonyl bond. A detailed treatment of these results will be the subject of a subsequent paper.

There has been some question about hindered rotation around the metal-arene bond in \( (\text{arene})\text{tricarbonylchromium complexes} \)\(^{47,48}\) and the orientation of the Cr(CO)_3 fragment in X-ray crystallographic studies.\(^{49-52}\) It is of interest to note from the line widths of the carbonyl resonances as shown in Figure 1 that there is no evidence for nonequivalence of the carbonyls in these complexes due to electronic effects.

**Conclusion**

The data obtained from this \( ^{13}C \) nmr study are best explained \( \text{via} \) a model in which there is a net withdrawal of electron density from the \( \sigma \) framework of the arene ring with little or no concomitant reduction in the \( \pi \)-electron density. This model is in complete agreement with the results of previous experiments discussed in the Introduction.

**Registry No.** C,H, , 71-43-2; C,H,F, 462-06-6; C,H,Cl, 108-90-7; C,H,CH, , 108-88-3; C,H,OCH, , 100-66-3; C,H,O,n-Bu, 1126-79-0; C,H,O,CH, , 93-58-3; C,H,NH, , 62-55-3; C,H,N(CH, ), 121-69-7; \((C,H,N)\text{Cr(CO)}_3\), 12082-08-5; \((C,H,F)\text{Cr(CO)}_3\), 12082-05-2; \((C,H,F)\text{Cr(CO)}_3\), 12082-03-0; \((C,H,CH, )\text{Cr(CO)}_3\), 12083-24-8; \((C,H,OCH, )\text{Cr(CO)}_3\), 12116-44-8; \((C,H,O,n-Bu)\text{Cr(CO)}_3\), 43202-61-5; \((C,H,O,CH, )\text{Cr(CO)}_3\), 12125-87-0; \((C,H,NH, )\text{Cr(CO)}_3\), 12108-11-1; \((C,H,N(CH, ))\text{Cr(CO)}_3\), 12109-10-3; \( ^{13}C\), 14762-74-4.