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A Fourier-Transform Carbon-13 Nuclear Magnetic Resonance Study of (Arene)tricarbonylchromium Complexes[1]

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^{13}C 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) ^{13}C 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) ^{13}C nmr chemical shifts and the $^1J_{^{13}C^1H}$ coupling constants indicates a net withdrawal of electron density by the $Cr(CO)_3$ fragment from the σ 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,[2] and (benzene)tricarbonylchromium has been found to undergo both acid-[3] and base[4,5]-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)tricarbonylchromium[2,6,7] and (phenol)tricarbonylchromium[8] and that aniline is a stronger base than (aniline)tricarbonylchromium.[6] 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.*,[9] have shown that under conditions analogous to those in which $BF_3 \cdot OD_2$ catalyzes deuterium exchange in (benzene)tricarbonylchromium, $BF_3 \cdot OH_2$ will protonate the chromium atom, thereby offering an alternative explanation for the greatly enhanced rate of exchange in the complex.

The solvolysis of (benzyl chloride)tricarbonylchromium[10] and the hydrolysis of (benzyl alcohol)tricarbonylchromium[11] have both been found to occur at a rate 10^5 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 McGlynn[12] and by Brown and Rawlinson,[13] 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.[14] 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,[15–18] and similar arguments have been made by Khandkarova and Gubin from studies of the polarographic reductions of free and complexed (acetophenone)tricarbonylchromium,[19] the polarographic oxidation of ferrocenyl-substituted (arene)tricarbonylchromium derivatives,[20] and the ^{19}F nmr chemical shifts of $Cr(CO)_3$ complexes of fluorinated biphenyls.[21]

In a somewhat contradictory fashion, studies of the transmission of substituent effects in complexed arenes by Reeves, *et al.*,[8,22] and by Brown and coworkers[23–25] have shown no significant reduction in the transmission of π-substituent effects in arenes upon complexation with $Cr(CO)_3$.

Preliminary ^{13}C nmr data for (benzene)tricarbonylchromium have been reported by Farnell, Randall, and Rosenberg,[26] while a study of the ^{13}C 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.[27] 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 ^{13}C nmr spectra of a series of derivatives of the type π-$(C_6H_5X)Cr(CO)_3$ [X = H, F, Cl, CH_3, OCH_3, O-*n*-Bu, CO_2CH_3, NH_2, $N(CH_3)_2$] and have compared these to results obtained from a study of monosubstituted benzene derivatives.

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Experimental Section

Materials. $Cr(CO)_6$ was purchased from the Pressure Chemical Co. and a sample of (methyl benzoate)tricarbonylchromium was purchased from the Strem Chemical Co. Arenes were stored over 4A molecular sieves and then used without further purification.

Complexes of the type π-$(C_6H_5X)Cr(CO)_3$ [X = H, F, Cl, CH_3, OCH_3, O-*n*-Bu, NH_2, $N(CH_3)_2$] were prepared by the method of Rausch, *et al.*,[28] by refluxing the respective arene with $(NH_3)_3$-$Cr(CO)_3$[29] 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.[30] 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: $\delta_{\mathrm{TMS}} = \delta_{\mathrm{CH_2Cl_2}} - 53.89$ ppm; $\delta_{\mathrm{TMS}} = \delta_{\mathrm{CCl_4}} - 95.99$ ppm. All chemical shifts were found to be reproducible to 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.[31,32] 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.[33] The assignment of the C(2,6) and C(3,5) carbon resonances follows the original work of Spiesecke and Schneider[34] and Nelson, Levy, and Cargioli[35] for the monosubstituted benzenes. The ^{13}C nmr chemical shifts for (C_6H_5X) and π-$(C_6H_5X)Cr(CO)_3$ derivatives [X = H, F, Cl, CH_3, OCH_3, O-*n*-Bu, CO_2CH_3, 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 π-electron density with varying substituent groups.[34,36-40] To determine the validity of this hypothesis we have calculated an optimal fit for the experimental ^{13}C nmr chemical shifts using the equation

$$\int_{\mathrm{H}}{}^{\mathrm{X}}\mathrm{C}(4) = fF_{\mathrm{X}} + rR_{\mathrm{X}} \qquad (1)$$

where $\int_{\mathrm{H}}{}^{\mathrm{X}}\mathrm{C}(4)$ is the change in the ^{13}C nmr chemical shift of the C(4) carbon resonance upon substitution of X for H 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,[41] 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.[42]

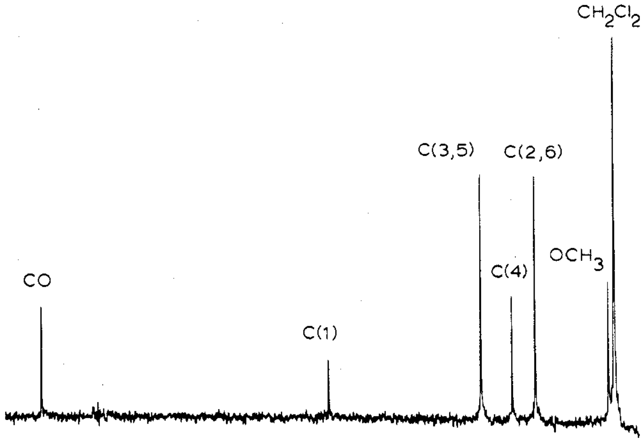

Figure 1. The ^1H-decoupled Fourier-transform pulsed ^{13}C nmr spectrum of $(C_6H_5OCH_3)Cr(CO)_3$ in methylene chloride solution; 512 scans, 10-sec pulse delay, 200-ppm window.

Table I. ^{13}C Nmr Chemical Shifts of C_6H_5X Derivatives[a]

X	C(1)[b]	C(2,6)[c]	C(3,5)	C(4)	YCH_3
H	-127.9_7				
F	-162.7_1	-115.0_4	-129.5_9	-123.5_8	
Cl	-134.2_6	-128.4_0	-129.3_8	-126.0_2	
CH_3	-137.0_1	-128.6_5	-127.9_1	-125.0_5	-21.2_3
OCH_3	-159.4_7	-113.5_7	-128.9_5	-120.2_2	-55.3_6
O-*n*-Bu	-158.8_6	-113.9_3	-128.7_0	-120.0_4	-66.6_9, -31.2_9, -18.3_5, -13.5_9
CO_2CH_3	-130.2_5	-129.3_8	-127.8_5	-132.2_5	-51.4_3
NH_2	-146.2_5	-114.6_1	-128.8_0	-117.8_5	
$N(CH_3)_2$	-150.1_9	-112.4_7	-128.6_5	-116.5_6	-41.2_0

[a] Nmr spectra were recorded in carbon tetrachloride solution, 20% by weight. Chemical shifts were measured relative to the internal CCl_4 solvent resonance and are reported relative to an internal TMS standard, using the conversion $\delta_{\mathrm{TMS}} = \delta_{\mathrm{CCl_4}} - 95.99$ ppm. [b] The C(1) carbon resonance was identified by the absence of an NOE upon ^1H irradiation. [c] The assignment of the C(2,6) *vs.* C(3,5) carbon resonances follows the work of Spiesecke and Schneider[34] and Nelson, Levy, and Cargioli.[35]

Analysis of the ^{13}C nmr chemical shift data for the C(4) carbon resonance in (C_6H_5X) derivatives *via* eq 1 yields values of f and r of 10 and 90%, respectively. The high linear correlation coefficient, $\bar{r} = 99.2\%$, 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 π-$(C_6H_5X)Cr(CO)_3$ complexes yields values of f and r which are 11 and 89%, respectively, $\bar{r} = 97.9\%$. Both the high linear correlation coefficient and the continued predominance of resonance substituent effects are of interest.

Maciel and Natterstad[40] 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)

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Table II. ^{13}C Nmr Chemical Shifts of π-$(C_6H_5X)Cr(CO)_3$ Derivatives[a]

X	CO	C(1)[b]	C(2,6)[c]	C(3,5)	C(4)	YCH_3
H	−233.34	−93.50				
F	−232.05	−146.16	−79.70	−93.93	−86.97	
Cl	−231.99	−113.16	−91.73	−93.81	−88.74	
CH_3	−233.64	−110.35	−94.91	−93.38	−90.21	−20.40
OCH_3	−233.53	−143.68	−78.68	−95.71	−85.95	−55.67
O-*n*-Bu	−233.67	−143.40	−79.07	−95.86	−85.72	−68.66, −30.98, −19.13, −13.66
CO_2CH_3	−231.23	−95.00[d]	−95.00[e]	−90.24	−95.43	−52.76
NH_2	−234.62	−131.41	−77.70	−97.00	−83.80	
$N(CH_3)_2$	−235.05	−135.68	−74.77	−97.47	−83.16	−39.55

[a] Chemical shifts were measured in dichloromethane solution relative to the internal CH_2Cl_2 solvent resonance and are reported relative to an internal TMS standard using the conversion $\delta_{TMS} = \delta_{CH_2Cl_2} - 53.89$ ppm. [b] The C(1) carbon resonance is identified by the absence of an NOE upon ^{1}H irradiation. [c] The assignment of the C(2,6) *vs.* C(3,5) carbon resonances was assumed to be the same as the assignment reported by Spiesecke and Schneider[34] for the parent C_6H_5X derivative. [d] The C(1) carbon resonance is not observed for this complex. From intensity ratios of the C(2,6) *vs.* C(3,5) carbon resonances it is most likely accidentally degenerate with the C(2,6) carbon resonance at −95.00 ppm. [e] The assignment of the C(2,6) *vs.* C(3,5) carbon resonances for this derivative follows the assignment of Nelson, Levy, and Cargioli[35] for the parent C_6H_5X derivative.

and C(4) positions in monosubstituted benzenes, and therefore a better analysis of the effect of substituents on the π-electron density could be attained by examining the *corrected* C(4) chemical shift, δ'

$$\delta' = \delta_{C(4)} - \delta_{C(3,5)} \qquad (2)$$

An analysis of the corrected chemical shifts, δ', *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[40] and imply that δ' is a direct measure of perturbations in the transmission of resonance substituent effects. A plot of δ' 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.

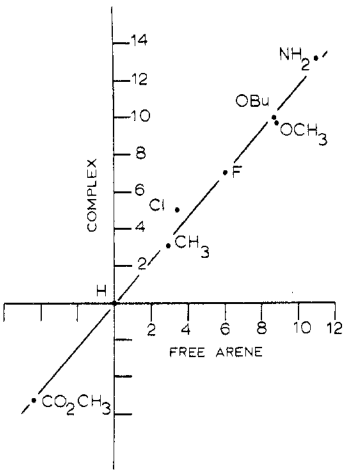

Figure 2. Plot of the corrected chemical shifts, δ', in ppm, for C_6H_5X derivatives *vs.* the corrected chemical shifts for π-$(C_6H_5X)Cr(CO)_3$ derivatives. Positive values of δ' imply corrected chemical shifts for the free and complexed arenes which are upfield of the corrected chemical shift for (C_6H_6) and π-$(C_6H_6)Cr(CO)_3$, respectively.

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

$$\mathcal{S}_H{}^XC(1) = fF_X + rR_X + sS_X + aA_X \qquad (3)$$

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 π-$(C_6H_5X)Cr(CO)_3$ 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 σ framework of the arene ring.

Changes in the $^1J_{CH}$ Coupling Constant upon Complexation. Emanuel and Randall[17] noted changes in the directly bound $^1J_{^{13}C^1H}$ 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 approximate expression for the $^1J_{CH}$ coupling constant of the form[43,44]

$$J_{XY} \propto (\Delta E^{-1})\alpha_X{}^2\alpha_Y{}^2|\psi_X(0)|^2|\psi_Y(0)|^2 \qquad (4)$$

where $\alpha_X{}^2$ is the s character of the hybrid orbital used by X for the X-Y bond, and $|\psi_X(0)|^2$ is the electron density at the nucleus.[45]

They argued that the increase in the $^1J_{CH}$ coupling constants for exocyclic methyl groups upon complexation was due to a change in the hybridization produced by an increased effective electronegativity of the arene ring. To explain the substantially larger changes in the $^1J_{CH}$ coupling constants of endocyclic ring carbons, they argued that the withdrawal of π-electron density from the arene ring reduced the screening of the ring carbon nucleus, thereby increasing the effective nuclear charge. This would increase the electron density at the carbon nucleus and thereby increase the magnitude of the coupling constant.

Anderson and Drago[46] have shown *via* a self-consistent charge molecular orbital calculation on bis(arene)-transition

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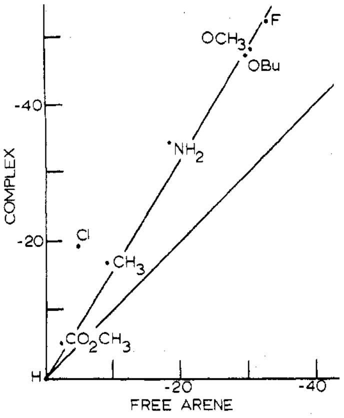

Figure 3. Plot of the C(1) chemical shifts, in ppm, for the C_6H_5X derivatives *vs.* the C(1) chemical shifts for π-$(C_6H_5X)Cr(CO)_3$ derivatives. The theoretical line of slope equal to unity is also shown. Negative values of the chemical shift for free and complexed arenes imply carbon resonances which are downfield of C_6H_6 and π-(C_6H_6)-$Cr(CO)_3$, respectively.

metal complexes that there is a significant overlap of transition metal hybrid orbitals with the σ 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. Since the coupling constants are observed to increase (see Table III), we must invoke an increase in the effective nuclear charge of the ring carbons upon complexation. Emanuel and Randall argued that the removal of electron density from the π framework would explain an increase in the effective nuclear charge, but it is also possible to explain this increase *via* a withdrawal of electron density from the σ framework of the arene ring.[21] 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 *via* an 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 σ framework of the arene ring, and the excellent agreement between calculated and experimental chemical shifts, $\bar{r} = 98.7\%$, 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 (arene)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.

Table III. $^1J_{^{13}C^1H}$ Nuclear Spin-Spin Coupling Constants (Hz) of Benzene and Anisole and Their $Cr(CO)_3$ Complexes

	Free arene	Complex
C_6H_6 [a]		
C(1)	158	175
$C_6H_5OCH_3$ [b]		
C(2,6)	159	173
C(3,5)	159	177
C(4)	162	177
OCH_3	143.5	145

[a] In chloroform solution. [b] In dichloromethane solution.

Conclusion

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

Registry No. C_6H_6, 71-43-2; C_6H_5F, 462-06-6; C_6H_5Cl, 108-90-7; $C_6H_5CH_3$, 108-88-3; $C_6H_5OCH_3$, 100-66-3; C_6H_5O-*n*-Bu, 1126-79-0; $C_6H_5CO_2CH_3$, 93-58-3; $C_6H_5NH_2$, 62-53-3; $C_6H_5N(CH_3)_2$, 121-69-7; $(C_6H_6)Cr(CO)_3$, 12082-08-5; $(C_6H_5F)Cr(CO)_3$, 12082-05-2; $(C_6H_5Cl)Cr(CO)_3$, 12082-03-0; $(C_6H_5CH_3)Cr(CO)_3$, 12083-24-8; $(C_6H_5OCH_3)Cr(CO)_3$, 12116-44-8; $(C_6H_5O$-*n*-Bu$)Cr(CO)_3$, 43202-61-5; $(C_6H_5CO_2CH_3)Cr(CO)_3$, 12125-87-0; $(C_6H_5NH_2)Cr(CO)_3$, 12108-11-1; $[C_6H_5N(CH_3)_2]Cr(CO)_3$, 12109-10-3; ^{13}C, 14762-74-4.

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