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Electronic Effects in $(CH_3)_nC_6H_{6-n}Mn(CO)_3^+$ Complexes (n = 0-6) as Evidenced by ^1H and ^{13}C Nmr Spectroscopy, ^{55}Mn Nqr Spectroscopy, and Carbonyl Ir Spectroscopy

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A spectroscopic analysis of electronic effects and transmission of electron density in $(CH_3)_nC_6H_{6-n}Mn(CO)_3^+$ complexes (n = 0-6) using ^1H and ^{13}C nmr of the aromatic ring atoms, ^{55}Mn nqr spectroscopy, and CO ir spectroscopy is reported. The nmr data for the complexes show substantial shielding of the ring nuclei compared to the free arenes, and this was ascribed to magnetic anisotropy of the ring caused by the metal. By comparison of the Mn(I) complexes to the isoelectronic Cr(0) systems, it was concluded that much more ring → metal electron migration occurs with Mn(I) than Cr(0). The ^{55}Mn nqr frequencies increase linearly with the number of methyl groups on the ring. The $C_5H_5^-$ ligand appears to be a much better electron donor than C_6H_6 based on the nqr spectra. Crystal lattice differences produced only 3% change in the ^{55}Mn coupling constant for a series of five anions in the $C_6H_6Mn(CO)_3^+$ salts. A larger effect (8%) was observed for the mesitylene salts. Only minute perturbations occur to the axial symmetry of the metal-ring bond in all salts as evidenced by small asymmetry parameters. The carbonyl ir frequencies show a linear correlation with ring substitution, and it is concluded that the electron density changes on the metal are transmitted in a corresponding fashion to the CO groups. All spectra are found to be internally consistent.

Introduction

The prevalence and importance in organometallic chemistry of aromatic systems that contain ring-metal π bonds has stimulated a great deal of study in the past 20 years.[1] Complexes containing benzene, such as the π-benzene tricarbonyl complexes of Cr(0), Mo(0), and W(0), have been subjects of vigorous work. The description of the metal-ring bond suggests that the metal orbitals mix with both the σ and π framework of the aromatic ring but to a greater extent with the π framework[2] and that not only ring (π) → metal electron migration occurs[3-5] but also some metal → ring (π^*) electron migration may take place.[6] Dipole moment measurements,[3] the stronger acidity of $(C_6H_5COOH)Cr(CO)_3$ compared to C_6H_5COOH,[4] the weaker basicity of $(C_6H_5NH_2)Cr(CO)_3$ compared to $C_6H_5NH_2$,[4] and the greater ^{35}Cl nqr frequency in $(C_6H_5Cl)Cr(CO)_3$ compared to C_6H_5Cl[5] are all suggestive of the dominance of ring (π) → metal electron migration over the back-bonding effect.

A thorough understanding of electron migration in a ring-metal bond requires a probe of electron density at each point in the molecule. The group VIb complexes, $C_6H_6M(CO)_3$, M = Cr(0), Mo(0), and W(0), are not ideal for study in this regard because of the difficulty of examining the metal spectroscopically. For this reason, an important analog of $C_6H_6Cr(CO)_3$ is the isoelectronic $C_6H_6Mn(CO)_3^+$ ion.[7] The ^{55}Mn nucleus is 100% abundant and has a spin of $^5/_2$ and thus can be studied by nuclear quadrupole resonance spectroscopy. Further, when studying the ring and carbonyl ligands in the Cr(0), Mo(0), and W(0) series, no variation in the metal oxidation state is realized and hence no marked changes in the transfer of electron density occur.

The value of having metal spectroscopic data, in this case ^{55}Mn nqr data, to correlate with the more traditional spectroscopic techniques is illustrated by results for the monosubstituted cyclopentadienyltricarbonylmanganese(I) complex.[8-10] The correlation between the α and β ring proton chemical shift and the ^{55}Mn nqr frequencies for a number of $RC_5H_4Mn(CO)_3$ compounds reveals that the ring feels essentially the same effects due to R as the manganese atom.[8] Such a correlation is unlikely unless direct ground state interactions between R and Mn are small. Although resonance effects dominate, both resonance and inductive effects are felt by the Mn atom[8,10] which tends to support the idea that both the σ and π frameworks of the aromatic ring are involved with the metal orbitals.[2] Substitution of a carbonyl by another ligand leads to large changes in the ^{55}Mn nqr frequency which correlate with the traditionally accepted σ-donor and π-acceptor properties of the ligand as well as bearing some relation to the CO ir intensities.[9]

In this paper, we report the ^1H and ^{13}C nmr spectra of the ring in $(CH_3)_nC_6H_{6-n}Mn(CO)_3^+$ (n = 0-6) along with a study of the ^{55}Mn nqr and carbonyl ir data. Correlation of the nmr parameters with those in the corresponding Cr(0) analogs permits assessment of the effect of the metal oxidation state on the ring. The manganese atom and carbonyl data reflect the cumulative effect of the ring electron density as the number of methyl groups is increased. All of the spectroscopic results are found to be internally consistent.

Experimental Section

Syntheses. The method employed for the synthesis of $Mn_2(CO)_{10}$ was an amalgamation of two procedures described in the literature.[11,12]

$Mn_2(CO)_{10}$. To a 1-l. autoclave equipped with a motor-driven stirrer and a heating jacket were added 80 ml (0.50 mol) of π-methylcyclopentadienyltricarbonylmanganese(I) (Ethyl Corp. or Strem), 300 ml of carefully dried diglyme, and 34.0 g (1.48 mol) of sodium metal. The bomb was flushed twice with nitrogen and twice with CO (~100 psi) and then pressurized to 700 psi with CO. The reaction

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mixture was heated to 160-190° with stirring for a period of 10-14 hr. During the course of the reaction the bomb was repressurized several times with CO to speed the reaction.

When complete, the bomb was cooled to room temperature, vented, and flushed with nitrogen. The contents were transferred to a 1000-ml flask and cooled in an acetone-Dry Ice bath. While the flask was being flushed with a rapid stream of nitrogen, 50-100 ml of water were added slowly using an eyedropper. After the excess sodium was destroyed, enough water was added to bring the total H_2O volume to 300 ml. Ethanol (100 ml) was added followed by 150 ml of H_3PO_4. The phosphoric acid was added slowly with cooling. The mixture was allowed to stir for an additional 2 hr during which time crystals separated from the liquid. These were filtered and washed with hot water and then 100 ml of ethanol. The yellow-green crystals that remained were sublimed at 0.1 mm and 80° to give pure $Mn_2(CO)_{10}$. Yields ranged from 19.4 to 25.4 g (29-40%).

$Mn(CO)_5Br$. This compound was prepared from $Mn_2(CO)_{10}$ using the procedure of Abel and Wilkinson.[13]

Arenetricarbonylmanganese(I) Salts. The procedure of Winkhaus, *et al.*,[14] was employed for the synthesis of all complexes. In the *p*-xylene synthesis, the reaction temperature was carefully controlled to prevent a significant amount of rearrangement to other isomers. Carbon and hydrogen analysis were carried out by Chemalytics, Tempe, Ariz., or using a Hewlett-Packard Model 185B C, H, and N analyzer at the University of Delaware. Analyses were found to be in good agreement with theoretical values in all cases.

Nqr Spectra. The nqr spectra were recorded on a system which has been described before.[15] Digital errors in the measuring frequency are ±0.003 MHz; however, much larger errors (±0.03 MHz) may be incurred by selecting the wrong line of the resonance multiplet as the true center frequency. Experimentally, it is found that the $^3/_2 \leftrightarrow {}^1/_2$ transition is lower in intensity than the $^5/_2 \leftrightarrow {}^3/_2$ transition so that in some compounds only the high-frequency signal was observed. No resonances were detected in π-durenetricarbonylmanganese(I) tribromide or triiodide.

^{13}C Nmr Spectra. ^{13}C spectra were recorded on a Bruker HFX-90 FT spectrometer. All complexes (I_3^- salts) and free arenes were run at 0.5 *M* concentration in 10% acetone-d_6-5% TMS-85% acetone solutions. Acetone is the only solvent in which all the complexes are sufficiently soluble to obtain usable spectra. Free hexamethylbenzene and benzenetricarbonylmanganese(I) triiodide were run as saturated solutions because of their somewhat lower solubility. The spectrometer was deuterium locked, proton decoupled, and spectra are referenced to TMS with downfield shifts being taken as positive. The sweep width was 5000 Hz and digital resolution was one channel (0.11 ppm). The toluene and xylene complexes were also recorded at 1.5 *M* to check the concentration effect and it was found to be less than 1 ppm for those compounds.

^{1}H Nmr Spectra. All proton spectra were recorded on a Perkin-Elmer R-12 60 MHz spectrometer in acetone-d_6 solution and deuteriochloroform solution using TMS as an internal standard and lock. Spectra were recorded on the I_3^- complexes. The estimated error in the signals is ±0.03 ppm. The effects of concentration changes and the counterion were checked in the proton spectra and found to impart a maximum difference of 0.2 ppm in Δ. To test for the possibility of complex lability in solution, an acetone-d_6 solution of benzene and π-benzenetricarbonylmanganese(I) triiodide was studied. No shift or line broadening in either spectral line was detected.

Infrared Spectra. All ir spectra were recorded on a Perkin-Elmer 180 high-resolution spectrometer in 0.1-mm NaCl cells using acetone as the solvent. On expansion of the *y* coordinate in the region of interest (2200-1900 cm^{-1}), very weak absorption bands at 2143, 2067, and 1997 cm^{-1} due to acetone appear. Since intensity integration was not desired and the bands are very weak compared to the A_1 and E modes of the carbonyl complex, they do not interfere with the assignments.

Results and Discussion

Nqr Spectra. Because of its $^5/_2$ spin, two nqr transitions, $^1/_2 \leftrightarrow {}^3/_2$ and $^3/_2 \leftrightarrow {}^5/_2$, can be observed for ^{55}Mn. From these the nuclear quadrupole coupling constant, e^2Qq/h in MHz, and the electric field gradient asymmetry, η, can be computed for manganese. The coupling constant for the molecule is related to that of the atom by the d orbital populations on manganese according to

$$(e^2Qq/h)_{\mathrm{mol}} = (e^2Qq/h)_{\mathrm{atom}} \left| N_{\mathrm{d}_{z^2}} + \frac{N_{\mathrm{d}_{xz}} + N_{\mathrm{d}_{yz}}}{2} - N_{\mathrm{d}_{xy}} - N_{\mathrm{d}_{x^2-y^2}} \right| \qquad (1)$$

In this work, no absolute calculation of the coupling constant was attempted because of the number of orbital population variables. Equation 1 is derived assuming that the d_{z^2} orbital is coincident with the ring-metal axis. Since Mn(I) is d^6 and diamagnetic[16] it is reasonable to assume that the d_{xz} and d_{yz} orbitals on Mn will mix extensively with the arene MO's to form bonds. The d orbital electron density on Mn(I) will then reside primarily in the d_{z^2}, $d_{x^2-y^2}$, and d_{xy} orbitals. If this is the case, the terms within the absolute value sign in eq 1 will sum to a negative value. Increasing the electron releasing power of the ring would then have the effect of increasing $N_{\mathrm{d}_{xz}}$ and $N_{\mathrm{d}_{yz}}$ and thus decreasing the magnitude of $(e^2Qq/h)_{\mathrm{mol}}$. This proved not to be the case in the $C_5H_5Mn(CO)_3$ moiety.[8] There the resonance frequencies and consequently the coupling constants of Mn(I) increase as the ring becomes more electron rich. Such an occurrence can only take place if the positive population terms in eq 1 dominate. Table I reveals that the same distribution also exists in $(CH_3)_nC_6H_{6-n}Mn(CO)_3^+$. This finding indicates that there must be a substantial rearrangement of metal electron density onto the carbonyls and perhaps back onto the ring because a large negative charge would otherwise build up on the Mn(I) atom.

Comparison of $C_5H_5Mn(CO)_3$ to $C_6H_6Mn(CO)_3^+$ reveals some predictable differences. While the two rings are isoelectronic in terms of the number of π electrons, the cyclopentadienide ligand produces a considerably higher nqr frequency. As might be predicted, $C_5H_5^-$ appears to be the better electron donor of the two; however, it is not possible to rule out differences in their π^*-acceptor abilities as also contributing because assigning, quite reasonably, the better π^*-acceptor function to benzene[9] also would lead to the same frequency trend. Most likely, both effects contribute and clearly lead to a somewhat different orbital population distribution on manganese.

The symmetry of the benzene, mesitylene, and hexamethylbenzene complexes is such that ideally the electric field gradient asymmetry parameter, η, at manganese should be zero. The small values of η actually found no doubt result from packing distortions and electrostatic contributions from neighboring ions in the crystal lattice. The other arenes which do not have at least threefold symmetry appear to cause negligible perturbation to the axial symmetry of the ring-metal bond. Similar effects are observed for monosubstitution of the $C_5H_5Mn(CO)_3$ complex.[8,10]

The variable and uncertain contribution of the crystal lattice to the nqr parameters is a complicating feature of the nqr technique. Very little is known about crystal lattice effects on organometallic ions in nqr spectroscopy. Because of the potentially flexible nature of the ions, it could be rather large. Cations, however, might be expected to be somewhat less sensitive to crystal effects than similar anions because of their lower polarizability. For these compounds

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Table I. ^{55}Mn Nuclear Quadrupole Resonance Data (MHz) for $LMn(CO)_3{}^+X^-$ Salts at 298°K[a]

L	X^-	ν		e^2Qq/h	η
		$^3/_2 \leftrightarrow {}^1/_2$	$^5/_2 \leftrightarrow {}^3/_2$		
C_6H_6	$Br_3{}^-$	7.712 (8)	15.420 (14)	51.40	0.014
	$I_3{}^-$	7.910 (3)	15.819 (5)	52.73	0.007
	$BF_4{}^-$	7.750 (30)	15.463 (70)	51.56	0.043
	$ClO_4{}^-$	7.742 (40)	15.460 (60)	51.55	0.034
	$B(C_6H_5)_4{}^-$	7.898 (3)	15.726 (6)	52.45	0.059
$CH_3C_6H_5$	$Br_3{}^-$	8.111 (16)	16.198 (25)	54.00	0.036
	$I_3{}^-$	7.998 (8)	15.947 (20)	53.18	0.049
	$BF_4{}^-$	8.429 (12)	16.834 (45)	56.13	0.033
1,4-$(CH_3)_2C_6H_4$	$Br_3{}^-$		16.385 (7)		
1,3,5-$(CH_3)_3C_6H_3$	$Br_3{}^{-b}$	8.676 (6)	17.356 (10)	57.84	0.00
		8.733 (4)	17.490 (5)	58.22	0.00
	$I_3{}^{-b}$	8.628 (8)	17.225 (15)	57.42	0.039
			16.968 (4)		
	$BF_4{}^-$	8.283 (2)	16.537 (10)	55.14	0.037
$(CH_3)_5C_6H$	$Br_3{}^-$	9.004 (6)	17.953 (9)	59.87	0.049
	$I_3{}^-$		17.959 (2)		
	$BF_4{}^-$		17.338 (2)		
$(CH_3)_6C_6$	$Br_3{}^-$	9.334 (10)	18.544 (12)	61.88	0.072
	$I_3{}^-$	9.287 (16)	18.512 (19)	61.74	0.051
	$BF_4{}^-$	9.545 (25)	19.085 (27)	63.62	0.014
$C_5H_5{}^{-c}$		9.65	19.28	64.29	0.0

[a] Parenthetical numbers are signal-to-noise ratios. [b] Doublet due to crystallographically inequivalent cations. [c] Reference 8 and citations therein.

the crystal effect is impossible to assess quantitatively because of the lack of structural data. The only reasonable approach is to study a large number of salts containing different anions to see how large an effect lattice differences actually have. This was done for the $C_6H_6Mn(CO)_3{}^+$ ion. Table I shows that large changes in the size, symmetry, and charge density of the anion produce a range of only 3% in the ^{55}Mn coupling constants. The biggest effect occurs in the mesitylene series where the $^5/_2 \leftrightarrow {}^3/_2$ transition is affected by almost 8% of the overall effect. Thus, the crystal effect in these compounds seems to be about the same magnitude as that found in organic compounds[17] and somewhat smaller than that in inorganic hexachlorometalates.[18] More surprising is the fact that the axial symmetry of the molecule, as evidenced by the small values of η, is relatively unperturbed in spite of the different lattice symmetries.

In Figure 1 a plot of the $\pm{}^5/_2 \leftrightarrow {}^3/_2$ transition frequency was made *vs.* the number of methyl groups on the ring for the $Br_3{}^-$ and $I_3{}^-$ salts. Using the $BF_4{}^-$ data, the same trend is observed, but the points are much more aberrant perhaps because of interionic interactions. The transition frequency rather than the coupling constant was used because in some cases the $^3/_2 \leftrightarrow {}^1/_2$ transition was too weak to be observed. The cumulative effect of the electron releasing power of the methyl groups is quite linearly felt at the Mn(I) atom and suggests that Mn(I) has not yet begun to approach charge saturation even with the hexamethylbenzene ligand. The correlation is not expected to be exact because of the possibility that not all the salts are isostructural. There is also a qualitative correlation between the ^{55}Mn nqr frequencies and the photoionization energy[19] of the free arenes.

The hexamethylbenzene ring produces resonance frequencies close to those found for the cyclopentadienide ring although still somewhat less. However, the carbonyl stretching frequencies are considerably different (*vide infra*), and it is not reasonable to assume that $(CH_3)_6C_6$ closely approximates $C_5H_5{}^-$ in its *detailed* effects on the metal orbital populations.

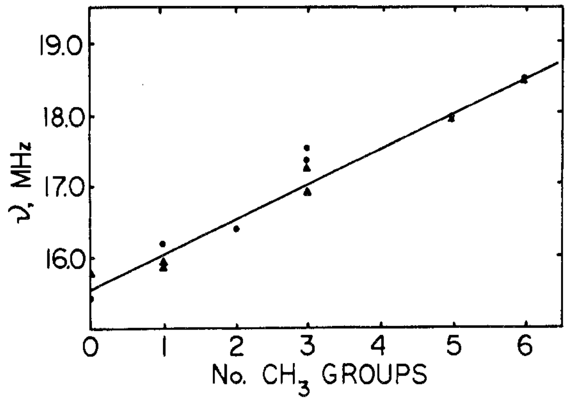

Figure 1. The correlation between the $\pm{}^3/_2 \leftrightarrow {}^5/_2$ nqr transition of ^{55}Mn for the $Br_3{}^-$ salts (●) and the $I_3{}^-$ salts (▲) and the number of methyl groups on the aromatic ring.

^{13}C Nmr Spectra. Cr(0), Mo(0), and W(0) arene carbon data have been reported previously[20,21] and reveal that the ring carbon atoms are more shielded in the complexes than they are in the free arenes. For example, in the benzene,[21] mesitylene,[20] and durene[20] complexes of these group VIb tricarbonyls the ^{13}C complex shift, Δ ($=\delta_{\text{uncomplexed}} - \delta_{\text{complexed}}$), is 30-37 ppm for the ^{13}CH carbons, 26-28 ppm for the ^{13}CMe carbons, and 0.1-0.6 for the $^{13}CH_3$ carbons. In Table II the Δ values for the Mn(I) series are reported. The chemical shifts for uncomplexed methylbenzenes in Table II have been reported before[22] but they were rerecorded so that the same solvent and concentration conditions could be used for all spectra. The free arene shifts are found to be in good, but not perfect, agreement with the published values.[22] It is noteworthy that the complex shift, Δ, is greater for the group VIb tricarbonyls than for $\text{-Mn}^{\text{I}}(CO)_3$. The origin of chemical shifts, particularly of ^{13}C in arene and olefin complexes, is a subject of some uncertainty.[20,21,23-26] Some of the most important factors appear to be paramagnetic effects (σ_P),[20,23,24] magnetic anisotropy of neighboring atoms,[25] and changes in the σ bond framework when an unsaturated molecule complexes with a metal.[23,26] Factors still important but less likely to produce large shifts include diamagnetic shielding (σ_d) and ring currents.[27,28] For carbon it may well emerge that no single concept can be used to account for the chemical shifts in all organometallic compounds, and for the present one is confined to discussing effects that are consistent with the data at hand while awaiting a sufficient body of ^{13}C data to evaluate their generality.

The dominant term in carbon chemical shifts is often sug-

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Table II. ^{13}C Nmr Chrmical Shifts[a] (ppm) for Free and Complexed Arenes Using I_3^- Salts

Compd	δ_{TMS}							Δ ($=\delta_{uncomplexed} - \delta_{complexed}$)						
	C_1	C_2	C_3	C_4	C_5	C_6	CH_3	C_1	C_2	C_3	C_4	C_5	C_6	CH_3
C_6H_6	129.2	129.2	129.2	129.2	129.2	129.2								
$C_6H_6Mn(CO)_3^+$	102.5	102.5	102.5	102.5	102.5	102.5		26.7	26.7	26.7	26.7	26.7	26.7	
$CH_3C_6H_5$	[138.4]	129.7	128.9	126.1	128.9	129.7	21.4							
$CH_3C_6H_5Mn(CO)_3^+$	[120.6]	100.9	103.5	98.2	103.5	100.9	20.7	[17.8]	28.8	25.4	27.9	25.4	28.8	0.7
$1,4-(CH_3)_2C_6H_4$	[135.2]	129.6	129.6	[135.2]	129.6	129.6	20.8							
$1,4-(CH_3)_2C_6H_4Mn(CO)_3^+$	[117.4]	101.4	101.4	[117.4]	101.4	101.4	19.4	[17.8]	28.2	28.2	[17.8]	28.2	28.2	1.4
$1,3,5-(CH_3)_3C_6H_3$	[138.1]	127.5	[138.1]	127.5	[138.1]	127.5	21.2							
$1,3,5-(CH_3)_3C_6H_3Mn(CO)_3^+$	[122.2]	97.5	[122.2]	97.5	[122.2]	97.5	20.6	[15.9]	30.0	[15.9]	30.0	[15.9]	30.0	0.6
$1,2,4,5-(CH_3)_4C_6H_2$	[133.9]	[133.9]	131.6	[133.9]	[133.9]	131.6	19.0							
$1,2,4,5-(CH_3)_4C_6H_2Mn(CO)_3^+$	[117.0]	[117.0]	102.2	[117.0]	[117.0]	102.2	20.2	[16.9]	[16.9]	29.4	[16.9]	[16.9]	29.4	−1.2
$(CH_3)_5C_6H$	[133.5]	[132.6]	[135.1]	[132.6]	[133.5]	129.8	20.6							
$(CH_3)_5C_6HMn(CO)_3^{+b}$	[113.7]	[107.6]	[115.8]	[107.6]	[113.7]	101.0	20.0	[19.8]	[25.0]	[19.3]	[25.0]	[19.8]	28.8	0.6
$(CH_3)_6C_6$	[132.5]	[132.5]	[132.5]	[132.5]	[132.5]	[132.5]	17.1							
$(CH_3)_6C_6Mn(CO)_3^+$	[114.3]	[114.3]	[114.3]	[114.3]	[114.3]	[114.3]	18.0	[18.2]	[18.2]	[18.2]	[18.2]	[18.2]	[18.2]	−0.9

[a] Bracketed values correspond to ring carbon atoms attached to CH_3 groups. [b] Assignments made on the basis of a consistency in shifts from the free durene.

Table III. The Difference Between ^1H Chemical Shifts for Uncomplexed and Complexed L in $LCr(CO)_3$ and $LMn(CO)_3^+I_3^-$ Complexes

	Δ, ppm ($=\delta_{uncomplexed} - \delta_{complexed}$)					
	CH			$-CH_3$		
L	Cr(0)[a]	Mn-(I)[b]	Mn-(I)[c]	Cr(0)[a]	Mn(I)[b]	Mn(I)[c]
C_6H_6	2.004		0.33			
$(CH_3)C_6H_5$	1.95[d]		0.24[d]	0.169	−0.30	−0.48
$1,4-(CH_3)_2C_6H_4$	1.824	0.53	0.13	0.176	−0.30	−0.43
$1,3,5-(CH_3)_3C_6H_3$	1.914	0.72	0.25	0.074	−0.35	−0.45
$1,2,4,5-(CH_3)_4C_6H_2$	1.648	0.49	0.03	0.082	−0.35	−0.46
$(CH_3)_5C_6H$	1.707	0.55	0.11	0.040[d]	−0.34[d]	−0.46[d]
$(CH_3)_6C_6$				0.014	−0.37	−0.40

[a] Calculated from data in ref 34 using $CDCl_3$ as the solvent. [b] This work using $CDCl_3$ as the solvent. [c] This work using acetone-d_6 as the solvent. [d] Average of a complex multiplet.

gested[29] to be σ_p which is proportional to three variables, ΔE^{-1}, $\langle r^{-3}\rangle_{2p}$, and ΣQ. ΔE is the mean excitation energy, $\langle r^{-3}\rangle_{2p}$ is the average of r^{-3} for the 2p electrons on C, and ΣQ contains elements of the atom charge and orbital overlap matrix for the molecule. It is rarely possible to accurately define these terms and thus the effect of σ_p is usually uncertain. However, qualitatively an increase in ΔE and/or r would cause σ_p to decrease and hence increase the shielding relative to the free arene. Upon complexation, ring $(\pi) \rightarrow$ metal electron migration would reduce the energy of the ring π orbitals and thus increase ΔE. The 2p orbitals on C would concomitantly be expected to contract as a result of the increased effective nuclear charge. The two effects oppose one another and thus tend to dampen the effect of σ_p. ΣQ variations related to a decrease in π-bond character of an arene upon complexation would cause an upfield shift[23] as is observed. However, in the present compounds it is surprising that Δ for Cr(0), Mo(0), and W(0) is so similar and that Mn(I) produces considerably *less* shielding than Cr(0) if σ_p dominates the complexing shift.

A more plausible explanation for the complex shift noted here lies in the effect of an electron-rich metal in close proximity to the carbon atoms. The magnetic anisotropy of a heavy atom near a resonant nucleus (*i.e.*, metal hydrides,[30] hydrogen halides,[31] σ-bonded organometallics[32]) is thought to produce the enormous shielding effect. Recently, this shielding has also been invoked to interpret ^{13}C shifts in Pd and Pt olefin complexes.[25] It might be expected that superimposed upon this shift would be some details of electron density changes at carbon. Mn(I) should produce less shielding at carbon than Cr(0) because the more electropositive element will have a counteracting deshielding effect by withdrawing electrons from the ring. The Δ values for the mesitylene and durene complexes of Cr(0)[20] and Mn(I) (Table II) show that the ^{13}CH carbons are 3-5 ppm less for Mn(I) than Cr(0) and the ^{13}CMe carbons are about 10 ppm less for Mn(I) than Cr(0). It is interesting that the ^{13}CMe carbons are deshielded more than the ^{13}CH carbons. It has been suggested from the proton nmr of the Cr(0), Mo(0), and W(0) analogs that more electron density is transferred to the metal from the CMe carbons than from the CH carbons of the ring.[33]

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The ^{13}C data suggest that on going from the Cr(0) to Mn(I) complex the CMe carbons sacrifice more electron density to the metal than do the CH carbons. The shift of the $^{13}CH_3$ signal upon complexation is small although in general it seems to be slightly larger in the Mn(I) complexes.

^1H Nmr Spectra. Proton nmr shifts for the Cr(0), Mo(0), and W(0) analogs of these Mn(I) complexes have been reported.[33,34] The shifts for the Cr(0) and Mn(I) compounds are shown in Table III. A significant solvent shift was found in acetone-d_6 when compared with $CDCl_3$. The same solvent effect has been noted for the Cr(0) analogs.[35] An interesting feature of the arene tricarbonyl Mn(I) spectra is that the ring protons are shifted only very slightly upfield from the uncomplexed arene. By contrast, in the Cr(0), Mo(0), and W(0) complexes the signals shift upfield by 2 ppm relative to the free arene.[33,34] Such behavior suggests that there may be competing effects operative. The 2-ppm upfield shift in group VIb complexes could result from the nearly complete quenching of the ring current by the metal tricarbonyl fragment.[34,35] However, an alternate explanation has been proposed which ascribes the shift to result largely from the magnetic anisotropy of the metal.[34] Both effects may in fact contribute. In the case of Mn(I), however, more electron density should be transferred to the metal than is the case with Cr(0), and this produces a deshielding effect which nearly cancels the heavy metal shielding or ring current quenching. In support of the substantially greater amount of e^- transfer to Mn(I), the methyl protons are deshielded by 0.3-0.5 ppm compared to those of the Cr(0) analog when $CDCl_3$ solution data were compared. Thus, the important features of both the ^1H and ^{13}C data are consistent with magnetic shielding of the ring arising from the close proximity of the transition metal coupled with a greater amount of ring → metal electron migration for Mn(I) compared to Cr(0). ^1H chemical shifts, unlike carbon, are not greatly affected by paramagnetic contributions and this lends additional support to the hypothesis that the σ_p is not dominating the complexing shift in these compounds. It must be emphasized, however, that considering the uncertainty in the origin of ^{13}C shifts, this explanation may not be the only reasonable one.

The constancy of the methyl proton chemical shift of about −0.35 ppm from toluene to hexamethylbenzene in the Mn(I) spectra suggests that each methyl group donates a roughly constant amount of electron density and that no saturation of electron density in the ring-metal system is reached. The same conclusion evolved from the ^{55}Mn nqr spectra above.

Table IV. Carbonyl Stretching Frequencies of $LMn(CO)_3{}^+I_3{}^-$ Salts in Acetone

L	ν_{CO}, (cm^{-1})	
	A_1	E
C_6H_6	2079	2023
$CH_3C_6H_5$	2076	2017
$1,4\text{-}(CH_3)_2C_6H_4$	2073	2010
$1,3,5\text{-}(CH_3)_3C_6H_3$	2070	2009
$1,2,4,5\text{-}(CH_3)_4C_6H_2$	2067	2008
$(CH_3)_5C_6H$	2065	2004
$(CH_3)_6C_6$	2061	1998
$C_5H_5{}^-$[a]	2024	1939

[a] Reference 9.

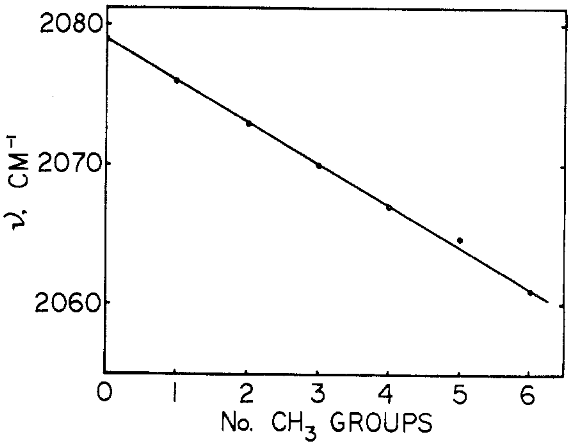

Figure 2. The correlation between $\nu_{CO}(A_1)$ and the number of methyl groups on the aromatic ring.

Ir Spectra. Carbonyl stretching data for the benzene-, toluene-, and mesitylenetricarbonylmanganese(I) perchlorates have been reported[14] and were found to be in reasonably good agreement with those found here. Of interest is the shift in the CO stretching frequency as a function of methyl substitution of the ring (Table IV). From the CO frequencies alone it is impossible to separate σ and π effects; however, as the metal electron density increases it is a widely established fact that the CO frequencies decrease.[36] Figure 2 shows that there is a linear and descending correlation between $\nu_{CO}(A_1)$ and the number of methyl groups on the ring. Fischer found a similar correlation with the Cr(0) analogs.[37] By the same token the correlation between the ^{55}Mn nqr frequencies and ν_{CO} in the Mn(I) complexes is excellent, suggesting that as the metal electron density increases it is transmitted in a corresponding fashion by the CO groups. A correlation between ^{59}Co nqr data and ν_{CO} has been noted in cobalt carbonyl compounds.[38]

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Registry No. C_6H_6, 71-43-2; $CH_3C_6H_5$, 108-88-3; $1,4\text{-}(CH_3)_2\text{-}C_6H_4$, 106-42-3; $1,3,5\text{-}(CH_3)_3C_6H_3$, 108-67-8; $1,2,4,5\text{-}(CH_3)_4C_6H_2$, 95-93-2; $(CH_3)_5C_6H$, 700-12-9; $(CH_3)_6C_6$, 87-85-4; $C_6H_6Mn(CO)_3{}^+Br_3{}^-$, 49564-30-9; $C_6H_6Mn(CO)_3{}^+I_3{}^-$, 49564-31-0; $C_6H_6Mn(CO)_3{}^+BF_4{}^-$, 49564-32-1; $C_6H_6Mn(CO)_3{}^+ClO_4{}^-$, 49564-33-2; $C_6H_6Mn(CO)_3{}^+B(C_6H_5)_4{}^-$, 49564-34-3; $CH_3C_6H_5Mn(CO)_3{}^+Br_3{}^-$, 49564-35-4; $CH_3C_6H_5Mn(CO)_3{}^+I_3{}^-$, 49564-36-5; $CH_3C_6H_5Mn(CO)_3{}^+BF_4{}^-$, 49564-37-6; $1,4\text{-}(CH_3)_2C_6H_4Mn(CO)_3{}^+Br_3{}^-$, 49564-38-7; $1,4\text{-}(CH_3)_2C_6H_4Mn(CO)_3{}^+I_3{}^-$, 49564-39-8; $1,3,5\text{-}(CH_3)_3C_6H_3Mn(CO)_3{}^+Br_3{}^-$, 49564-40-1; $1,3,5\text{-}(CH_3)_3C_6H_3Mn(CO)_3{}^+I_3{}^-$, 49564-41-2; $1,3,5\text{-}(CH_3)_3C_6H_3Mn(CO)_3{}^+BF_4{}^-$, 49564-42-3; $1,2,4,5\text{-}(CH_3)_4C_6H_2Mn(CO)_3{}^+I_3{}^-$, 49564-43-4; $(CH_3)_5C_6HMn(CO)_3{}^+Br_3{}^-$, 49564-44-5; $(CH_3)_5C_6HMn(CO)_3{}^+I_3{}^-$, 49564-45-6; $(CH_3)_5C_6HMn(CO)_3{}^+BF_4{}^-$, 49564-46-7; $(CH_3)_6C_6Mn(CO)_3{}^+Br_3{}^-$, 49564-47-8; $(CH_3)_6C_6Mn(CO)_3{}^+I_3{}^-$, 49564-48-9; $(CH_3)_6C_6Mn(CO)_3{}^+BF_4{}^-$, 49564-49-0; $Mn_2(CO)_{10}$, 10170-69-1; ^{13}C, 14762-74-4; Mn, 7439-96-5.

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