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# $^{55}$Mn NQR AND INFRARED INTENSITIES OF THE CARBONYL STRETCHING VIBRATIONS IN GROUP V AND OLEFIN DERIVATIVES OF CYCLOPENTADIENYLMANGANESE TRICARBONYL

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## SUMMARY

Carbonyl IR intensity and $^{55}$Mn NQR measurements are reported for a series of olefin and Group V donor atom derivatives of $C_5H_5Mn(CO)_3$. The ratio of infrared intensities of the symmetric and antisymmetric carbonyl stretching vibrations for most compounds are rather insensitive to changes in the donor ligand which suggests that the $\pi$-bonded ring acts as a buffer of the vibronic contributions that the ligand can make to the CO groups. This observation is consistent with previous results on $C_5H_5Fe(CO)_2L$ and $Co(CO)_2(NO)L$ systems. A simple MO calculation is presented for compounds of the type *cis*-$X_3M(CO)_2L$ which further supports this explanation. Details of the individual shifts in the intensity data are also presented. $^{55}$Mn NQR data for the Group V donor derivatives reveal that the $\nu(\pm 5/2 \rightleftarrows \pm 3/2)$ transition frequency parallels what is conventionally accepted as the trend in $\sigma$-donor ability and $\pi$-acceptor ability of the ligands. Within the olefin series the trend in the electric field gradient asymmetry parameter at manganese parallels the ring strain of the olefin.

## INTRODUCTION

The use of the frequencies of carbonyl stretching vibrations as a probe in the study of $\sigma$- and $\pi$-bonding in metal carbonyl derivatives has fallen into disrepute in recent years[1,2]. At the same time other probes, such as Raman intensities[3], $^{31}$P and $^{183}$W NMR[4], $^{13}$C NMR[5], photoelectron spectroscopy[6,7], $^{55}$Mn and $^{59}$Co NQR[8,9], and infrared intensity measurements[2,10–15] have been used to analyze bonding effects. However, all of these techniques suffer from the fact that the number of parameters influencing the observed results is large. This makes interpretation of the data in terms of simple bonding models often difficult or impossible.

Because of these problems, a given system can probably best be examined by use of a combination of techniques. Since different techniques are sensitive to different parameters, a comparison of the results for two techniques may indicate the strengths and weaknesses of each in investigating the metal–ligand bonding in metal carbonyls. With this in mind, we have measured the $^{55}$Mn NQR and the IR intensities of the carbonyl-stretching vibrations in a series of compounds of the type $C_5H_5Mn(CO)_2L$ (L = Group V donor ligand or an olefin).

## EXPERIMENTAL

Compounds were prepared by methods reported previously[16-19]. Melting points were in good agreement with published values[16-19], and all compounds gave good C, H analyses.

The NQR spectra were recorded using a Wilks NQR-1A spectrometer, and frequency measurements were made as described earlier[20]. Errors in the resonance frequencies are estimated to be ±0.015 MHz due to the difficulty of identifying the center peak of the resonance multiplet.

Infrared spectra were measured on a Perkin–Elmer Model 180 spectrophotometer using 1.0 mm NaCl cells. Spectra were recorded in the linear absorbance mode using a spectral slit width of 1.0–1.5 $cm^{-1}$, an expanded scale, and a scanning speed of 3.0–11 $cm^{-1}$ per minute.

The integrated absorption intensity of an infrared band is calculated from the expression

$$I = \frac{2.303}{cl} \int_{\nu_1}^{\nu_2} \log I_0/I \mathrm{d}\nu$$

where $c$ is the concentration, $l$ the path length of the cell (1.0 mm) and $\int_{\nu_1}^{\nu_2} \log I_0/I \mathrm{d}\nu$ is the area under the band between frequencies $\nu_1$ and $\nu_2$. The interval on either side of the peak maximum over which integration was carried out was chosen to be 3–4 times the width of the band at half height. No wing corrections were made. Areas were obtained using a planimeter. Intensity values reported are the average of 4–8 measurements in the concentration range $6 \cdot 10^{-4}$–$20 \cdot 10^{-4}$ $M$ in $CS_2$. Since the slopes of lines obtained by plotting the intensities of the two modes in each molecule as a function of concentration are nearly equal, there is little difference between the ratios obtained from the intercepts in the above plots and those obtained from the average value for the 4–8 measurements.

All computer calculations were carried out on a Burroughs 5500 computer at the University of Delaware.

## DISCUSSION

### *IR intensity measurements.*

The intensity ratio $I_s/I_a$ of the symmetric and antisymmetric stretching vibrations in metal dicarbonyl compounds is dependent upon the angle, $2\theta$, between the CO vibrators and upon intramolecular electronic effects[15]:

$$\frac{I_s}{I_a} = \left(\frac{\mu_s'}{\mu_a'} \cot \theta\right)^2 \qquad (1)$$

where $\mu_s'$ and $\mu_a'$ are the MCO dipole moment derivatives for the symmetric and antisymmetric carbonyl vibrations. In general, $\mu_s' \neq \mu_a'$, so that attempts[21] to calculate $\theta$ from IR intensities using the abbreviated equation $\frac{I_s}{I_a} = (\cot \theta)^2$ are invalid[11,22]. On the other hand if $\theta$ is known, the intensity ratio can be used to obtain the relative magnitudes of $\mu_s'$ and $\mu_a'$.

Information concerning the bonding in a metal carbonyl compound can be derived from the ratio $\mu_s'/\mu_a'$ in equation (1). Because of the competition for electron density by the two carbonyl groups during the symmetric stretch, $\mu_s'/\mu_a' < 1$ in the absence of appreciable vibronic contributions to $\mu_s'$[15,22]. If a good $\pi$-acceptor ligand is *trans* to the CO groups, vibronic contributions may increase $\mu_s'$ so that $\mu_s'/\mu_a' \geq 1$. Thus, the magnitude of $\mu_s'/\mu_a'$ is thought to be a measure of the bonding abilities of the ligands *trans* to CO[15,22]. This conclusion is supported in the tricarbonyl series by the fact that $\mu_s'/\mu_a' = 0.6$ for the compound $(CH_3)_5$dienMo$(CO)_3$[23] in which the pentamethylenetriamine group is incapable of $\pi$-bonding with the metal, while $\mu_s'/\mu_a' = 1.0$ for $C_6H_6Cr(CO)_3$[24] in which vibronic contributions can arise from the benzene ring. Recent molecular orbital calculations[25] also support this conclusion.

In the crystal structure of $C_5H_5Mn(CO)_3$[26] the three-fold axis of the $M(CO)_3$ linkage passes through the center of the cyclopentadienyl group. Thus, the $C_5H_5^-$ ligand can be considered effectively as a tridentate ligand occupying the three *fac* sites in the octahedron *trans* to the carbonyl groups. The $\mu_s'/\mu_a'$ value of 0.84 for $C_5H_5Mn(CO)_3$ is intermediate between that for $(CH_3)_5$dienMo$(CO)_3$ and that for $C_6H_6Cr(CO)_3$. This suggests that some vibronic contributions to $\mu_s'$ are present, but that the $C_5H_5^-$ group functions as a weaker $\pi$-acceptor ligand than does $C_6H_6$ in $C_6H_6Cr(CO)_3$[15,25,27].

In the simplest model the compounds $C_5H_5Mn(CO)_2L$ can be considered as structurally analogous to $C_5H_5Fe(CO)_2L$ derivatives simply by substituting a CO in $C_5H_5Mn(CO)_3$ by L and assuming no other appreciable change in geometry. In this model the L group is located *cis* to the carbonyls while the $C_5H_5^-$ group is located *trans* to the carbonyls. Crystal structures of $C_5H_5Mn(CO)_2P(C_6H_5)_3$* and $[\pi\text{-}CH_3\text{-}C_5H_4Mn(CO)_2]_2$diars[29] support this model. While crystal structures of other Group V donor atom derivatives of the type $C_5H_5Mn(CO)_2L$ have not been reported, values of $\theta$ obtained from the crystal structures of compounds of the type $C_5H_5Fe(CO)_2L$[30] suggest that the OC–M–CO angle is relatively insensitive to the nature of the L group. Nevertheless, it is important to point out that $\mu_s'/\mu_a'$ calculated from observed intensities varies by about 4% per degree variation in $\theta$ in the vicinity of 45–55°. Therefore, small changes in the $\mu_s'/\mu_a'$ ratio could be a result of an alteration in the angle $\theta$ rather than a change in the nature of the bonding in the compound.

Infrared intensity results and MCO dipole moment derivative ratios for several compounds of the type $C_5H_5Mn(CO)_2L$ are listed in Table 1. The most striking observation is the fact that $I_s/I_a$ and $\mu_s'/\mu_a'$ are essentially constant regardless of the nature of the ligand L. Among the dicarbonyl Group V derivatives, only $C_5H_5Mn(CO)_2Sb(C_6H_5)_3$ and $C_5H_5Mn(CO)_2As(OC_6H_5)_3$ have $\mu_s'/\mu_a'$ values which differ appreciably from other members of the series. A constant value of $\mu_s'/\mu_a'$ has been reported previously for the compounds $C_5H_5Fe(CO)_2L$ (L = Cl, I, CN, $SnCl_3$)[15]. Thus, it appears that $\pi$-acceptor ligands *trans* to the carbonyl groups in a pseudooctahedral complex tend to level the influence of $\pi$-bonding ligands *cis* to the carbonyls on vibronic contributions to $\mu_s'$. This is reflected in the fact that $\mu_s'/\mu_a'$ for $C_5H_5Mn(CO)_2NHC_5H_{10}$ is identical to the values for $C_5H_5Mn(CO)_2P(C_6H_5)_3$ and $C_5H_5Mn(CO)_2$-

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* We are indebted to a referee for informing us of this crystal structure[28].

TABLE 1

INFRARED INTENSITIES AND MCO DIPOLE MOMENT DERIVATIVE RATIOS FOR MANGANESE AND COBALT DICARBONYL COMPOUNDS

| $C_5H_5Mn(CO)_2L$ | $\nu_s{}^a$ | $\nu_a{}^a$ | $I_s{}^b$ | $I_a{}^b$ | $\mu_s'/\mu_a'{}^c$ |
|---|---|---|---|---|---|
| CO | 2024 | 1939 | 7.0(0.1) | 21.9(0.2) | 0.84 |
| $(C_4H_9)_3P$ | 1929 | 1863 | 9.2(0.1) | 11.6(0.2) | 0.93 |
| $(C_6H_5)_3P$ | 1934 | 1874 | 9.6(0.3) | 12.1(0.2) | 0.93 |
| $(C_6H_{11})_3P$ | 1928 | 1848 | 9.2(0.1) | 12.0(0.1) | 0.91 |
| $(C_6H_5O)_3P$ | 1963 | 1900 | 9.6(0.6) | 12.4(0.7) | 0.91 |
| $(C_6H_5)_3As$ | 1935 | 1872 | 9.8(0.1) | 12.2(0.1) | 0.93 |
| $(C_6H_5O)_3As$ | 1974 | 1918 | 10.1(0.4) | 10.9(0.1) | 1.00 |
| $(C_6H_5)_3Sb$ | 1934 | 1874 | 10.2(0.1) | 11.3(0.2) | 0.99 |
| $C_5H_{10}NH$ | 1920 | 1840 | 8.9(0.3) | 11.4(0.6) | 0.92 |
| Cyclopentene | 1958 | 1896 | 9.2(0.1) | 10.8(0.1) | 0.96 |
| Cycloheptene | 1958 | 1895 | 9.6(0.1) | 11.3(0.2) | 0.96 |
| Cyclooctene | 1956 | 1893 | 9.7(0.1) | 11.2(0.1) | 0.97 |
| Norbornylene | 1961 | 1900 | 8.8(0.1) | 11.0(0.1) | 0.93 |
| Norbornadiene | 1963 | 1903 | 8.9(0.1) | 11.6(0.1) | 0.91 |

| $Co(CO)_2(NO)L^e$ | $\nu_s{}^a$ | $\nu_a{}^a$ | $I_s{}^b$ | $I_a{}^b$ | $\mu_s'/\mu_a'{}^c$ |
|---|---|---|---|---|---|
| CO | 2101 | 2033 | 2.91 | 19.2 | 1.07 |
| $(C_6H_5)_3P$ | 2028 | 1971 | 6.17 | 10.4 | 1.09 |
| $(C_6H_5)_3P$ | 2035 | 1980 | 6.80 | 11.7 | 1.08 |
| $(C_6H_5O)_3P$ | 2061 | 2004 | 5.10 | 8.90 | 1.07 |
| $(C_6H_5)_3As$ | 2037 | 1982 | 6.37 | 11.5 | 1.09 |
| $(C_6H_5)_3Sb$ | 2036 | 1984 | 5.68 | 9.66 | 1.08 |

[a] $cm^{-1}$ in $CS_2$ ($\pm 1$ $cm^{-1}$). [b] In units of $10^4$ $l \cdot mole^{-1} \cdot cm^{-2}$. Numbers in parentheses are standard deviations from the mean. [c] Calculated from eqn. (1) using values of $\theta$ 46° for $C_5H_5Mn(CO)_2L$, $\theta$ 56° for $C_5H_5Mn(CO)_3$, $\theta$ 55° for $Co(CO)_2(NO)L$ and $\theta$ 70° for $Co(CO)_3NO$. [d] Intensity data have also been reported previously for this compound. [e] Data taken from ref. 13.

$P(OC_6H_5)_3$ even though piperidine is incapable of $\pi$-bonding to the metal, while the phosphines and phosphites are potential $\pi$-acids[22]. This interpretation is also consistent with the fact that $\mu_s'/\mu_a'$ for $C_5H_5Fe(CO)_2SnCl_3$ is no greater than that for $C_5H_5Fe(CO)_2Cl$ in spite of the fact that $SnCl_3^-$ is considered to be a better $\pi$-acceptor ligand[31].

In light of the good correlation between measured infrared intensities of the carbonyl stretching vibrations in $M(CO)_5L$ derivatives and those calculated from a simple molecular orbital model[25], similar molecular orbital calculations were carried out on the compounds *cis*-$M(CO)_2X_3L$, assuming a value of $-4.35$ eV for the energy of the *d* orbitals for an $M^0$ metal.

The model used, parameters, and method of calculating intensities were similar to those described previously[25,32]. The input parameter $\sigma$ corresponds to the fractional charge assumed to be donated to the central metal by the ligand in question (CO, L, X) through the $\sigma$ framework, while $\alpha$ corresponds to the energy of the $\pi$-acceptor orbital on the ligand. Although the energy assumed for the metal orbitals may not correspond to the actual energy for Mn, the observed trends within the framework of this simple model should be relatively independent of the metal *d* orbital energy.

TABLE 2

INFRARED INTENSITIES AND MCO DIPOLE MOMENT DERIVATIVES BASED ON MOLECULAR ORBITAL CALCULATIONS ON THE COMPOUNDS $X_3M(CO)_2L$

| $X$ | $L$ | $I_s{}^a$ | $I_a{}^a$ | $\mu'_s/\mu'_a{}^b$ |
|---|---|---|---|---|
| $\sigma$ 0.65<br>$\alpha$ $\infty$ | $\sigma$ 0.50<br>$\alpha$ $\infty$ | 0.47 | 14.9 | 0.18 |
| | $\sigma$ 0.50<br>$\alpha$ $-3.0$ | 1.44 | 14.6 | 0.31 |
| | $\sigma$ 0.50<br>$\alpha$ $-5.0$ | 2.38 | 13.9 | 0.41 |
| $\sigma$ 0.65<br>$\alpha$ $-3.0$ | $\sigma$ 0.50<br>$\alpha$ $\infty$ | 3.00 | 15.8 | 0.44 |
| | $\sigma$ 0.50<br>$\alpha$ $-3.0$ | 2.74 | 15.6 | 0.42 |
| | $\sigma$ 0.50<br>$\alpha$ $-5.0$ | 2.42 | 14.7 | 0.41 |

[a] In units of $10^4$ l·mole$^{-1}$·cm$^{-2}$. [b] Calculated from eqn. (1) assuming $\theta$ 45°.

Values of $\mu'_s/\mu'_a$ were determined from the calculated intensities using equation (1).

Results in Table 2 suggest that if the ligands X are incapable of $\pi$-bonding, the magnitude of $\mu'_s/\mu'_a$ increases significantly as the acceptor ability of L increases. Thus, vibronic contributions to $\mu'_s$ can arise from ligands *cis* to CO as well as those *trans* to CO. On the other hand, if X serves as a $\pi$-acceptor ligand, the $\mu'_s/\mu'_a$ value is relatively insensitive to the nature of L. The latter conclusion is consistent with the experimental intensity results for $C_5H_5Mn(CO)_2L$ and $C_5H_5Fe(CO)_2L^{15}$.

The high $\mu'_s/\mu'_a$ value for $C_5H_5Mn(CO)_2As(OC_6H_5)_3$ along with the high carbonyl stretching frequencies[17] and low value of $I_a$ suggest that $As(OC_6H_5)_3$ is a particularly good $\pi$-acceptor ligand. The low $I_a$ value arises because of the decrease in electron density in the $M(CO)_2$ fragment of the molecule when L is a good $\pi$-acceptor[15,22]. The reason for the high $\mu'_s/\mu'_a$ ratio for $C_5H_5Mn(CO)_2Sb(C_6H_5)_3$ is unclear. Since structural changes, particularly variations in the angle $\theta$, affect $\mu'_s/\mu'_a$, the observed result may be due to geometrical rather than electronic factors.

The $\mu'_s/\mu'_a$ ratios for the cyclic olefin derivatives are somewhat higher than those for the Group V derivatives suggesting somewhat larger vibronic contributions to $\mu'_s$ in the case of the olefins. It is not clear whether this enhancement arises from increased backbonding to the $C_5H_5^-$ group or from appreciable backbonding to the olefinic ligand. The slightly lower $\mu'_s/\mu'_a$ ratios for the bridgehead olefins than for the non-bridgehead olefins is most likely a result of geometrical differences which arise when a bridgehead carbon is present. In fact the structure of $C_5H_5Mn(CO)_2$(norbornadiene)[33] is considerably different from those of the $C_5H_5$-$Mn(CO)_2L$ derivatives mentioned earlier.

It is interesting to compare the infrared intensity results for the series $Co(CO)_2$-$(NO)L^{13}$ with those for the series $C_5H_5Mn(CO)_2L$. In all cases $\mu'_s/\mu'_a > 1$ for the cobalt compounds, indicating sizeable vibronic contributions to $\mu'_s$. This result is not unexpected considering the good $\pi$-acceptor character of the NO group. In addition, the pseudotetrahedral geometry allows vibronic contributions to arise from the group L in the dicarbonyl compounds. The lack of sensitivity of $\mu'_s/\mu'_a$ to the nature of L, however, suggests that the principal vibronic contribution to $\mu_s'$ arises from the nitrosyl group while the effect of the L group is leveled out.

### *NQR spectra*

$^{55}$Mn has a nuclear spin of 5/2. Thus, two signals, $\nu(\pm 5/2 \rightleftarrows \pm 3/2)$ and $\nu(\pm 3/2 \rightleftarrows \pm 1/2)$, should appear. From these it is possible to compute the NQR coupling constant, $e^2Qq/h$, and the electric field gradient asymmetry parameter, $\eta$. $\eta$ can vary between 0 and 1. In practice it was found that if the signal-to-noise ratio of the high frequency transition was less than about 8/1, the low frequency signal could not be assigned with certainty. For this reason $e^2Qq/h$ and $\eta$ could be extracted for only about half the olefin derivatives studied and for none of the Group V atom derivatives. Very qualitatively, however, the high frequency $^{55}$Mn transition mimics the coupling constant even though the transition frequency is sensitive to $\eta$. A change in $\eta$ from 0.0 to 0.5 causes less than a 5% decrease in a frequency of 19.0 MHz. Data are compiled in Table 3.

In the cycloolefin series, the large values of $\eta$ demonstrate that there is a sizable asymmetric distortion in the arrangement of electron density about the manganese atom. The parent compound, $C_5H_5Mn(CO)_3$, has axial electric field gradient sym-

TABLE 3

$^{55}$Mn NQR DATA IN $\pi$-$C_5H_5Mn(CO)_2L$ COMPOUNDS AT 298 K[a] IN MHz

| L | $\nu(\pm 5/2 \rightleftarrows \pm 3/2)$ | $\nu(\pm 3/2 \rightleftarrows \pm 1/2)$ | $e^2Qq/h$ | $\eta$ |
|---|---|---|---|---|
| CO (ref. 35) | 19.29 | 9.65 | 64.29 | 0.0 |
| *cis*-Cyclooctene | 17.93(25) | 11.12(8)<br>11.15(8) | 61.93 | 0.45 |
| Cyclopentene | 18.33(20) | 10.87(4) | 61.61 | 0.39 |
| Cycloheptene | 17.81(16) | 11.27(4)<br>11.23(4) | 60.77 | 0.35 |
| Vinylene carbonate | 16.63(25) | 10.70(8) | 57.82 | 0.49 |
| Norbornylene | 18.96(8) | — | | |
| Endic anhydride[b] | 17.90(5) | — | | |
| 1,2,3,6-Tetrahydrophthalic anhydride | 17.69(4) | — | | |
| 2,5-Norbornadiene | 17.27(3) | — | | |
| Piperidine | 17.18(3) | — | | |
| Pyridine | 17.62(4) | — | | |
| $C_6H_5CN$ | 18.22(6) | — | | |
| $CH_3CN$ | 18.71(6) | — | | |
| | 18.63(6) | — | | |
| $P(CH_3)_3$ | 18.13(4) | — | | |
| $P(i\text{-}C_3H_7)_3$ | 18.44(4) | — | | |
| $P(n\text{-}C_4H_9)_3$ | 18.66(5) | — | | |
| $P(C_6H_5)_3$ | 18.82(3) | — | | |
| $P(OC_6H_5)_3$ | 19.78(8) | — | | |
| $As(C_6H_5)_3$ | 19.38(5) | — | | |
| $As(OC_6H_5)_3$ | 20.92(6) | — | | |
| $Sb(C_6H_5)_3$ | 19.78(6) | — | | |

[a] Parenthetical numbers are signal-to-noise ratios. [b] *endo,cis*-Bicyclo[2.2.1]-5-heptene-2,3-dicarboxylic anhydride.

metry. It is impossible to develop a detailed bond model to describe the distortion because of unknown and possibly somewhat variable orientation of the electric field gradient principal axes. However, it may be important that the trend in decreasing $\eta$ for the *cis*-cyclooctene, cyclopentene, cycloheptene series parallels an increase in the olefin ring strain[34], and also parallels the decreasing rate that the olefin is replaced by $P(C_6H_5)_3$[18]. As the strain within the olefin increases, the strength of the Mn–olefin bond which acts to relieve the strain, increases[18]. Vinylene carbonate, which should be a relatively poor $\sigma$-donor compared to the other olefins, has the highest $\eta$ value.

In contrast to the IR intensity results, the NQR frequencies for the Group V donor atom derivatives are sensitive to the nature of the L group. The trend in the frequencies roughly parallels the conventionally accepted trend in both $\pi$-acceptor and $\sigma$-donor abilities of the ligands. Whether or not $e^2Qq/h$ will also parallel these trends must await the detection of $\nu(\pm 3/2 \rightleftarrows \pm 1/2)$. For instance the order of decreasing $\pi$-acceptor ability and increasing $\sigma$-donor ability among nitrogen donor ligands follows the sequence nitrile, pyridine, piperidine. The NQR frequencies for derivatives of these compounds decrease in the same order. The trend in resonance frequencies for phosphorus donor atom ligands, namely $P(OC_6H_5)_3 > P(C_6H_5)_3 > P(alkyl)_3$, is also that for $\pi$-acceptor ability and the reverse of the trend in $\sigma$-donor ability. The highest NQR frequency observed results from $C_5H_5Mn(CO)_2As(OC_6H_5)_3$, suggesting that $As(OC_6H_5)_3$ is a particularly good $\pi$-acceptor ligand or a particularly weak $\sigma$-donor. This is consistent with the high carbonyl stretching frequencies and unique infrared intensity results for $C_5H_5Mn(CO)_3As(OC_6H_5)_3$ in comparison with the $P(OC_6H_5)_3$ derivative. Whereas there is a smooth trend in NQR frequencies in the sequence $Sb(C_6H_5)_3 > As(C_6H_5)_3 > P(C_6H_5)_3$, the IR intensity data show the phosphine and arsine to be similar, but different from the stibine.

As with the olefins it is extremely difficult to identify the precise reasons of the detailed shifts in all of the Group V compounds because, in addition to competitive Mn–L bonding differences, there are geometric factors which can be variable. A method used for analyzing bond trends resulting from ring substitution in the parent compound, $\pi$-$C_5H_5Mn(CO)_3$, is valid when near axial symmetry is maintained at the manganese atom[9]. There it was assumed that the $d_{z^2}$ orbital of manganese points into the center of $C_5H_5^-$ ring; thus the $d_{xz}$ and $d_{yz}$ orbitals are used in large portions in the MO's employed for $\sigma$-bonding with the $C_5H_5^-$ ring and the CO groups. The $d_{xy}$ and $d_{x^2-y^2}$ orbitals have largely $\pi$ and $\delta$ bonding symmetry. The $^{55}Mn$ resonance frequency then varies proportionally with the population of the $d$ orbitals according to $[N_{d_{z^2}} + (N_{d_{xz}} + N_{d_{yz}})/2 - N_{d_{x^2-y^2}} - N_{d_{xy}}]$. This bracketed quantity has been shown[9] to have positive sign in $C_5H_5Mn(CO)_3$. Although axial symmetry is not maintained when a ligand, L, replaces a carbonyl group, the equation predicts that an increase in Mn→L $\pi$-bonding will result in the observed higher resonance frequency. A decrease in Mn←L $\sigma$-bonding should result in lower frequency according to the bracketed quantity, however. The frequency differences are small, hence a non-negligable fraction of the variations could result from intermolecular interaction and packing effects which change from compound to compound.

It is clear from our results that the NQR and IR intensity measurements show different trends as the ligand is varied. This undoubtedly arises from the fact that $^{55}Mn$ NQR spectroscopy makes use of a probe atom directly involved in the Mn–L bond, whereas the carbonyl intensities are a more indirect probe. In the intensity results, other ligands can buffer the potential effects of L. In the NQR results the ligands directly affect the probe site. Unfortunately, the NQR data seem to be complicated by a greater variety of molecular changes which makes their interpretation difficult.

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