Figure 3. A point-charge model calculation of the asymmetry parameter of X as a function of nonlinearity of the MXM unit as shown. The principal axis of the electric field gradient is also indicated as a function of the angle (y is perpendicular to the MXM unit).

A less clear correlation exists in the bismuth chloride series. The Bi–Cl bond lengths are 2.47–2.52, 2.50–2.52, and 2.52[23] or 2.66 Å[24] in $BiCl_3$, $BiCl_4^-$, and $BiCl_6^{3-}$, respectively, and the ^{35}Cl resonance frequencies for terminal linkages in this series fall in the ranges of 19.1–15.4, 15.4–13.5, and 13.3–12.6 MHz.

The electronic structure of the bridging halogen atoms is difficult to establish because of their nonaxially symmetric electric field gradient tensor. The ratio of the resonance frequency for terminal to bridging halogen atoms covers a broad range in these compounds. The difference in Bi–Br–Bi angles ranging from 90–97° in $BiBr_4^{-}$ [19] to 82–85° in $Bi_2Br_9^{3-}$ [25] contributes to some of this variation, particularly as the angle approaches 70 or 110°. Figure 3 is based on the point-charge

model[41] and shows the effect of changes in the bridge angle on the asymmetry parameter of the bridging element. The halogen resonance frequency can change to 16% as the angle changes. Other factors, such as bond length and the number of bridging vs. terminal halogen atoms, play a role in the electric field gradient of the bridging halogen atom.

The most interesting electronic feature of the Bi(III) core is the effect of the $6s^2$ electron pair. This effect can be most directly noted when Bi(III) is compared to Sb(III) and Tl(III) in structurally similar compounds. In $M_2Br_9^{3-}$ salts, the electric field gradient of the terminal bromine atoms is greater in Sb(III)–Br bonds than in Bi(III)–Br bonds, reflecting the greater covalency of the Sb–Br bonds compared to that of Bi–Br bonds.

The presence of the $6s^2$ electron pair in Bi(III) may be used to rationalize the electric field gradient differences in $Bi_2Cl_9^{3-}$ compared to $Tl_2Cl_9^{3-}$.[38] The terminal Tl–Cl bonds appear to be much more covalent than the Bi–Cl bonds because Bi(III) experiences reduced effective nuclear charge as a result of the presence of the $6s^2$ pair.

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Electronic Structure Properties of Exo-Substituted Cyclohexadienylmanganese Complexes Based on ^{55}Mn NQR Spectroscopy

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The series of tricarbonylcyclohexadienylmanganese(I) complexes, $C_6H_6XMn(CO)_3$, X = H⁻, $CH(CO_2C_2H_5)_2^-$, and CN⁻, have been examined by ^{55}Mn NQR spectroscopy. The very large value of the electric field gradient asymmetry parameter results from a difference in population of the d_{xz} and d_{yz} orbitals on manganese. The asymmetry parameter in this series of compounds is inversely proportional to the coupling constant which can only occur if the difference in the population of these two orbitals remains constant. Comparison of calculated transition probabilities to theoretical values for the $\pm^5/_2 \leftrightarrow \pm^3/_2$ and $\pm^3/_2 \leftrightarrow \pm^1/_2$ transitions of ^{55}Mn show the same trend and provide support for Cohen's tables. A forbidden transition for ^{55}Mn was observed for what we believe is the first time by using a superregenerative oscillator.

Introduction

The electronic structures of cyclohexadienyl transition-metal tricarbonyl complexes have come under scrutiny by using theoretical methods with an eye to understanding their geometric deformations,[1] reactivity,[2] NMR spectra,[3] and place in the scheme of metal-ring fluxionality.[4] Although NMR spectroscopy is useful for studying the ring,[3] experimental

methods capable of probing small changes in the ground-state electronic properties of the metal in these complexes are less handy. This fact limits the availability of data with which one might explain the behavior of the complexes and analyze the theoretical conclusions. Nuclear quadrupole resonance spectroscopy is a potentially useful technique for examining small changes in the electronic structure of metals. It has been applied to an increasing extent to this role.[5]

In this project the electric field gradient properties of the metal atom in tricarbonylcyclohexadienylmanganese(I), **1**,

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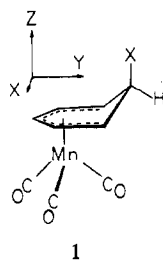
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have been probed by using ^{55}Mn NQR spectroscopy. Substitution of the ring at the exo position of the methylene carbon might modulate the electron density at the metal in a way that provides experimental information about the orbital usage in the complex. The ^{55}Mn NQR spectrum reflects the changes in the electron distribution among the metal orbitals.

Experimental Section

exo-$C_6H_6XMn(CO)_3$ complexes (X = H$^-$, CN$^-$, CH(CO$_2$C$_2$H$_5$)$_2^-$) were prepared by methods described in the literature.[6-8] The complex where X = C$_6$H$_5^-$ was also prepared[9] but failed to yield NQR data. All of the syntheses gave yellow crystalline products whose NMR and IR spectra compared favorably with the literature data.

exo-$C_6H_7Mn(CO)_3$ can be recrystallized very effectively by dissolving the complex in a minimum amount of warm methanol and filtering to remove insoluble decomposition products. The filtrate was then poured into ice-cold distilled water. The flocculent pale yellow crystalline precipitate was isolated by filtration and dried over P$_2$O$_5$ under vacuum.

The NQR spectra were obtained on a spectrometer system which has been described before.[10] Uncertainty in the measurement of the center line of the resonance multiplet produces a possible error of about 0.01 MHz in the resonance frequency. The nuclear quadrupole coupling constant and asymmetry parameter for ^{55}Mn were then calculated from the eigenvalue equation[11] for $I = {}^5/_2$ by using a computer program.[12]

Results and Discussion

The crystal structures of tricarbonylcyclohexadienyl-manganese(I)[13] and tricarbonyl[(bis(ethoxycarbonyl)-methyl)cyclohexadienyl]manganese(I)[14] show the ring to be nonplanar and the entire complex to have the structure of **1**. The ^{55}Mn atom possesses an $I = {}^5/_2$ nucleus so that two NQR transitions are observed. The electric field gradient at manganese can be interpreted in terms of the population of the d orbitals on manganese. Equation 1 relates the coupling

$$(e^2Qq/h)_{mol} = (e^2Qq/h)_{at}[N(d_{z^2}) + (N(d_{xz}) + N(d_{yz}))/2 - N(d_{xy}) - N(d_{x^2-y^2})] \quad (1)$$

constant in the molecule to the atomic coupling constant according to the orbital electron populations, N. When this equation is used, the z principal axis of the electric field gradient tensor is assumed to coincide with the principal axis of the d_{z^2} orbital. This condition probably does not exist in structure **1**. On the other hand, symmetry requires that the z principal axis lie on the mirror plane of the molecule. It is likely to cant toward the center carbon atom in the π-electron ribbon. The d_{z^2} orbital also will lie in this mirror plane but not necessarily in the same axis system as the EFG tensor. Hence we cannot apply eq 1 to these complexes in a quantitative way. It can be applied qualitatively because information

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Table I. ^{55}Mn NQR Data at 300 K

compd	$\pm^3/_2 \leftrightarrow \pm^1/_2$	$\pm^5/_2 \leftrightarrow \pm^3/_2$	e^2Qq/h	η
$C_6H_7Mn(CO)_3$,[a]	9.457 (100)	14.363 (125)	50.156	0.518
$C_6H_6CH(CO_2C_2H_5)_2Mn(CO)_3$	10.133 (3)	13.385 (4)	48.267	0.668
$C_6H_6CNMn(CO)_3$	10.400 (14)	13.311 (16)	48.012	0.712
$C_6H_6Mn(CO)_3^+X^-$,[b]			51.94	0.031
$C_5H_5Mn(CO)_3$,[c]			64.29	0.0

[a] The forbidden $\pm^5/_2 \leftrightarrow \pm^1/_2$ transition was observed at 23.827 (2) MHz. [b] Average of five compounds from ref 16. [c] Reference 15.

on similar, but higher symmetry, complexes such as C_5H_5-$Mn(CO)_3$ and $C_6H_6Mn(CO)_3^+$ is available.[15,16] A brief discussion of the salient features of these latter two complexes is pertinent to analyzing the cyclohexadienyl systems.

$C_6H_6Mn(CO)_3^+$ and $C_5H_5Mn(CO)_3$ are respectively axially symmetric and pseudoaxially symmetric molecules. The z principal axis of the manganese electric field gradient tensor coincides with the d_{z^2} orbital and points into the center of the ring. By placing various substituents on the ring, we have determined that the bracketed quantity in eq 1 carries a positive sign.[15,16] Of course, this arises from the fact that the sum of the populations of the d_{z^2}, d_{xz}, and d_{yz} orbitals is greater than that of the $d_{x^2-y^2}$ and d_{xy} orbitals. According to the nuclear quadrupole coupling constant values, the C_6H_6 ring in $C_6H_6Mn(CO)_3^+$ donates about 0.2 fewer electrons to the $Mn(CO)_3^+$ fragment than the $C_5H_5^-$ ring donates in C_5H_5-$Mn(CO)_3$. This analysis assumes that the extent of metal-to-ring back-bonding is about the same in the two. The trend in the CO stretching frequencies in these two compounds is compatible with this direction of electron shift.[16]

$C_6H_7Mn(CO)_3$ differs from $C_5H_5Mn(CO)_3$ and C_6H_6Mn-$(CO)_3^+$ in that the axial symmetry of the molecule is destroyed, giving rise to a nonzero asymmetry parameter in the electric field gradient at manganese. The asymmetry parameter is related to the d orbital populations according to eq 2. The

$$\eta = \{{}^3/_2[N(d_{xz}) - N(d_{yz})]/(e^2Qq/h)_{mol}\}(e^2Qq/h)_{at} \quad (2)$$

relative importance of the d_{z^2} and d_{yz} metal orbitals (on the mirror plane) in the cyclohexadienyl–metal bond probably differs somewhat from that in the benzene and cyclopentadienyl rings.

Comparison of the NQR data for $C_6H_7Mn(CO)_3$ and $C_6H_6Mn(CO)_3^+$ shown in Table I reveals that the coupling constant decreases and η increases when the ring is reduced. The nonzero asymmetry parameter is mostly a result of the difference in the population between the d_{xz} and d_{yz} orbitals in $C_6H_7Mn(CO)_3$. We feel that symmetry plays a lesser role in the asymmetry parameter because only small values of η are observed in $C_4H_4NMn(CO)_3$[17] and in ring-substituted $C_5H_5Mn(CO)_3$ compounds.[15] The large values of η in $C_6H_6XMn(CO)_3$ are somewhat deceptive because they do not result from a large difference in the population of the d_{xz} and d_{yz} orbitals. In fact, the difference in the orbital population is computed to be only about 0.1 electron by assuming $(e^2Qq/h)_{at}$ for ^{55}Mn is about 200 MHz.[18] This is a result of the fact that $(e^2Qq/h)_{mol}$ has a rather small value in these complexes. The molecular orbital calculations of Whitesides et al. show a comparable difference ($\sim$0.2 e) between the populations of these two orbitals.[19]

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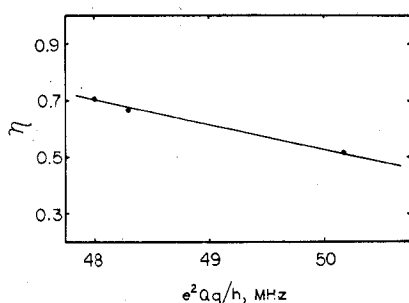(19) T. H. Whitesides, personal communication.

Figure 1. The relationship between the ^{55}Mn electric field gradient asymmetry parameter and the coupling constant.

The molecular orbital calculations of Hoffmann and Hofmann[1] suggest that the out-of-plane deformation involving the CH_2 unit of the ring in $C_6H_7Mn(CO)_3$ results from an electronic factor. The phase of the contribution of hydrogen in the CH_2 unit to the ring MO's is opposite that of the metal d_{yz} orbital. As a result, a secondary repulsive interaction occurs between the metal and the CH_2 group. The orbital combination shown in structure **2** depicts this destabilizing interaction.
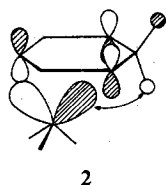
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Experimental evidence for orbital contact between the metal atom and the CH_2 group is not particularly easy to extract. Our approach was to substitute the ring at the exo position of the CH_2 group and then measure the effect this has on manganese electric field gradient. If direct orbital contact exists, then the manganese EFG might be altered in a more dramatic way than if the electronic character of the substituent is transmitted through the saturated bonds in the ring. We were somewhat limited by the availability of compounds of this type, but $C_6H_6XMn(CO)_3$ (X = H⁻, CN⁻, CH($CO_2C_2H_5)_2$⁻) were prepared in high enough yield to permit a study by NQR spectroscopy.

The asymmetry parameter, η, is sensitive to the difference in the population of orbitals in the xz and yz plane. For this reason it is possible that η will be sensitive to the contact shown in structure **2**. The values of η increase in the series X = H⁻, CH($CO_2C_2H_5)_2$⁻, and CN⁻, but this is accompanied by a small and proportional decrease in $(e^2Qq/h)_{mol}$. The inverse relationship is shown in Figure 1. Equation 2 reveals that e^2Qq/h and η will be inversely proportional only if the difference in orbital population between d_{xz} and d_{yz} is constant through the series. Consequently, the relative population of the manganese orbitals does not appear to be affected in any significant way by substitution of the ring at the exo position. As to how much effect on the orbital populations substitution at the exo position should have with and without orbital contact, we do not know, but it is apparent that the metal orbital populations are not altered when the ring is substituted in this way. Therefore, the results do not prove or disprove the orbital contact proposal, although they do suggest that the substituent site preference (endo or exo) at the saturated position does not undergo direct electronic control by the metal. The decrease in the EFG

Table II. Comparison of Experimental and Theoretical Transition Probabilities for a Series of Olefin–Manganese Tricarbonyl Compounds

η	$\nu_1 = \pm^3/_2 \leftrightarrow \pm^1/_2$		$\nu_2 = \pm^5/_2 \leftrightarrow \pm^3/_2$		ν_1/ν_2	
	W_{exptl}	W_{theor}	W_{exptl}	W_{theor}	W_{exptl}	W_{theor}
0.0^a	0.28	2.64	0.13	1.66	2.2	1.59
0.5^b	1.06	2.18	0.61	1.65	1.7	1.32
0.7^c	0.14	1.97	0.09	1.67	1.5	1.18

^{a} Average of $C_6H_6Mn(CO)_3^+$ salts of Br$_3^-$, I$_3^-$, BF$_4^-$, ClO$_4^-$, B(C$_6$-H$_5)_4^-$.[16] ^{b} $C_6H_7Mn(CO)_3$. ^{c} $C_6H_6CNMn(CO)_3$.

observed at ^{55}Mn for X = H⁻, CH($CO_2C_2H_5)_2$⁻, and CN⁻ is in keeping with the withdrawal of electron density in this series by an inductive mechanism through the saturated bonds of the ring.

The series of compounds in Table I offers an opportunity to test a theory proposed 25 years ago by Cohen[20] concerning the relationship of the intensity of NQR signals to the EFG asymmetry parameter. The signal-to-noise ratio, I, of a resonance line is related to the transition probability, W, between two energy levels and the frequency of the signal, ν, according to eq 3. The transition probability depends upon η. In the

$$I = \nu^2 W \tag{3}$$

series of compounds $C_6H_6Mn(CO)_3^+$ and $C_6H_6XMn(CO)_3$ the values of η change dramatically but do so without a drastic structural change in the complex. Hence the total electric field gradient changes symmetry without undergoing a comparable change in magnitude. We can calculate from the experimental data values of W and compare them to Cohen's theoretical values. To eliminate factors such as instrumental bias, differences in coil filling factors, etc., we achieve a much more satisfactory comparision between experimental and theoretical values by comparing the *ratio* of I/ν^2 for the $\pm^3/_2 \leftrightarrow {}^1/_2$ transition and the $\pm^5/_2 \leftrightarrow \pm^3/_2$ transition to the ratio of W values taken from Cohen's tables for these transitions. This can be done for each value of η, and the results are tabulated in the last column of Table II. The correlation between the calculated and observed ratios is not quantitative, but it is apparent that the trend is followed. In practice the general improvement in the signal-to-noise ratio of the $\pm^3/_2 \leftrightarrow \pm^1/_2$ transition of manganese as η becomes larger allowed us to observe the weak signals in $C_6H_6CH(CO_2C_2H_5)_2Mn(CO)_3$ in this study and also in $C_5H_5Mn(CO)_2$·olefin complexes in earlier work.[21] In other $C_5H_5Mn(CO)_2$·L complexes, we could not detect the $\pm^3/_2 \leftrightarrow \pm^1/_2$ transition presumably because η is small. At least in this limited series Cohen's tables give a satisfactory description of the trend in signal-to-noise ratios as a function of η for an $I = {}^5/_2$ nucleus.

The high intensity of the signals in $C_6H_7Mn(CO)_3$ combined with the large value of η permitted detection of the forbidden $\pm^5/_2 \leftrightarrow \pm^1/_2$ transition in that compound. To our knowledge this is the first time that a $\Delta m_I = \pm 2$ transition has been observed for an $I = {}^5/_2$ nucleus by using a superregenerative oscillator.

Registry No. $C_6H_7Mn(CO)_3$, 12108-14-4; $C_6H_6CNMn(CO)_3$, 72580-16-6; $C_6H_6CH(CO_2C_2H_5)_2Mn(CO)_3$, 50725-63-8.

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