strengths of electron-transfer bands, proton association constants, formal oxidation potentials, and rates of dissociation.

Registry No. Fe(CN)$_5$L^{3-} (L = 4-methylpyridine), 37475-65-3; Fe(CN)$_5$L^{3-} (L = pyridine), 37475-75-5; Fe(CN)$_5$L^{3-} (L = 4-chloropyridine), 37475-74-4; Fe(CN)$_5$L^{3-} (L = isonicotinaldehyde hemiacetal), 37475-73-3; Fe(CN)$_5$L^{4-} (L = isonicotinate), 37475-64-2; Fe(CN)$_5$L^{3-} (L = 4,4′-bipyridine), 37475-72-2; Na$_3$(CN)$_5$L (L = isonicotinamide), 37475-71-1; Na$_3$Fe(CN)$_5$L (L = pyrazine), 37475-70-0; Na$_2$Fe(CN)$_5$L (L = 4-pyridylpyridinium), 37475-69-7; Fe(CN)$_5$L^{3-} (L = isonicotinaldehyde), 37475-68-6; Fe(CN)$_5$L^{2-} [L = 1-methyl-4-(4-pyridyl)pyridinium], 37475-67-5; Na$_2$Fe(CN)$_5$L (L = methylpyrazinium), 37475-66-4.

Acknowledgment. The authors gratefully acknowledge financial support from the following: the Conselho National de Pesquisas, the Fundacao de Amparo a Pesquisa do Estado de Sao Paulo (predoctoral fellowship to H. E. T), the Atlantic Petroleum Co. of Brasil, the Agency of International Development, the National Science Foundation, the National Academy of Sciences, and the Atlantic Richfield Corp. Also acknowledged gratefully are the aid and encouragement of Professors Ernesto Giesbrecht, Pawel Krumholtz, and Henry Taube.

Contribution from the University Chemical Laboratory, Cambridge, United Kingdom, and the Department of Chemistry, University of British Columbia, Vancouver, Canada

Mossbauer Measurements of the Electric Field Gradient at Iron in Some Pentacoordinate Phosphine-Carbonyl-Iron(0) Complexes

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Received June 23, 1972

We report experimental and theoretical studies of the electric field gradient at trigonal-bipyramidally coordinated Fe in phosphine derivatives of Fe(CO)$_5$. Theoretical calculations are based on the assumption (supported by experimental evidence) that the effect of substitution may be treated as a perturbation. It is shown that, although substitution which preserves the axial symmetry has little effect on the electric field gradient at Fe, both the asymmetry parameter η and the sign of the ^{57}Fe^m quadrupole splitting ΔE_Q [$\Delta E_Q = {}^1/_2 e^2qQ(1 + {}^1/_3\eta^2)^{1/2}$] are very sensitive to breaking of the threefold symmetry by substitution, but $|\Delta E_Q|$ is not. Mossbauer spectra in applied magnetic fields of 35–50 kG give values for η and the sign of ΔE_Q for four derivatives of Fe(CO)$_5$. The results are considered in the light of the theoretical investigations. It is concluded that determination of η and the sign of ΔE_Q is a sensitive method for detecting lack of axial symmetry in derivatives of Fe(CO)$_5$ but cannot easily be used to answer more detailed stereochemical questions.

Introduction

An interesting feature of the Mossbauer spectra of Fe(CO)$_5$ and its pentacoordinate phosphine and arsine derivatives of the types LFe(CO)$_4$, L$_2$Fe(CO)$_3$, L$^{(b)}$Fe$_2$(CO)$_8$, and L$^{(c)}$Fe(CO)$_3$ is that the magnitude of the ^{57}Fe quadrupole splitting $|\Delta E_Q|$ is quite insensitive both to the nature of the ligand and to the symmetry of the complex. [L represents a tertiary phosphine or arsine, and L$^{(b)}$ and L$^{(c)}$ represent a di(tertiary phosphine or arsine) acting as a bridging or chelating group, respectively.] At 80°K all complexes of the above four types for which Mossbauer data are available[3-9] have $|\Delta E_Q|$ values within about ±15% of the value for Fe(CO)$_5$ itself, even when the symmetry of the complex is quite different. An examination of the Mossbauer quadrupole interaction in some of these compounds in the presence of an applied magnetic field seemed attractive, since this technique allows one to determine the sign of the electric field gradient (EFG) at the iron nucleus and to estimate the value of the asymmetry parameter η. Both of these quantities should be more sensitive than the quadrupole splitting to replacement of carbonyl groups if such substitution breaks the axial symmetry.[10]

Very few determinations of the sign of the EFG in Fe(0) complexes have been reported. For Fe(CO)$_5$, studies of oriented polycrystalline samples have shown that the quadrupole coupling constant e^2qQ is positive.[3] Collins and Travis[11] have reported the Mossbauer spectra of butadieneiron tricarbonyl and cyclobutadieneiron tricarbonyl in applied magnetic fields of 26 kG. They found that e^2qQ was negative in the butadiene compound and positive in the cyclobutadiene derivative, but a satisfactory explanation of this sign reversal was not given. Magnetic perturbation studies on a few derivatives in which the (π-C$_5$H$_5$)Fe(CO)$_2$ moiety is bonded to a tin atom have revealed positive signs for e^2qQ at Fe in every case.[12,13] No attempt has been made to interpret these results, since the nature of the molecular orbitals is not well understood.

The approximate invariance of $|\Delta E_Q|$ in pentacoordinate phosphine and arsine derivatives of Fe(CO)$_5$ suggests that replacement of CO may be regarded as a perturbation of the electronic structure of the Fe atom in Fe(CO)$_5$. In the next

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section the dependence on substitution of the EFG at Fe is calculated on the basis of this assumption. Mossbauer spectra in applied magnetic fields are then reported for an example of each of the four types of derivative mentioned above. The results are considered in the light of the theoretical investigations.

Simple Molecular Orbital Model for the EFG at Iron in Trigonal-Bipyramidal Iron(0) Carbonyls

It is well established[14] that the EFG at the nucleus of a covalently bound atom is determined mainly by asymmetry of the charge distribution in the innermost valence shell. In the case of diamagnetic Fe(0) complexes this is the 3d shell with its (nominally) d^8 configuration. The purpose of this section is to discuss how the EFG at Fe arising from the 3d electrons varies on substitutional replacement of CO in $Fe(CO)_5$. All other contributions to the EFG will be neglected.

The model presented is, of course, equally applicable to the isoelectronic trigonal-bipyramidal Co(I)-substituted carbonyls. Some discussion of Co(I) systems with threefold symmetry has already been given,[15] but our purpose is to go beyond this and consider the effects of breaking the threefold symmetry.

The components V_{ij} of the EFG at Fe are given by

$$V_{ij} = \langle \Psi | \sum_{\text{el}} v_{ij} | \Psi \rangle \tag{1}$$

$$= 2\sum_{\alpha}(1 - R_\alpha)\langle \psi_\alpha | v_{ij} | \psi_\alpha \rangle \tag{2}$$

where

$$v_{ij} = -er^{-5}(3x_ix_j - r^2\delta_{ij}) \tag{3}$$

In eq 1-3 Σ_{el} denotes the sum over all electrons, $|\Psi\rangle$ is the Slater determinant formed from the doubly occupied valence molecular orbitals ψ_α, and the Sternheimer factors R_α are explicitly inserted into eq 2 to correct for distortion of closed inner shells by the charge distribution $2e\psi_\alpha{}^*\psi_\alpha$. The functions ψ_α of interest are those which contain a d-orbital component[16]

$$\psi_\alpha = \phi_\alpha + \sum_\mu c_{\alpha\mu}\text{d}_\mu \tag{4a}$$

$$= \phi_\alpha + (\sum_\mu c^*{}_{\alpha\mu}c_{\alpha\mu})^{1/2}\,\text{d}_\alpha \tag{4b}$$

where

$$\text{d}_\alpha = (\sum_\mu c_{\alpha\mu}\text{d}_\mu)/(\sum_\mu c^*{}_{\alpha\mu}c_{\alpha\mu})^{1/2} \tag{4c}$$

In eq 4 the d_μ are an orthonormal basis of Fe 3d orbitals (say the conventional real d orbitals), and ϕ_α is the linear combination of all other orbitals participating in ψ_α. If eq 4b is inserted into eq 2 we obtain

$$V_{ij} = (1 - R_\text{d})\sum_\alpha N_\alpha \langle \text{d}_\alpha | v_{ij} | \text{d}_\alpha \rangle = (1 - R_\text{d})\sum_\nu N_\nu \langle \text{d}_\nu | v_{ij} | \text{d}_\nu \rangle \tag{5}$$

where N_α, N_ν are effective populations,[17,18] and the second summation in eq 5 runs over all *distinct* linear combinations d_ν which occur among the d_α. For a molecule with low symmetry there will be many distinct d_ν, but we are concerned with the case in which the parent unsubstituted complex $[Fe(CO)_5]$ has sufficiently high symmetry $[D_{3h}]$ that no irreducible representation is repeated in the reduction of the representation spanned by a basis of five orthonormal d orbitals. In this case only five distinct d_ν occur. On substitution the symmetry may be lowered, and the discussion below centers on the consequent changes in the set of d_ν.

Note that, whereas eq 5 contains only diagonal matrix elements, off-diagonal elements may appear if eq 4a is inserted into eq 2. However, if $i = j = z$ then, because the operator v_{zz} has no off-diagonal matrix elements between the conventional real d orbitals, eq 5 always reduces to the often cited[14,15] equation

$$v_{zz} = -{}^4/_7 e(1 - R_\text{d})\langle r^{-3}\rangle_\text{d}[N_{z^2} + {}^1/_2(N_{xz} + N_{yz}) - (N_{x^2-y^2} + N_{xy})] \tag{6}$$

The structural types discussed in this paper are illustrated in Figure 1. Consider first the parent carbonyl $Fe(CO)_5$ (structure I). The transformation properties of metal and ligand valence orbitals under the D_{3h} point symmetry group[19] of $Fe(CO)_5$ are given in Table I. It is convenient to classify the valence molecular orbitals as σ or π types, although this distinction is not exact for orbitals belonging to the A_2'' and E' representations. Of the Fe 3d orbitals, d_{z^2} can participate only in ligand→Fe σ bonding, while $(\text{d}_{x^2-y^2}, \text{d}_{xy})$ and $(\text{d}_{xz}, \text{d}_{yz})$ can participate in Fe→ligand π bonding. The $(\text{d}_{x^2-y^2}, \text{d}_{xy})$ orbitals, since they belong to E', may also be involved in σ bonding to some extent. A schematic diagram of the relevant orbital levels is given in Figure 2. The numerical prefixes used to distinguish different orbitals belonging to the same representation are chosen to agree with the approximate molecular orbital calculation of Hillier.[20]

From Table I it is evident that the conventional real d orbitals are appropriate d_ν for use in eq 5. Further, by symmetry the EFG at Fe must be axially symmetric and thus is completely determined[21] by the one component V_{zz}, where the z axis is parallel to the threefold symmetry axis. Thus eq 6 applies with

$$N_{xz} = N_{yz} = N_{e''} \tag{7}$$

$$N_{x^2-y^2} = N_{xy} = N_{e'} \tag{8}$$

$$N_{z^2} = N_{a_1'} \tag{9}$$

The value of $N_{a_1'}$ is determined by the extent to which the (nominally empty) d_{z^2} orbital participates in formation of the $5a_1'$ and $6a_1'$ σ molecular orbitals. The values of $N_{e'}$ and $N_{e''}$ are determined by the extent to which the empty e' and e'' ligand π orbitals (and in the case of E' the Fe $4p_x$, $4p_y$ orbitals) are mixed into the $3e''$ and $6e'$ molecular orbitals.

Inserting eq 7-9 into eq 6 we obtain

$$V_{zz} = -{}^4/_7 e(1 - R_\text{d})\langle r^{-3}\rangle_\text{d}[N_{a_1'} + N_{e''} - 2N_{e'}] \tag{10}$$

$$= {}^4/_7 e(1 - R_\text{d})\langle r^{-3}\rangle_\text{d}(\pi - \sigma) \tag{11}$$

where

$$\pi = 2N_{e'} - N_{e''} \tag{12}$$

$$\sigma = N_{a_1'} \tag{13}$$

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(21) For the theory of EFG tensors see M. H. Cohen and F. Reif, *Solid State Phys.*, 5, 321 (1957).

Table I. Symmetry Species of Metal and Ligand Valence Orbitals in $Fe(CO)_5$

	Orbitals	Symmetry species under D_{3h}
Metal	$3d_{z^2}$	A_1'
	$(3d_{x^2-y^2}, 3d_{xy})$	E'
	$(3d_{xz}, 3d_{yz})$	E''
	4s	A_1'
	$(4p_x, 4p_y)$	E'
	$4p_z$	A_2''
Ligand	apical σ	$A_1' + A_2''$
	equatorial σ	$A_1' + E'$
	apical π	$E' + E''$
	equatorial π	$A_2' + A_2'' + E' + E''$

It is anticipated that $2 > \pi > \sigma$, since in the absence of covalent bonding $\pi = 2$ and $\sigma = 0$, while $\pi < \sigma$ corresponds to a situation in which it would be difficult to justify the usual "d^8" nominal configuration for the iron atom. Note that σ increases with increasing "σ-donor character" of the ligands, whereas π decreases with increasing "π-acceptor character."

The observation[3,4] that in $Fe(CO)_5$ $|\Delta E_Q| = 2.60$ mm sec^{-1} with V_{zz} positive confirms that $\pi > \sigma$. Taking[22,23] $Q(^{57}Fe^m) = +0.2 \times 10^{-24}$ cm^2 and $\langle r^{-3}\rangle_d = 2.6 \times 10^{25}$ cm^{-3} we obtain

$$(1 - R_d)(\pi - \sigma) = 0.58$$

It is interesting to compare this number with the value of

$$(\pi - \sigma) = 1.54 - 1.23 = 0.31$$

obtained from the Mulliken orbital populations calculated by Schreiner and Brown.[15a,24] The two numbers appear to be consistent if one takes into account the uncertainties associated with the value of $Q(^{57}Fe^m)$ and with the molecular orbital calculation.[25] Also, it is not certain that Mulliken orbital populations are directly comparable with empirical values of $(\pi - \sigma)$.

The replacement of one or more CO groups by other ligands will cause changes in the electronic structure of the iron atom. In this paper we are concerned with ligands (specifically tertiary phosphines) which are not too different from CO in their ligating properties. Thus it is reasonable to regard substitutional replacement of CO as a perturbation of the Fe atom in $Fe(CO)_5$.

In general, substitution will lower the point symmetry of the complex to a subgroup of D_{3h}. Thus the perturbation may be split into a sum of parts, one of which spans the unit representation of D_{3h}, while the remainder span those other representations of D_{3h} which go to the unit representation of the subgroup on descent in symmetry. The first part will be termed "symmetric" and the remaining parts "symmetry breaking." Both types of perturbation can lead to changes in the N_ν appropriate to eq 5, but the symmetry of $Fe(CO)_5$ is sufficiently high that only symmetry-breaking perturbations can lead to changes in the form of the d_ν.[26]

Apical-apical disubstitution of $Fe(CO)_5$ (structure III) leaves the D_{3h} symmetry unchanged. Thus only the symmetric perturbation is allowed, and the EFG is still given by eq 10-13, although the value of $(\pi - \sigma)$ may be changed. Apical monosubstitution (structure II) leads to C_{3v} symmetry with an A_2'' symmetry-breaking perturbation. This may mix E' and E'' levels, but since the threefold symmetry is not broken the EFG must still be axially symmetric and will be given by eq 6. The threefold symmetry ensures that $N_{x^2-y^2} = N_{xy}$ and $N_{xz} = N_{yz}$, so that eq 11 is unchanged in form.

Rather more spectacular effects are observed if one considers the case of equatorial-equatorial disubstitution (structure IV). The symmetry is reduced to C_{2v} by a symmetry-breaking perturbation belonging to the $E'c$ component of E'.[27] Both the different electronic structure of the substituent and possible small distortions from strict trigonal-bipyramidal geometry may contribute to the $E'c$ perturbation.

This perturbation can mix the lowest empty molecular orbital $7a_1'$ into the $e'c$ component of the highest filled orbital $6e'$. This mixing is likely to be significant since the two orbitals will only be separated by a few electron volts. As a result of this mixing the d_α in eq 4 for $\psi_\alpha = 6e'c$ becomes a linear combination of $d_{x^2-y^2}$ and d_{z^2}, say

$$d_{6e'c} = d_{x^2-y^2} \cos\alpha + d_{z^2} \sin\alpha \qquad (14)$$

where the mixing parameter α is a measure of the symmetry-breaking perturbation and is zero if the perturbation is negligible.

The only other filled molecular orbitals which may be perturbed in such a way as to alter the form of their d components are the σ orbitals $5e'c$, $6a_1'$, and $5a_1'$. These all lie at much lower energies (at least 10 eV on the basis of Hillier's calculation[20]) than the empty orbitals with which they must be mixed. Thus any such mixing will be much smaller than the perturbation of $6e'c$ and will therefore be neglected. (Note that it follows from the properties of Slater determinants that mixing of filled orbitals with filled orbitals does not change V_{ij}.)

On this assumption any $(d_{x^2-y^2}, d_{xy})$ participation in $5e'$ will produce a small axially symmetric EFG opposing the EFG arising from the d_{z^2} components of $5a_1'$ and $6a_1'$. In order to simplify our equations we shall not consider $5e'$ explicitly but instead note that its contribution can be accounted for by subtracting an amount $(N_{5e'c} + N_{5e's})$ from $N_{a_1'}$.

Inserting the appropriate d_ν into eq 5 we obtain

$$V_{ij} = (1 - R_d)[(N_{a_1'} - N_{e's} + N_{e''})\langle d_{z^2}|v_{ij}|d_{z^2}\rangle + N_{e'c}\langle d_{x^2-y^2}\cos\alpha + d_{z^2}\sin\alpha|v_{ij}|d_{x^2-y^2}\cos\alpha + d_{z^2}\sin\alpha\rangle] \qquad (15)$$

where we have used the equations

$$\langle d_{xz}|v_{ij}|d_{xz}\rangle + \langle d_{yz}|v_{ij}|d_{yz}\rangle + \langle d_{xy}|v_{ij}|d_{xy}\rangle = 0 \qquad (16)$$

$$\langle d_{z^2}|v_{ij}|d_{z^2}\rangle + \langle d_{xy}|v_{ij}|d_{xy}\rangle = 0 \qquad (17)$$

Also, we have set $N_{e''c} = N_{e''s} = N_{e''}$, which is exactly true in the unperturbed complex and is likely to remain a good approximation for small perturbations.

The principal axes of V_{ij} are determined by symmetry for the group C_{2v}. In terms of principal axes with Ox parallel to the twofold axis of C_{2v}, eq 5 becomes eq 18

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(25) For evidence on uncertainty in the value of $Q(^{57}Fe^m)$ see Table I of ref 22 and references therein; for the molecular orbital calculations compare the self-consistent configurations of ref 24 with those of ref 20.

(26) The precise condition for the d_ν in eq 5 to be unaffected by a symmetric perturbation is the same as that for them to be orthogonal and independent, namely, that no irreducible representation be repeated in the reduction of the representation spanned by a basis of five orthonormal d orbitals under the point group of the unperturbed complex.

(27) The components of E″ and E′ will be denoted Ec and Es (c = cosine, s = sine) where, if ϕ is the azimuthal angle, Ec transforms like cos $m\phi$ and Es like sin $m\phi$. The integer m is 1 for (d_{xz}, d_{yz}) and 2 for $(d_{x^2-y^2}, d_{xy})$.

$$\mathrm{V}^{\mathrm{IV}} = {}^{4}/_{7}e(1 - R_{\mathrm{d}})\langle r^{-3}\rangle_{\mathrm{d}} \begin{bmatrix} -{}^{1}/_{2}[(\cos 2\alpha - \sqrt{3}\sin 2\alpha)\pi_{\mathrm{IV}} - \sigma_{\mathrm{IV}}] & 0 & 0 \\ 0 & -{}^{1}/_{2}[(\cos 2\alpha + \sqrt{3}\sin 2\alpha)\pi_{\mathrm{IV}} - \sigma_{\mathrm{IV}}] & 0 \\ 0 & 0 & (\pi_{\mathrm{IV}}\cos 2\alpha - \sigma_{\mathrm{IV}}) \end{bmatrix} \tag{18}$$

where

$$\pi_{\mathrm{IV}} = N_{\mathrm{e'c}} \tag{19}$$

and

$$\sigma_{\mathrm{IV}} = N_{\mathrm{a_1}'} - (N_{\mathrm{e's}} - N_{\mathrm{e''}}) \tag{20}$$

The quantity σ_{IV} largely reflects the influence of σ bonding since $(N_{\mathrm{e's}} - N_{\mathrm{e''}})$ is small (only 9% of $N_{\mathrm{a_1}'}$ for Schreiner and Brown's Mulliken populations[15a]). By arguments similar to those given above it may be anticipated that $0 < \sigma_{\mathrm{IV}} < \pi_{\mathrm{IV}}$.

It is of particular interest to analyze the dependence of V^{IV} on α for fixed π_{IV} and σ_{IV}. The magnitude $|\Delta E_{\mathrm{Q}}|$ of the quadrupole splitting of an $I = {}^{3}/_{2}$ nuclear level (*e.g.*, $^{57}\mathrm{Fe^m}$) is given by[28]

$$|\Delta E_{\mathrm{Q}}| = {}^{2}/_{7}e^{2}Q(1 - R_{\mathrm{d}})\langle r^{-3}\rangle_{\mathrm{d}}(\pi_{\mathrm{IV}}{}^{2} = 2\pi_{\mathrm{IV}}\sigma_{\mathrm{IV}}\cos 2\alpha + \sigma_{\mathrm{IV}}{}^{2})^{1/2} \tag{21}$$

As α increases from zero,[29] $|\Delta E_{\mathrm{Q}}|$ increases rather slowly for small α and is actually independent of α if σ_{IV} is negligible.[10] At $\alpha = 0$ the asymmetry parameter[21] $\eta = 0$, and (for Q positive, as in $^{57}\mathrm{Fe^m}$) the sign of ΔE_{Q} is positive. As α increases from zero, η goes from zero to unity, to zero, to unity, and so on. Each time η passes through unity the sign of ΔE_{Q} changes, leading to a discontinuity in the dependence on α of ΔE_{Q} but not in that of $|\Delta E_{\mathrm{Q}}|$.

The first change of sign comes when V_{xx} in eq 18 vanishes. This occurs at a value α_1 given (in degrees) by

$$\alpha_1 = {}^{1}/_{2}\cos^{-1}(\sigma_{\mathrm{IV}}/2\pi_{\mathrm{IV}}) - 30 \tag{22}$$

It is readily shown that $0 < \alpha_1 < 15°$ if $\pi_{\mathrm{IV}} > \sigma_{\mathrm{IV}} > 0$.

The general conclusion to be drawn from eq 21 and 22 is that only a small symmetry-breaking perturbation is required to change the sign ΔE_{Q} but that the accompanying change in $|\Delta E_{\mathrm{Q}}|$ will be modest. For example, if the Mulliken populations calculated for $\mathrm{Fe(CO)_5}$ by Schreiner and Brown[15a] are inserted into eq 19 and 20 it is found that $\alpha_1 = 3.5°$, for which value $|\Delta E_{\mathrm{Q}}|$ is increased by 11% above its value at $\alpha = 0$.

Apical-equatorial substitution (structure V) causes the D_{3h} symmetry to be reduced to C_s by symmetry-breaking perturbations $\mathrm{E'c} + \mathrm{A_2}'' + \mathrm{E''c}$. Energy considerations suggest that mixing of $7\mathrm{a_1}'$ into $6\mathrm{e'c}$ by the E′c perturbation will be the most important effect. If no other mixing occurred, the problem would be identical with the case of C_{2v} symmetry discussed above. However, other possibilities for perturbative mixing of orbitals also exist, and these, of course, will lead to additional parameters.

For example, $7\mathrm{a_1}'$ may also be mixed into $3\mathrm{e''c}$, which Hillier[20] places only 2.4 eV below 6e′ in $\mathrm{Fe(CO)_5}$. The modified d component of 3e″c may be written

$$\mathrm{d_{e''c}} = \mathrm{d}_{xz}\cos\beta + \mathrm{d}_{z^2}\sin\beta \tag{23}$$

If we maintain the assumption that $N_{\mathrm{e''c}} = N_{\mathrm{e''s}} = N_{\mathrm{e''}}$ and take cartesian axes with Oz parallel to the apical-apical direction and Oz, Ox contained in the mirror plane of C_s, then the EFG at Fe is given by eq 24

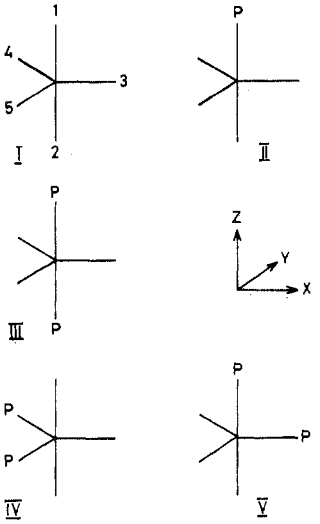

Figure 1. Structural types considered in this paper.

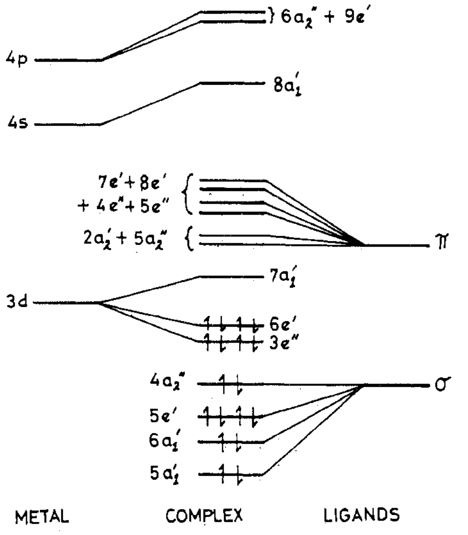

Figure 2. Schematic diagram of valence molecular orbital levels in $\mathrm{Fe(CO)_5}$.

Table II. ^{59}Co Nqr Data for Certain Co(I) Complexes[a,b]

Compd[c]	Transition energies, MHz		e^2qQ, MHz	η
	$\pm{}^{3}/_{2} \leftrightarrow \pm{}^{5}/_{2}$	$\pm{}^{5}/_{2} \leftrightarrow \pm{}^{7}/_{2}$		
$\mathrm{Cl_3Sn[Co(CO)_4]}$[d]	23.37	35.02	163.45	0.0
$\mathrm{Cl_3Sn[Co(CO)_3PPh_3]}$	22.84	34.86	163.39	0.208
$\mathrm{Ph_3Sn[Co(CO)_4]}$	15.03	22.55	105.38	0.022
$\mathrm{Ph_3Sn[Co(CO)_3PPh_3]}$	16.28	24.52	114.53	0.095
$\mathrm{Ph_3Ge[Co(CO)_4]}$	15.74	23.64	110.34	0.046
$\mathrm{Ph_3Ge[Co(CO)_3PPh_3]}$		24.22		

[a] Taken from ref 15a and 30. [b] All at 77°K except $\mathrm{Cl_3Sn[Co(CO)_4]}$ at 298°K; data in ref 15 and 30 show that e^2qQ is unlikely to change by more than about 2% between 298 and 77°K. [c] Ph = $\mathrm{C_6H_5}$. [d] In this case a $\pm{}^{1}/_{2} \leftrightarrow \pm{}^{3}/_{2}$ transition at 11.67 MHz was also observed.

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(28) The most direct method of obtaining this result is to calculate the symmetrized parameter S_{02} [see M. G. Clark, *J. Chem. Phys.*, 54, 697 (1971)].

(29) Negative α corresponds to interchange of the x and y axes.

$$\mathrm{V^V} = \frac{4}{7}e(1 - R_\mathrm{d}')\langle r^{-3}\rangle_\mathrm{d} \begin{bmatrix} -\frac{1}{2}[\pi_\mathrm{V}'(\cos 2\alpha - \sqrt{3}\sin 2\alpha) - \pi_\mathrm{V}''(1 - \cos 2\beta) - \sigma_\mathrm{V}] & 0 & -\frac{\sqrt{3}}{4}\pi_\mathrm{V}''\sin 2\beta \\ 0 & -\frac{1}{2}[\pi_\mathrm{V}'(\cos 2\alpha + \sqrt{3}\sin 2\alpha) + \frac{1}{2}\pi_\mathrm{V}''(1 - \cos 2\beta) - \sigma_\mathrm{V}\pi] & 0 \\ -\frac{\sqrt{3}}{4}\pi_\mathrm{V}''\sin 2\beta & 0 & [\pi_\mathrm{V}'\cos 2\alpha - \frac{1}{4}\pi_\mathrm{V}''(1 - \cos 2\beta) - \sigma_\mathrm{V}] \end{bmatrix} \quad (24)$$

where α is defined by the form of $\mathrm{d}_{6\mathrm{e}'\mathrm{c}}$ given in eq 14 and

$$\pi_\mathrm{V}' = N_{\mathrm{e}'\mathrm{c}} \quad (25)$$

$$\pi_\mathrm{V}'' = N_{\mathrm{e}''} \quad (26)$$

$$\sigma_\mathrm{V} = N_{\mathrm{a}_1'} - (N_{\mathrm{e}'\mathrm{s}} - N_{\mathrm{e}''}) \quad (27)$$

It is anticipated that $|\beta| < |\alpha|$; if $\beta = 0$, eq 24 is identical with eq 18, as noted above.

The data presently available do not justify a detailed analysis of eq 24. However, it should be noted that, as in the case of structure IV, only a small perturbation is required to change the sign of ΔE_Q, although the accompanying change in $|\Delta E_\mathrm{Q}|$ may be modest.

A priori prediction of the effective populations which appear in the equations of this section is unlikely to be easy. At an empirical level the effective populations in structures I-III have been discussed in the case of the isoelectronic Co(I) complexes.[15] Data[15a,30] on Co(I) complexes also provide support for our assumption that replacement of CO by tertiary phosphine ligands may be regarded as a perturbation. Table II gives ^{59}Co nqr data for pairs of complexes $\mathrm{XCo(CO)_4}$ and $\mathrm{XCo(CO)_3P(C_6H_5)_3}$ with X = $\mathrm{SnCl_3}$, $\mathrm{Sn(C_6H_5)_3}$, and $\mathrm{Ge(C_6H_5)_3}$. Presumably[15] these compounds all have structures II or III, so that the change in $(\pi - \sigma)$ caused by substitution of $\mathrm{P(C_6H_5)_3}$ is 8.3% in the case of X = $\mathrm{Sn(C_6H_5)_3}$ and less than 3% in both other cases. The nonzero η values observed are consistent with the greater sensitivity of that parameter to intermolecular interactions in the solid state.[10]

Finally, we note that the σ orbitals $5\mathrm{a}_1' + 6\mathrm{a}_1' + 5\mathrm{e}' + 4\mathrm{a}_2''$ may be transformed into localized orbitals, one per metal-ligand bond. Thus it is reasonable to conjecture that the contributions to the EFG due to these orbitals might be additive.[31] By use of the equations given in Table I of ref 31 the effective population $N_{\mathrm{a}_1'}$ may be expressed as

$$N_{\mathrm{a}_1'} = {}^1/_2(\sigma_1{}^\mathrm{tba} + \sigma_2{}^\mathrm{tba})\sin^2\theta + {}^1/_3(\sigma_3{}^\mathrm{tbe} + \sigma_4{}^\mathrm{tbe} + \sigma_5{}^\mathrm{tbe})\cos^2\theta \quad (28)$$

In eq 28 θ is a mixing parameter describing the distribution of d_{z^2} between apical and equatorial bonds,[32] and σ_i depends upon the ligand occupying the *i*th position (numbered as in structure I, Figure 1) and whether this position is apical (tba = trigonal-bipyramidal apical) or equatorial (tbe = trigonal-bipyramidal equatorial). The value of $N_{\mathrm{a}_1'}$ may be more sensitive to apical or to equatorial substitution, depending on the value of θ in eq 28.

Results and Discussion

The zero-field Mossbauer quadrupole splittings for the compounds studied here have been reported previously[4,8] and are given in Table III together with the η values and signs of ΔE_Q deduced in the present investigation.

Table III. ^{57}Fe Quadrupole Coupling Parameters for Some Phosphine Derivatives of $\mathrm{Fe(CO)_5}$

Compd[a]	$\lvert\Delta E_\mathrm{Q}\rvert$,[f] mm sec^{-1}	Sign of ΔE_Q[b]	η
$\mathrm{Fe(CO)_5}$	2.60[c]	+[d]	0.0
$\mathrm{Ph_3PFe(CO)_4}$	2.54[c]	+	0.0
$\mathrm{(Ph_3P)_2Fe(CO)_3}$	2.76[c]	+	0.0
diphos$\mathrm{Fe_2(CO)_8}$	2.46[e]	+	0.0
diphos$\mathrm{Fe(CO)_3}$	2.12[e]	−	0.8

[a] Ph = $\mathrm{C_6H_5}$, diphos = $\mathrm{(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2}$. [b] $Q(^{57}\mathrm{Fe^m})$ is positive.[22] [c] Reference 4. [d] Reference 3. [e] Reference 8. [f] At liquid nitrogen temperature.

The infrared spectrum[33] of $\mathrm{(C_6H_5)_3PFe(CO)_4}$ shows three CO stretching bands consistent with the C_{3v} symmetry of structure II. The X-ray crystal structure analyses of $\mathrm{(C_6H_5)_2HPFe(CO)_4}$[34] and the phosphorus-bridged dimer[35] $\mathrm{[Fe(CO)_4P(CH_3)_2]_2}$ show apical substitution of the parent $\mathrm{Fe(CO)_5}$ trigonal-bipyramidal structure, and there can be little doubt that $\mathrm{(C_6H_5)_3PFe(CO)_4}$ has structure II. It has been shown[33,36] that $\mathrm{[(C_6H_5)_3P]_2Fe(CO)_3}$ has apical-apical disubstitution (D_{3h} symmetry with only one infrared-active carbonyl band) and hence has structure III. At 4.2°K in longitudinal applied magnetic fields of 35-42 kG, both compounds have Mossbauer spectra showing positive ΔE_Q and $\eta \simeq 0$. These results are as predicted by eq 11 for $\pi > \sigma$. The similarity of the quadrupole splitting values for these compounds and the $\mathrm{Fe(CO)_5}$ parent shows that replacement of an apical carbonyl by a phosphine produces only a small perturbation of the EFG at the iron nucleus. The changes in $(\pi - \sigma)$ of −2% and +6% are comparable with those observed in analogous Co(I) systems (Table II).

Manuel[37] has reported identical three-band infrared carbonyl spectra for $\mathrm{(C_6H_5)_3PFe(CO)_4}$ and diphos$\mathrm{Fe_2(CO)_8}$ [diphos = 1,2-bis(diphenylphosphino)ethane]. However, we have observed[8] further splitting resulting in a four-band spectrum for the bridged diphos$\mathrm{Fe_2(CO)_8}$. While these results for diphos$\mathrm{Fe_2(CO)_8}$ appear to rule out apical substitution in a square-pyramidal structure (C_{4v} symmetry with only two infrared-active CO modes), they leave open the possibilities of equatorial substitution in a trigonal-bipyramidal structure or basal substitution in a square-pyramidal structure. It is also possible that a four-band spectrum could result from apical substitution in a trigonal-bipyramidal structure with the asymmetric substituent splitting the

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doubly degenerate E mode found in C_{3v} symmetry. The Mossbauer spectrum of diphos$Fe_2(CO)_8$ in a longitudinal magnetic field of 41.5 kG at 4.2°K is shown in Figure 3. It is clear that ΔE_Q is positive and $\eta \simeq 0$. This result eliminates both an equatorially substituted trigonal-bipyramidal structure[38] and a basally substituted square-pyramidal structure and confirms apical substitution with trigonal-bipyramidal coordination. The zero asymmetry parameter shows that the Fe-P bond effectively has axial symmetry insofar as it affects the EFG. It is worth noting that although the ligand symmetry is presumably responsible for the extra carbonyl band in the infrared spectrum, it appears to have no measurable effect on the EFG.

The structure of diphos$Fe(CO)_3$ has not been firmly established. This compound shows three strong CO stretching bands, consistent with either C_{2v} or C_s symmetry. The pattern of the bands is similar to that found for other (chelate)$Fe(CO)_3$ derivatives[8] and especially to that of diars$Fe(CO)_3$ [diars = 1,2-bis(dimethylarsino)benzene]. The nmr spectra of both diphos$Fe(CO)_3$ and diars$Fe(CO)_3$ suggest that in solution the $Fe(CO)_3$ moiety is attached to the ligand in a way which preserves the original ligand symmetry,[8] a result which seems to favor structure IV. It is possible that rapid exchange of apical and equatorial positions in solution could average the signal, although the nmr spectrum of diars$Fe(CO)_3$ in the *As*-CH_3 region remains a singlet even on cooling to −80°.[8] On the other hand an X-ray study[39] of solid diars$Fe(CO)_3$ indicated structure V for this complex, with only minor distortions from the ideal trigonal-bipyramidal bond angles.

The Mossbauer spectrum of diphos$Fe(CO)_3$ at 4.2°K in a longitudinal magnetic field of 50 kG, shown in Figure 4, is very different from those of the other three derivatives reported here (*cf.* Figure 3). In this case ΔE_Q is clearly negative and the asymmetry parameter is large. Although a detailed fit of this spectrum was not attempted, comparison with the computed spectra of Collins and Travis[11] indicates $\eta \simeq 0.8$ for diphos$Fe(CO)_3$. This result confirms our conclusion that, in derivatives of $Fe(CO)_5$, η and the sign of ΔE_Q are much more sensitive than $|\Delta E_Q|$ to a substitution which breaks the axial symmetry, but it does not establish the geometry of diphos$Fe(CO)_3$. The model presented above shows that, whether the symmetry is C_{2v} or C_s, ΔE_Q can have either sign, and η any value in the permitted range[21] $0 \leqslant \eta \leqslant 1$, depending on subtle details of the electronic structure of the complex.

In the present case some information can be gained by careful consideration of $|\Delta E_Q|$. From eq 21 it is seen that for constant effective populations $|\Delta E_Q{}^{IV}| \geqslant |\Delta E_Q{}^{I}|$; under the same condition eq 24 implies that $|\Delta E_Q{}^{V}|$ may be greater or less than $|\Delta E_Q{}^{I}|$ depending on whether[28]

$$4\pi_V{}'\sigma_V(1 - \cos 2\alpha) - \pi_V{}''(1 - \cos 2\beta)[\pi_V{}'(\cos 2\alpha - \sqrt{3} \sin 2\alpha) - \sigma_V - \pi_V{}'']$$

is positive or negative, respectively. Thus the observation that $|\Delta E_Q|$ for diphos$Fe(CO)_3$ is 18% *less* than that for $Fe(CO)_5$ might be taken as supporting structure V. However, two other factors must also be considered. First, it is likely that some cancelation of individual changes in σ and π is involved in the invariance of $(\pi - \sigma)$ under apical substitution. Tertiary phosphine ligands[40] are better σ donors and worse π acceptors than CO; thus both π and σ should if anything increase on substitution. In the case of structure IV eq 21 indicates that this would lead to a further increase in $|\Delta E_Q|$. Second, the effective populations may not be equally sensitive to apical and equatorial substitution. (In the case of $N_{a_1}{}'$ this is immediately apparent from inspection of eq 28.) However, insufficient information is available for us to make a detailed assessment of this effect. Thus although the first two points mentioned above favor structure V for diphos$Fe(CO)_3$, the last prevents us from reaching an unambiguous conclusion.

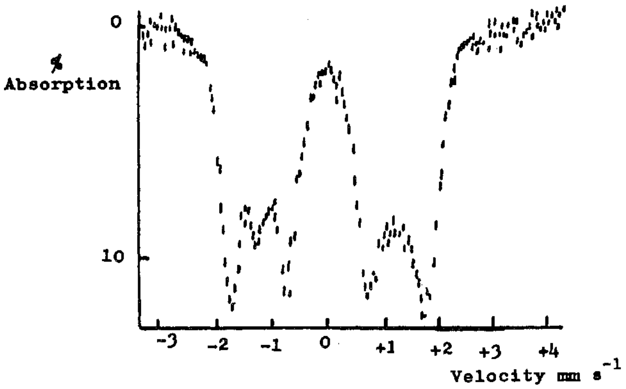

Figure 3. ^{57}Fe Mossbauer spectrum of diphos$Fe_2(CO)_8$ at 4.2°K in an applied longitudinal magnetic field of 41.5 kG.

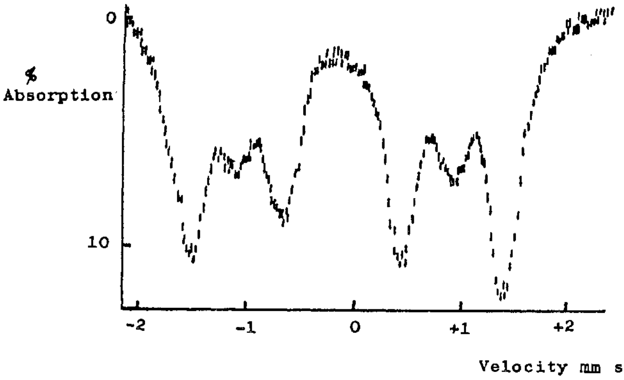

Figure 4. ^{57}Fe Mossbauer spectrum of diphos$Fe(CO)_3$ at 4.2°K in an applied longitudinal magnetic field of 50 kG.

The work reported in this paper shows that although determination of η and the sign of ΔE_Q from magnetically perturbed ^{57}Fe Mossbauer spectra is a sensitive method for detecting lack of axial symmetry in derivatives of $Fe(CO)_5$, it cannot easily be used to answer more detailed stereochemical questions.

Experimental Details

The compounds studied were prepared by methods previously described.[8,33,41] Applied-field Mossbauer spectra were obtained using an Oxford Instruments liquid helium cryostat and superconducting magnet system, as reported elsewhere.[42] Because of the large quadrupole interaction all the compounds gave rise to well-resolved splitting patterns, with no overlap of the halves of the spectra in applied fields up to 50 kG.

Registry No. $Ph_3PFe(CO)_4$, 38894-53-0; $(Ph_3P)_2Fe(CO)_3$,

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38894-54-1; diphos$Fe_2(CO)_8$, 39022-97-4; diphos$Fe(CO)_3$, 38894-55-2.

Acknowledgments. W. R. C. and J. R. S. are grateful to the National Research Council of Canada for financial support. J. R. S. also thanks the Royal Society for the award of a bursary. M. G. C. gratefully acknowledges the financial support provided by a fellowship of St. John's College, Cambridge. Dr. D. B. Patterson is thanked for a helpful discussion.

Contribution No. 4465 from the Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91109, and Contribution from the Los Alamos Scientific Laboratory, University of California, Los Alamos, New Mexico 87544

Potential Constants of Manganese Pentacarbonyl Bromide from the Vibrational Spectra of Isotopic Species[1]

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Received July 31, 1972

Infrared and Raman spectra are reported for $Mn(^{12}C^{16}O)_5Br$, $Mn(^{13}C^{16}O)_5Br$, and $Mn(^{12}C^{18}O)_5Br$ as solids and in CH_2Cl_2 solutions. Most of the fundamental vibrations have been definitively assigned. Compliance constants with standard deviations and their equivalent force constants have been calculated for a general quadratic valence potential field. Changes in the σ- and π-bonding systems in going from $Cr(CO)_6$ to $Mn(CO)_5Br$ are deduced by a detailed examination of the internal valence potential constants.

Introduction

The present paper seeks to establish the transferability of the general quadratic potential field calculated for $M(CO)_6$[2] to $Mn(CO)_5Br$. Although the use of ^{13}CO and $C^{18}O$ would be expected to aid considerably in the calculations, the lowering of symmetry from O_h to C_{4v} is so great that a large number of potential constants must be constrained in the calculation. In order to establish suitable constraints one must rely upon information from other systems, such as $M(CO)_6$.

Apart from the question of transferability, the complete normal-coordinate calculation for $Mn(CO)_5Br$ is of considerable interest due to the very large number of partial vibrational analyses in recent years on $M(CO)_5L$ systems. Almost all of these investigations have been concerned with elucidating the nature of the M-L bond by characterizing the CO stretching frequencies within an "energy-factored" CO force field.

The simplest and by far most heavily used approach is that due to Cotton and Kraihanzel[3] (C-K) which involves the relations between cis and trans CO,C′O′ interaction constants based on a π-bonding model. Many of the investigators using the C-K field have carefully mentioned the inherent approximations, and yet the ordering of a large number of ligands as to π-acceptor or π-donor ability has been widely accepted with little questioning of the effects of possible electrostatic interactions or changes in the σ-bonding system.[4] Such π-bonding orderings must be eyed with suspicion in view of the calculation of Jones, *et al.*,[2] who showed that the relations in the C-K field do not compare well at all with the values for the $M(CO)_6$ harmonic, general quadratic valence potential field.

It should be noted that the present calculation is based on a compliance field although force constants are also presented. The use of compliance constants in vibrational analyses is more fully described in previous papers.[5,6] Their chief advantage over force constants in the present calculation lies in the more complete description of the potential constants involving internal coordinates leading to redundant symmetry coordinates (*i.e.*, the CMC and CMX angle bending).

Experimental Section

Synthesis of Enriched $Mn(CO)_5Br$ Species. The normal, ^{13}CO, and $C^{18}O$ species were prepared by the reaction[7] of $Mn_2(CO)_{10}$ with Br_2 in CCl_4 solution. Normal $Mn_2(CO)_{10}$ was obtained from Alfa Inorganics and the enriched species were prepared by the reaction of manganese acetate in isopropyl ether with enriched CO under pressure.

Carbon monoxide enriched to 93% ^{13}C was obtained from Mound Laboratory of Monsanto Research Corp., Miamisburg, Ohio. The oxygen-enriched carbon monoxide contained 99% ^{18}O and was prepared from $^{15}N^{18}O$ as described earlier.[2]

The purity of each compound was checked by comparison of the CO stretching frequencies with those of normal $Mn(CO)_5Br$.[8] The pattern of the primary absorptions for the enriched species is similar to the spectrum of the normal compound but is shifted to lower energy. By using this spectral comparative method sufficient reaction of the $Mn_2(CO)_{10}$ was guaranteed, and any impurity of $Mn_2(CO)_8Br_2$ could be detected and removed by recrystallization.

Observation of Spectra. The Raman spectra were obtained for the solids and solutions on a Cary 81 with a Spectra-Physics Model 125 He-Ne laser source. Solid-state Raman spectra were obtained from powders, and the solution spectra were obtained with CH_2Cl_2 as solvent. The CH_2Cl_2 solutions were contained in glass capillary tubes; laser power at the capillary was 25 mW. No decomposition of the solutions was noticed over the period of observation (about 1 hr at most). The observation of so few Raman lines for concentrated CH_2Cl_2 solutions in contrast to the powder spectra is attributed to solubility limitations and pronounced solvent line broadening. Slit widths were typically 3-5 cm^{-1} with very high

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