Obviously, the magnitude of the effects causing preference for one structure over the other need not be large, in view of previous data[13,19–21] on simple derivatives suggesting that in many cases the two pentacoordinate conformations differ by only a few kilocalories. In the case of the relatively nonrigid trigonal bipyramidal VF_5, an estimate of 1.8 kcal/mol has been given.[19]

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Calculated and Observed Field Gradients in $[M(CO)_{5-x}P_x]^n$ Complexes[1]

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Abstract: Using nqr or Mössbauer spectroscopy the field gradient at the metal nucleus, eq_{zz}, has been determined in isoelectronic pentacoordinate complexes, $[M(CO)_{5-x}P_x]^n$, where P is $P(C_6H_5)_3$ or $P(OCH_3)_3$ and M is Mn ($n = -1$), Fe ($n = 0$), or Co ($n = +1$). Values of $eq_{d_{z^2}}$ and eq_{p_z} were calculated for the metal ions Mn(-1), Fe(0), and Co($+1$) in different electron configurations, using SCF atomic functions. The one-electron 4p orbital contribution to the field gradient is comparable in magnitude with the 3d term. Theoretical estimates of eq_{zz} for $Fe(CO)_5$ based on eigenvectors from molecular orbital studies are in reasonable agreement with the experimental field gradient. Relative values of $eq_{d_{z^2}}$ for the three metal ions are compared with relative values of eq_{zz} observed for $[Mn(CO)_5]^-$ and $Fe(CO)_5$ and estimated for the hypothetical $[Co(CO)_5]^+$. It is concluded that the populations of the planar d orbitals increase relative to the axial, in the order Mn < Fe < Co. The effect of phosphorus ligand substitution on eq_{zz} is difficult to interpret, since a simple trend is not observed. It is deduced that $[Mn(CO)_{5-x}P_x]^-$ and $[Co(CO)_{5-x}P_x]^+$ complexes have positive values of eq_{zz} and e^2Qq.

The electric field gradient at the metal nucleus in compounds of the transition metals in low valence states can be expressed to a good approximation as

$$eq_{zz} = eq_{d_{z^2}}[N_{d_{z^2}} + {}^1\!/_2(N_{d_{xz}} + N_{d_{yz}}) - (N_{d_{xy}} + N_{d_{x^2-y^2}})] + eq_{p_z}[N_{p_z} - {}^1\!/_2(N_{p_x} + N_{p_y})] \quad (1)$$

where $eq_{d_{z^2}}$ and eq_{p_z} are the expectation values for the field gradient operator for a single electron in a valence d_{z^2} or p_z orbital, respectively. The N's are electron populations of the various orbitals. In evaluating field gradient data for different transition metals in similar chemical environments, or for the same element in different chemical situations, it is essential to have some idea of how $eq_{d_{z^2}}$ and eq_{p_z} vary with changing effective nuclear charge or electronic configuration at the metal. We have chosen to investigate this question by study of isoelectronic species of the form $[M(CO)_{5-x}P_x]^n$, where M is Mn ($n = -1$), Fe ($n = 0$), or Co ($n = +1$) and P is a phosphine or phosphite. ^{55}Mn ($I = {}^5/_2$) and ^{59}Co ($I = {}^7/_2$) are 100% abundant in nature, so that field gradient information is obtainable by nuclear quadrupole resonance (nqr) spectroscopy. From Mössbauer spectroscopy of ^{57}Fe (^{57}Fe^m has $I = {}^3/_2$), it is possible to obtain information regarding the field gradient at iron. By utilizing the best available values for the nuclear quadrupole moments, eQ, the quadrupole coupling constants, $e^2q_{zz}Q/h$, may be converted to estimates of field gradients, eq_{zz}. Previous nqr[3] and Mössbauer[4–6] spectral work on five-coordinate species in these series has shown the presence of fairly large field gradients at the central metal. Since the metals in these diamagnetic systems obey the 18-electron "krypton rule," *i.e.*, have all their valence orbitals occupied, the field gradients must arise from differential levels of occupancy of these orbitals. In this contribution we examine from both theoretical and experimental viewpoints the effect on eq_{zz} of changing the central metal nuclear charge and electronic configurations. In addition, we have measured experimentally the effects of substitutions on the parent $[M(CO)_5]^n$ species by triphenylphosphine and trimethyl phosphite.

Experimental Section

Materials. Dimanganese decacarbonyl, $Mn_2(CO)_{10}$, was obtained from Pressure Chemical Co. or prepared according to a standard procedure[7] and stored under argon. Dicobalt octacarbonyl, $Co_2(CO)_8$, (Pressure Chemical Co.) was stored at 0° under argon or nitrogen. Triiron dodecacarbonyl, $Fe_3(CO)_{12}$ was obtained from Strem Chemicals, Inc., or prepared by a standard method.[8] It was purified by extraction with pentane.

Triphenylphosphine, PPh_3, and trimethyl phosphite, $P(OCH_3)_3$, were purchased from Aldrich Chemical Co.

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The manganese anions, without exception, are quite susceptible to oxidation by air, although the Ni(1,10-phen)$_3{}^{2+}$ salts are considerably more stable than their Na$^+$ or Li$^+$ counterparts. The anions containing PPh$_3$ as a ligand are especially air sensitive. All preparations and handling of the manganese salts were carried out in a glove box with an argon atmosphere.

The iron complexes are affected by air only over an extended period of time, if at all. The cobalt cations are air stable as the tetraphenylborate salts. Preparations of these compounds, however, involved use of air-sensitive starting materials, so Schlenk techniques, using a nitrogen atmosphere, were employed.

NaMn(CO)$_5$ was prepared from Mn$_2$(CO)$_{10}$ and dilute sodium amalgam in THF, as described elsewhere.[9] To prepare LiMn(CO)$_5$, a suspension of a sixfold excess of lithium sand (Foote Mineral Co.) in Et$_2$O was stirred vigorously using a glass-covered stirring bar. After about 1 hr, shiny platelets of lithium metal appeared on the liquid surface, and Mn$_2$(CO)$_{10}$ was then added. The mixture was stirred for about 4 hr and then filtered. Solvent was removed at room temperature to give the product.

Tris(1,10-phenanthroline)nickel(II) was prepared as the sulfate or bromide salt by treating a methanolic solution of the ligand with a stoichiometric amount of hydrated NiSO$_4$ or NiBr$_2$. The resultant dark rose solution was treated with Drierite, filtered, and evaporated to dryness, leaving the pale pink Ni(1,10-phen)$_3{}^{2+}$ salt.

Ni(1,10-phen)$_3$[Mn(CO)$_5$]$_2$ was obtained by adding a slight excess of the cation to a methanol solution of NaMn(CO)$_5$. The dark red precipitate which formed immediately was collected by filtration, washed with many portions of water and then with a small portion of methanol, and finally dried under vacuum.

The Ni(1,10-phen)$_3{}^{2+}$ salts of the P(OCH$_3$)$_3$-substituted anions were generally prepared in the same manner from their sodium salts. The Ni(1,10-phen)$_3$[Mn(CO)$_{5-x}$(P(OCH$_3$)$_3$)$_x$]$_2$ compounds occur as very dark purple or black needles, soluble in acetone and THF.

NaMn(CO)$_4$P(OCH$_3$)$_3$ was prepared by adaptation of a published procedure for synthesis of NaMn(CO)$_4$PPh$_3$.[10] NaMn(CO)$_3$(P(OCH$_3$)$_3$)$_2$ was prepared from CH$_3$Mn(CO)$_3$[P(OCH$_3$)$_3$]$_2$[11] by treatment with sodium amalgam.

The Ni(1,10-phen)$_3{}^{2+}$ salts of the PPh$_3$-substituted anions are more difficult to obtain in a pure state, since, aside from their greater sensitivity to air, washing with water (and for the disubstituted species, washing with methanol or ethanol) tends to convert the anion into the corresponding hydride complex.[10,12]

NaMn(CO)$_4$PPh$_3$ was obtained by a published procedure[10] and converted to the Ni(1,10-phen)$_3{}^{2+}$ salt in the usual manner.[13] The crude product was collected by filtration, redissolved in acetone, filtered, pumped dry, washed with a small volume of THF and a large volume of Et$_2$O, and finally dried. A dark brown solid, soluble in acetone and slightly soluble in THF, was thus obtained.

The complexes Fe(CO)$_4$P(OCH$_3$)$_3$ and Fe(CO)$_3$[P(OCH$_3$)$_3$]$_2$ were obtained by treatment of a benzene solution of Fe$_3$(CO)$_{12}$ with about 1.5 mol of P(OCH$_3$)$_3$ per mole of iron.[14] After the initial bubbling ceased, the mixture was heated to boiling for about 3 hr. Then the suspension was filtered and the residue extracted with benzene. The filtrate was pumped to dryness and the residue was sublimed at ~0.01 mm. Fe(CO)$_4$P(OCH$_3$)$_3$ was collected at ~40° and Fe(CO)$_3$[P(OCH$_3$)$_3$]$_2$ at ~60°.

The corresponding triphenylphosphine complexes, Fe(CO)$_4$PPh$_3$ and Fe(CO)$_3$(PPh$_3$)$_2$, were prepared according to the method of Cotton and Parish.[15]

$\{$Co(CO)$_2$[P(OCH$_3$)$_3$]$_3\}$BPPh$_4$ and $\{$Co(CO)[P(OCH$_3$)$_3$]$_4\}$BPh$_4$ were prepared as described in the literature.[16] $\{$Co[P(OCH$_3$)$_3$]$_5\}$BPh$_4$ was prepared by adaptation of a literature procedure.[17] An acetone solution of Co(NO$_3$)$_2\cdot$6H$_2$O was treated with twice the needed amount of the drying agent 2,2-dimethoxypropane and was stirred for 0.5 hr. Ten moles of P(OCH$_3$)$_3$ per mole of Co(NO$_3$)$_2$ was then added. The dark green solution was stirred for 5 min, after which the theoretical amount of NaBPh$_4$ was added, followed by a large portion of Et$_2$O. The yellow solid, $\{$Co[P(OCH$_3$)$_3$]$_5\}$BPh$_4$, which formed almost immediately, was collected by filtration, recrystallized from acetone–water, washed with Et$_2$O, and dried.

The previously unknown complex $\{$Co(CO)$_3$[P(OCH$_3$)$_3$]$_2\}^+$ was obtained as a mixture with the tris(phosphite) complex when a pentane solution of P(OCH$_3$)$_3$ was slowly added to a pentane solution of excess Co$_2$(CO)$_8$ at $\leq -20°$. The work-up of the product, including conversion of the [Co(CO)$_4$]$^-$ salt to the tetraphenylborate($-$I), was carried out as described for the tris- and tetrakis-substituted complexes. The complex was characterized by its ir (Table I) and nmr spectra (virtual triplet at τ ~6.5, superimposed on the known resonances due to $\{$Co(CO)$_2$[P(OMe)$_3$]$_3\}^+$).

Table I. Complexes of the Type [M(CO)$_{5-x}$P$_x$]^n and Their Solution (Acetone) Infrared Spectra in the Carbonyl Region[a]

	M, *n*					
P, *x*	Mn, −1		Fe, 0		Co, +1	
−, 0	A$_1''$	1898 s	A$_1''$	2020 s		
						b
	E$'$	1862 vs	E$'$	1994 vs		
PPh$_3$, 1	A$_1$	1938 s	A$_1$	2048 s		
	A$_1$	1844 s	A$_1$	1971 s		*b*
	E	1812 vs	E	1940 vs		
PPh$_3$, 2			A$_1'$	1950 vw	A$_1'$	2072 vw
		c				
			E$'$	1894 vs	E$'$	2008 vs
P(OCH$_3$)$_3$, 1	A$_1$	1952 s	A$_1$	2058 s		
	A$_1$	1857 s(sh)	A$_1$	1982 s		*b*
	E	1824 vs	E	1949 vs		
P(OCH$_3$)$_3$, 2			A$_1'$	1995 vw	A$_1'$	2108 vw
	E$'$	1786 s	E$'$	1908 vs	E$'$	2025 vs
P(OCH$_3$)$_3$, 3			A$_1$	1937 s^c	A$_1$	2037 s
		d	B$_1$	1879 vs	B$_1$	1982 vs
			(hydrocarbon)			
P(OCH$_3$)$_3$, 4		*b*		*b*	A	1970 s
P(OCH$_3$)$_3$, 5		*b*		*b*		

[a] Frequencies given in cm^{-1}. [b] Compound not reported. [c] Acetone infrared spectrum is unreported. [d] An infrared spectrum has been reported for this compound in CHCl$_3$.[11] However, since we have noted that Mn(CO)$_5{}^-$ reacts with chlorinated solvents to form Mn(CO)$_5$Cl, it is likely that the reported spectrum is attributable to Mn(CO)$_2$(P(OCH$_3$)$_3$)$_3$Cl.

Some of the compounds studied, the manganese anions in particular, are too air sensitive to be analyzed by conventional means. However, by utilizing a tared metal sleeve which was filled with sample, sealed, and reweighed, accurate carbon analyses were obtained. These results were in excellent agreement with the calculated per cent C for both NaMn(CO)$_5$ and LiMn(CO)$_5$. The technique also indicated the absence of hydrogen from both samples. A further check on sample purity involved allowing a sample to decompose in air, then analyzing the residues to check for a 1:1 molar ratio of alkali metal to transition metal. For NaMn(CO)$_5$ the observed ratio was very close to 1. The LiMn(CO)$_5$ residues gave variable results, but infrared and nmr spectral evidence indicated that the material was of the same purity as the sodium compound.

All compounds were additionally characterized by their infrared spectra in the carbonyl region (Table I), which were found to comply with the patterns expected from group theoretical consideration. To facilitate direct comparisons, we report in Table I acetone ir data for several of the complexes for which this information was not previously available.

The results of the analyses carried out by the microanalytical laboratory are listed in Table II, provided in the microfilm edition. See paragraph at end of paper regarding microfilm material.

Instrumental. The nuclear quadrupole resonance spectra were obtained on a Wilks Scientific Corporation (Model NQR 1A) spectrometer, or on the apparatus described by LaRossa and Brown.[18] A 30-sec time constant was normally employed. Fre-

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quencies were measured as described elsewhere.[3] In most instances the frequencies are accurate to within ±0.01 MHz.

The Mössbauer spectrometer is of the constant acceleration type,[19] velocity-calibrated with an iron metal absorber. The source was ^{57}Co diffused into Cu.

Calculation of Field Gradients

The electronic field gradient at a nucleus, eq_{zz}, can be expressed as the sum of the field gradients due to all external charges. The electronic contribution to eq_{zz} is given by[20]

$$eq_{zz,\mathrm{elec}} = \sum_i eq_i = e\sum_i \int \Psi_{\mathrm{M}}(3\cos^2\theta_i - 1)/r_i^3\Psi_{\mathrm{M}}^* \mathrm{d}\tau \qquad (2)$$

where ψ_{M} is the molecular electronic wave function and θ_i and r_i are polar coordinates in the diagonalized field gradient axis system.

If only electrons occupying metal valence orbitals are considered, eq_{zz} is given by eq 1. This expression is frequently simplified further by assuming that only d electrons contribute to the electric field gradient.

It should be noted that in using eq 1 to calculate eq_{zz}, no allowance is made for the contribution of core electrons to the field gradient. If the core electrons were distributed spherically about the nucleus, their effect on eq_{zz} would be zero. However, as shown by Sternheimer,[21] these electrons are polarized by the valence electrons, so that they do contribute to the net field gradient. The magnitude of the Sternheimer effect due to valence electrons is small, and approximately constant for a group of similar compounds.[22] Its neglect should therefore not substantially affect conclusions regarding trends in eq_{zz} in an isoelectronic series of molecules.

To evaluate eq_{zz} from eq 2 we make the assumption, discussed elsewhere,[23,24] that only valence shell electrons centered on the quadrupolar nucleus contribute to the field gradient. This limits us to 3d, 4s, and 4p orbitals. We express Ψ_{M} as a product of sums of atomic functions, Ψ_λ, which are linear combinations of Slater-type orbitals[25]

$$\Psi_\lambda = \sum_j c_{j\lambda}\chi_{j\lambda} \qquad (3)$$

where the subscript j refers to the jth basis function of symmetry λ. The basis functions χ are Slater-type orbitals with integer quantum numbers

$$\chi_j(r, \theta, \phi) = R_{j\lambda}(r)Y^{\lambda\mathrm{m}}(\theta, \phi) \qquad (4)$$

and $R_{j\lambda}(r)$ is the radial part of the function

$$R_{j\lambda}(r) = (2n_{j\lambda})!^{-1/2}(2\zeta_{j\lambda})^{n_{j\lambda}+1/2}r^{n_{j\lambda}-1}e^{-\zeta_{j\lambda}r} \qquad (5)$$

$Y^{\lambda\mathrm{m}}(\theta, \phi)$ are the normalized complex spherical harmonics.

Integrals of the type

$$\int Y^{\lambda\mathrm{m}}(\theta, \phi)(3\cos^2\theta - 1)Y^{\lambda'\mathrm{m}'}(\theta, \phi)\sin\theta\, \mathrm{d}\theta\mathrm{d}\phi \qquad (6)$$

are zero unless $\lambda = \lambda'$ or $\lambda = \lambda' \pm 2$, although when $\lambda = \lambda' = 0$, the integral also equals zero because of spherical symmetry. Thus the only nonzero integrals are those involving the 4s–3d, 3d–3d, and 4p–4p pairs of orbitals.

The formal oxidation states of the metals in the isoelectronic series $[\mathrm{Mn(CO)_5}]^-$, $\mathrm{Fe(CO)_5}$, and $[\mathrm{Co(CO)_5}]^+$, are −1, 0, or +1, respectively. Clementi orbitals are available for Mn(−1), Fe(0), and Co(+1) for a $4s^23d^6$ configuration (^{5}D state). Using these, the results of the calculation for the field gradient due to a single electron in a metal $3d_{z^2}$ orbital are as listed in Table III.

Table III. Calculated Values of One-Electron Atomic Orbital Field Gradient Contributions

Metal (charge)	Configuration	$10^{15}eq_i$, esu/cm^3
Mn(−1)	$4s^23d^6$	−6.70 $(eq_{d_{z^2}})^a$
Fe(0)	$4s^23d^6$	−9.23 $(eq_{d_{z^2}})^a$
Co(+1)	$4s^23d^6$	−12.16 $(eq_{d_{z^2}})^a$
Fe(0)	$4s^13d^64p^1$	−8.79 $(eq_{d_{z^2}})^b$
		−4.97 $(eq_{p_z})^b$

[a] Atomic orbitals of ref 25 are utilized. [b] Atomic orbitals of ref 31 are utilized.

The atomic field gradients for Mn(−1) and Fe(0), in s^2d^6 configuration, have previously been calculated,[26] using Clementi's functions. Our results for these two cases are in agreement with the earlier result.

The electronic configuration $4s^23d^64p^0$ is almost certainly an inaccurate description of the orbital population distribution in $[\mathrm{M(CO)_5}]^n$ species. Molecular orbital calculations on $\mathrm{Fe(CO)_5}$[27–30] indicate that a more reasonable configuration is $4s^13d^64p^1$. Values of eq_i for 3d and 4p electrons can be calculated using the wave functions of Strange, *et al.*,[31] for Fe(0) in the $4s^13d^64p^1$ configuration (^{7}P state). Using these orbitals, the expectation values for the integrals $\langle\psi_{1s}|V_{zz}|\psi_{3d}\rangle$, $\langle\psi_{3d}|V_{zz}|\psi_{3d}\rangle$, and $\langle\psi_{4p}|V_{zz}|\psi_{4p}\rangle$ (where $V_{zz} = (3\cos^2\theta - 1)/r^3$) were evaluated. The first of these integrals is essentially zero. Values for the other two are given in Table III.

It is especially interesting that eq_{p_z} is on the same order of magnitude as $eq_{d_{z^2}}$. It is also noteworthy that $eq_{d_{z^2}}$ for Fe(0) in the ^{7}P state differs by only about 5% from that for Fe(0) in the ^{5}D state. The results of the calculations based on accurate atomic wave functions thus indicate that *configurational changes can be expected to make only minor changes in the orbital field gradient contributions, whereas changes in central metal effective nuclear charge occasion large variations.* Roothan–Hartree–Fock atomic orbitals for the $s^1d^6p^1$ configuration have not been computed for Mn(−1) or Co(+1). Thus, corresponding calculations cannot be carried out for these ions. Since, however, the values of $eq_{d_{z^2}}$ for Fe(0) in the $s^1d^6p^1$ and s^2d^6 configurations are closely similar, the values of $eq_{d_{z^2}}$ for Mn(−1) and

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Table IV. Nqr Data for $[M(CO)_{5-x}P_x]^n$ Complexes (25°)

	ν_1, MHz	ν_2, MHz	ν_3, MHz	$\lvert e^2Qq_{zz}\rvert/h$	η
$Ni(1,10\text{-phen})_3[Mn(CO)_5]_2$	9.42	18.67		62.4	0.08
	9.66	18.99		63.5	0.12
$LiMn(CO)_5$	10.16	20.07		67.1	0.10
$NaMn(CO)_5$	10.48	19.24		65.0	0.26
$Ni(1,10\text{-phen})_3[Mn(CO)_4P(OCH_3)_3]_2$	11.52	22.92		76.5	0.05
$Ni(1,10\text{-phen})_3[Mn(CO)_4PPh_3]_2$	12.92[a]	25.31		84.7	0.13
		25.69		85.8	0.06
$\{Co(CO)_3[P(OCH_3)_3]_2\}BPh_4$	~9.7	19.26	29.12	136.1	0.13
$\{Co(CO)_2[P(OCH_3)_3]_3\}BPh_4$	15.68	18.09	28.56	136.3	0.47
$\{Co[P(OCH_3)_3]_5\}BPh_4$		21.93	32.92	153.7	0.04
$\{Co(CO)_3(PPh_3)_2\}Co(CO)_4$[b]		22.77	34.20	159.7	0.05

[a] Average of two very closely spaced resonances. [b] K. Ogino and T. L. Brown, *Inorg. Chem.*, **10,** 517 (1971).

Table V. Mössbauer Data for $Fe(CO)_{5-x}P_x$ Complexes

	Temp, °K	$\lvert\Delta E_q\rvert$, mm/sec	Sign of $\lvert\Delta E_q\rvert$[b]	η	e^2Qq_{zz}/h,[f] MHz	Ref
$Fe(CO)_5$	77	2.60	+[c]	0.0[d]	60.5	6
	78	2.57			59.8	*g*
	253	2.57			59.8	*h*
$Fe(CO)_4PPh_3$	77	2.54	+[d]	0.0[d]	59.1	6
	Ambient	2.42			56.3	5
$Fe(CO)_3(PPh_3)_2$	77	2.76	+[d]	0.0[d]	64.2	6
$Fe(CO)_4P(OCH_3)_3$	4.2	2.27	+	~0.0	52.8	*a*
	Ambient	2.26			52.6	*a*
$Fe(CO)_3[P(OCH_3)_3]_2$	4.2	2.20	+	~0.0	51.2	*a*
	Ambient	2.28			53.0	*a*
$Fe(CO)_4P[N(CH_3)_2]_3$	Ambient	2.22	*e*		51.6	5
$Fe(CO)_3\{P[N(CH_3)_2]_3\}_2$	Ambient	2.27	*e*		52.8	5

[a] This work. [b] $Q(^{57}Fe^m)$ is positive. [c] Reference 5. [d] Reference 33. [e] Not determined, but assumed to be positive. [f] For $^{67}Fe^m$, 1 mm/sec ≡ 11.63 MHz. [g] R. H. Herber, W. R. Kingston, and G. K. Wertheim, *Inorg. Chem.*, **2**, 153 (1963). [h] M. Kalvius, V. Zahn, P. Kienle, and H. Eicher, *Z. Naturforsch. A*, **17**, 494 (1962).

Co(+1) in the $s^1d^6p^1$ configuration should thus be quite similar to the values found for the s^2d^6 configuration.

Nqr Results and Discussion

The ^{55}Mn and ^{59}Co nqr frequencies for Mn and Co compounds, respectively, are given in Table IV. Since $[Co(CO)_3(P(OCH_3)_3)_2]^+$ was isolated as a mixture with $[Co(CO)_2(P(OCH_3)_3)_3]^+$, the resonances of both complexes were observed in the sample. Those due to the tris(phosphite) complex were identified by comparison with the spectrum of that pure compound. It is interesting, but unfortunate, that the nqr resonances of $[Co(CO)(P(OCH_3)_3)_4]BPh_4$ were not observed, despite repeated attempts and despite the fact that the other cobalt complexes produce intense resonance signals.

In a few cases, two sets of resonances were found, as a result of crystallographic nonequivalence within the unit cell. For $Ni(1,10\text{-phen})_3[Mn(CO)_5]_2$, the nqr results are consistent with the known crystal structure.[32] The sets of data for this molecule are easily paired as given in Table IV, since the alternative pairing would lead to an imaginary value for η. The signals arising from the anion more severely distorted from axial symmetry, which Frenz and Ibers label molecule I, are probably those associated with the larger value of η, 0.12. For the two complexes in which two sets of signals were found, the average value of $\lvert e^2qQ_{zz}/h\rvert$ is used in the discussion to follow.

With the exception of the $NaMn(CO)_5$ compound, the asymmetry parameter is within about 0.15 of zero in all instances in which the geometry about the metal is expected to possess axial symmetry. The rather large value of η in $NaMn(CO)_5$ suggests that the Na^+ may be coordinated to a radial CO group of the $Mn(CO)_5^-$. In any event, the geometry about Mn in the sodium salt is such as to strongly perturb the ion away from axial symmetry. The expected large departure from axial symmetry is observed in $\{Co(CO)_2[P(OCH_3)_3]_3\}BPh_4$, in which there are presumably two axial and one equatorial phosphites.

Mössbauer data for the complexes $Fe(CO)_{5-x}P_x$ are presented in Table V. The sign of $\lvert\Delta E_q\rvert$ (and hence, of $e^2q_{zz}Q/h$ and eq_{zz}) has been shown to be positive for $Fe(CO)_5$[4] and its PPh_3 derivatives;[33] the present study shows this to be the case for the $P(OCH_3)_3$-substituted compounds as well.

Attempts to synthesize compounds containing the $Co(CO)_5^+$ ion have so far been unsuccessful. It is possible to estimate $e^2q_{zz}Q/h$ for $Co(CO)_5^+$, however, by employing determinations of $e^2q_{zz}Q/h$ for isoelectronic pairs of Fe and Co complexes, *e.g.*, $[M(CO)_3(PPh_3)_2]^n$ and $[M(CO)_3(P(OCH_3)_3)_2]^n$. The relationship in eq 7 is employed to approximate $\lvert e^2Qq_{zz}/h\rvert$ for the

$$\frac{\dfrac{\lvert e^2Qq_{zz}\rvert}{h}([Co(CO)_5]^+)}{\dfrac{\lvert e^2Qq_{zz}\rvert}{h}([Co(CO)_3P_2]^+)} = \frac{\dfrac{\lvert e^2Qq_{zz}\rvert}{h}(Fe(CO)_5)}{\dfrac{\lvert e^2Qq_{zz}\rvert}{h}(Fe(CO)_3P_2)} \qquad (7)$$

hypothetical cation $[Co(CO)_5]^+$. The assumption made is that changes in electronic configuration on going

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from $Fe(CO)_3P_2$ to $[Co(CO)_3P_2]^+$ are the same as those which would occur between $Fe(CO)_5$ and $[Co(CO)_5]^+$. Slater, *et al.*, have utilized[34] a similar relationship, in comparing the known quadrupole coupling constants of ferrocene and cobaltocenium ion. They predict $e^2q_{zz}Q/h$ for $[Co(CO)_5]^+$ to be +170 MHz.

For the two pairs of complexes for which $e^2q_{zz}Q/h$ are known, we calculate $(e^2q_{zz}Q/h)([Co(CO)_5]^+) = 150$ MHz (P = Ph_3) or 161 MHz (P = $P(OCH_3)_3$). The average value of 156 MHz is used in the discussion which follows. Because of the close structural and electronic similarities between $[M(CO)_5]^n$ and $[M(CO)_3P_2]^n$ complexes, our estimate of $e^2q_{zz}Q/h$ for $Co(CO)_5^+$ is probably more accurate than the previous estimate.

For more direct comparison of the field gradients in the different metal complexes, the values of $e^2q_{zz}Q/h$ are divided by eQ/h to determine the field gradient eq_{zz}. Values of Q for the three nuclei, taken from the recent literature, are $Q(^{55}Mn) = +0.40$ b,[35] $Q(^{57}Fe^{m}) = +0.19$ b,[36] and $Q(^{59}Co) = +0.40$ b.[37] The field gradients thus calculated from the data of Tables IV and V are listed in Table VI.

Table VI. Observed Field Gradients, eq_{zz}, for the Complexes $[M(CO)_{5-x}P_x]^{n}$ [a,b]

	M, n		
x, P	Mn, −1	Fe, 0[c]	Co, +1
0	±2.17	+4.39	±5.4[d]
1, $P(OCH_3)_3$	±2.64	+3.83	—
2, $P(OCH_3)_3$		+3.72	±4.69
3, $P(OCH_3)_3$			±4.70
4, $P(OCH_3)_3$	—	—	
5, $P(OCH_3)_3$	—	—	±5.30
1, PPh_3	±2.94	+4.29	—
2, PPh_3		+4.66	±5.51

[a] The field gradients are given in units of 10^{15} esu/cm^3. [b] A dash indicates the complex is unknown. [c] Low temperature quadrupole splittings were used to obtain the iron field gradients. [d] This value was estimated as described in the text.

Several MO calculations have been reported for $Fe(CO)_5$.[27–30] Using the reported orbital populations and the values listed in Table III for the orbital field gradient contributions, for Fe in the $4s^13d^64p^1$ configuration, the total valence electronic contribution to the field gradient can be estimated using eq 1. When this is done for the populations reported by Schreiner and Brown,[28] a value for eq_{zz} of $+3.2 \times 10^{15}$ esu/cm^3 is obtained. Using the results of the calculation by Trautwein and Harris,[30] eq_{zz} is computed to be $+4.6 \times 10^{15}$ esu/cm^3. (Hillier[29] does not report the individual orbital populations, so the corresponding calculation cannot be carried out for his MO results.) The estimates based on the MO calculations are in reasonable agreement with the eq_{zz} value deduced from the observed quadrupole splitting in $Fe(CO)_5$, $+4.4 \times 10^{15}$ esu/cm^{-3}.

The 4p orbital contribution to eq_{zz} in transition metal complexes has been generally ignored on the grounds that $q_{d_{z^2}}$ should be considerably larger than q_{p_z} and that 4p orbital populations are likely to be much smaller than the 3d. Korol'kov and Makhanek report[38] that for Cu(I) the expectation values for $1/r^3$ are 1.17 and 8.1 au for 4p and 3d electrons, respectively. Our calculations using the SCF orbitals of Strange, *et al.*,[31] yield 1.9 and 4.74 au for the analogous values for Fe(0) in the ^7P state.

Inclusion of the appropriate angular terms in arriving at the values for eq_i listed in Table III reduces the difference between the 3d and 4p electron contributions even further. The 4p orbital contribution to the calculated value of eq_{zz} in $Fe(CO)_5$, using available MO eigenvectors as described above, is on the order of 10–20%. Thus, while the 3d orbitals do make the major contributions, the 4p orbitals play a significant role. In discussing changes in the orbital populations in related compounds, the p_z orbital changes may be assumed to parallel those in d_{z^2}, while the p_x and p_y orbital changes should follow those for d_{xy}, $d_{x^2-y^2}$.

The sign of the field gradient is known only for the iron complexes. If, however, we consider the $[M(CO)_5]^n$ species, it is reasonable to assume that the sign of eq_{zz} does not change. The only alteration in the isoelectronic sequence $Mn(CO)_5$, $Fe(CO)_5$, and $Co(CO)_5^+$ is an increase in the central metal nuclear charge. While this should cause a steady contraction of the valence orbitals centered on the metal, it should not alter their *relative* populations sufficiently to cause the sign to change.

Furthermore, one would expect at least a smooth relationship in the manner in which eq_{zz} varies in the series $Mn(CO)_5^-$, $Fe(CO)_5$, and $Co(CO)_5^+$.[39] If either $Mn(CO)_5$ or $Co(CO)_5^+$ possessed a sign for eq_{zz} different from that for $Fe(CO)_5$, the value for the other, regardless of which sign is assumed, would not fit well. For example, assume that eq_{zz} for $Mn(CO)_5^-$ is −2.17. Then the difference in eq_{zz} between $Mn(CO)_5^-$ and $Fe(CO)_5$ would be on the order of 6.6. This would suggest that eq_{zz} for $Co(CO)_5^+$ should be on the order of $10–11 \times 10^{15}$ esu/cm^3, a factor of two greater than the estimated value.

Assuming then that eq_{zz} is positive for all three isoelectronic species, it is of interest to compare the variation in eq_{zz} seen experimentally with the calculated variation in $eq_{d_{z^2}}$, as given in Table III. The variation in the calculated quantity is the result of a full unit difference in charge on the central metal in the series Mn(−1), Fe(0), and Co(+1). The variation in effective nuclear charge on the central metal experienced by the valence electrons in the series $Mn(CO)_5^-$, $Fe(CO)_5$, and $Co(CO)_5^+$ must be considerably smaller than for the atoms, since much of the electronic charge which would otherwise accumulate on the metal in the more negatively charged species is transferred to the CO groups.

The observed variation in eq_{zz} exceeds the calculated variation in $eq_{d_{z^2}}$ for the isoelectronic monatomic species. It therefore appears that there is a shift in the relative magnitudes of the terms of opposite sign in eq 1, such that the radial orbitals become relatively more

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populated as compared with the axial, with increased charge on the central metal. Since the radial orbitals are more heavily populated than the axial in all three complexes, assuming positive values for eq_{zz}, this amounts to saying that the $[M(CO)_5]^n$ species becomes more anisotropic with increasing charge on the central atom. It should be noted, however, that the differential electronic populations involved in creating the nonzero field gradients are not large; the difference in d_{z^2} and $d_{x^2-y^2}$ populations from Schreiner and Brown's molecular orbital results for $Fe(CO)_5$ is, for example, only 0.2 electron. Assuming this were correct for $Fe(CO)_5$, the analogous differential populations for $Mn(CO)_5^-$ and $Co(CO)_5^+$ might be on the order of 0.1 and 0.3, respectively. It would be of interest to know the chemical shift anisotropies for ^{55}Mn and ^{59}Co in these two ions; the prediction is that the anisotropy is smaller for ^{55}Mn.

It is difficult to draw many firm conclusions from the limited data available for substituted systems. The most reliable interpretations can be placed on those systems for which the substitution occasions no structural changes in terms of bond angles. This includes the disubstituted systems, in which the phosphines or phosphites are located axially, and the pentakis(phosphite) compound, $Co[P(OCH_3)_3]_5^+$.

The values for $Co(CO)_5^+$ and $Co(P(OCH_3)_5^+$ must be regarded as essentially the same, since the former value is only an estimate. The result tells little about the binding of $P(OCH_3)_3$ as compared with CO, since so many parameters (both σ- and π-bonding capabilities of CO and $P(OCH_3)_3$ in both apical and radial positions) are involved. The results for the $[M(CO)_3P_2]^n$ compounds as compared with the parent compounds are more interesting. Since eq_{zz} for the cobalt compounds were employed to estimate eq_{zz} for $Co(CO)_5^+$, the data for the Fe compounds provide the only entirely independent data for examination. Substitution of $P(OCH_3)_3$ for axial CO groups leads to a decrease in eq_{zz}, whereas an increase is seen upon PPh_3 substitution.

Bancroft and Libbey have recently reported[40] the Mössbauer spectra of an extensive series of low spin iron(II) compounds, from which they have derived a series of ligand partial field gradient (pfg) parameters. Since the complexes are all six-coordinate, it is not to be expected that the derived pfg parameters are transferable to five-coordinate compounds. Nevertheless, the results are of interest here because they represent the only pfg parameters for ligands such as CO, phosphines, and phosphites. Although the pfg parameters do not transfer quantitatively, one might ask whether their *relative* values remain the same in the five-coordinate systems. The pfg parameters reported by Bancroft and Libbey for CO, $P(OCH_3)_3$, and PPh_3 are −0.55, −0.65, and −0.53, respectively. Taking account of only the relative values, it would thus be predicted that axial substitution of CO in the five-coordinate systems by PPh_3 would result in an increase in $e^2q_{zz}Q/h$, whereas replacement by $P(OCH_3)_3$ would result in a decrease, as observed. It thus appears that the relative values of pfg parameters for these three ligands do remain the same, even though the relative importances of σ- and π-bonding surely change in going from six-coordinate Fe(II) to five-coordinate Fe(0).

The changes in eq_{zz} upon substitution of one phosphine or phosphite in place of CO cannot be readily explained in the absence of structural data, since it is not clear how much the central metal is displaced from the plane of the radial CO groups. These displacements may be large enough to make a significant contribution to changes in eq_{zz}. This is especially true in the case of the mono-substituted Fe compounds, in which the changes are small. Thus we base our discussion on the bis-substituted derivatives of $Fe(CO)_5$.

The radial CO stretching frequency (E mode) may be used as a gauge of relative π-accepting and σ-donating capacities of axial CO, $P(OCH_3)_3$, and PPh_3 in the complexes $Fe(CO)_5$ and $Fe(CO)_3P_2$. Substantial decreases are observed in this frequency in the order $Fe(CO)_5 > Fe(CO)_3[P(OCH_3)_3]_2 > Fe(CO)_3(PPh_3)_2$. The CO frequency variation may be ascribed in large measure to differences in π-accepting capability of the axial ligands. Thus, in this series of complexes we order the ligands CO > $P(OCH_3)_3$ > PPh_3, as regards π-acid behavior, in accord with conventional notions.

The values of eq_{zz} observed for these complexes indicate that, according to eq 1, PPh_3 must be acting as either a strong π-acceptor or weak σ-donor relative to CO, since the value of the term $N_{d_{z^2}} + {}^1/_2(N_{d_{xz}} + N_{d_{yz}})$ must be smaller for $Fe(CO)_3(PPh_3)_2$ as compared with $Fe(CO)_5$. Since the ir data indicate that PPh_3 is a poorer π-acceptor than CO, we conclude that the phosphine also functions as a poorer σ-donor in $Fe(CO)_3(PPh_3)_2$. The behavior of $P(OCH_3)_3$ cannot be analyzed so simply since the value of eq_{zz} for $Fe(CO)_3[P(OCH_3)_3]_2$ is consistent with *either* poorer π-accepting or better σ-donating capacity of the ligand relative to CO.

Unfortunately the values of eq_{zz} for the bis-substituted Mn complexes are not available. However, the data for mono-substituted Mn complexes suggest that the $Mn(CO)_3P_2^-$ derivatives might both exhibit field gradients substantially larger than that of $Mn(CO)_5^-$. This result would lead to the conclusion that both PPh_3 and $P(OCH_3)_3$ behave as poorer σ-donors relative to CO in the Mn series.

These results are consistent with the idea that low valent metals, such as Fe(0) and Mn(−1) in the complexes studied, are relatively resistant to σ-donation by ligands which cannot adequately drain away excess electron density through π back-bonding. A single ordering of ligands as regards σ- and π-bonding capacities may therefore not be applicable to all organometallic systems.

Supplementary Material Available. Analytical data will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JACS-74-4149.

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