istries with force constants, the separation of steric and electronic effects, and the specific role of the organolithium compounds in nucleophilic addition reactions.[48] It is also important to test the hypothesis with nucleophiles derived from reagents other than organolithium compounds.

We have begun an investigation of the reactions of organomagnesium halides with tungsten and chromium hexacarbonyls. Our initial results indicate these reactions provide products identical with those resulting from organolithium–metal carbonyl reactions but seem to be more amenable to a kinetic study.[49]

Acknowledgments.—The authors are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for Grants 1404-G3 (M. Y. D.) and 1705-G3 (D. J. D.) which supported this research. In addition, we thank Professor T. L. Brown for helpful discussion in the preparation of this article.

(48) Several of these investigations are presently underway in our laboratory.

(49) Reactions of methyl- and phenylmagnesium bromides with tungsten and chromium hexacarbonyls and subsequent ethylation produced complexes identical with those well characterized in the phenyl- and methyllithium reactions.[1] Benzyl- and cyclohexylmagnesium chlorides produced carbene-type ligands hitherto unreported. Further studies of these reactions are forthcoming from our laboratories.

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Mössbauer Spectra of Some Linear and Triangular Polynuclear Iron Carbonyls

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The Mössbauer spectra of ^{57}Fe in a number of trinuclear carbonyls were studied at liquid nitrogen temperature. In the linear $Mn_2Fe(CO)_{14}$ the quadrupole splitting is only 0.43 mm/sec, whereas in the triangular species $(C_2H_5)_4N[Fe_2M(CO)_{12}]$ (M = Mn, Tc, Re) it is much greater (Δ = 0.91, 0.91, and 0.89 mm/sec, respectively). An estimate of 0.15 mm/sec is given for the quadrupole splitting of the unique iron atom in $Fe_3(CO)_{12}$. The isomer shifts are very similar for all of the compounds studied: δ 0.34–0.35 mm/sec relative to sodium nitroprusside. Charge distributions were estimated by analysis of these data. In the linear compound, the small quadrupole splitting was taken as evidence of the rather high σ donation of terminal carbonyls, which also explained the very small quadrupole splitting observed for the unique iron atom in $Fe_3(CO)_{12}$. In the triangular species the environment of the iron atoms may be described as an octahedron with distortions along both the three- and fourfold axes. In comparison with the quadrupole coupling in $Co_2(CO)_8$, it is shown that the observed quadrupole splitting is approximately equal to the contribution of the tetragonal distortion. This part of the field gradient is attributed to the higher metal orbital population in the metal–metal bonds compared with metal–carbon bonds of bridging carbonyls. A value of 0.11 was obtained for the difference in σ donation from terminal and bridging carbonyls to the iron atom.

Introduction

The iron carbonyls were among the first compounds to be studied by the Mössbauer method soon after it was recognized as a source of molecular structure information. Although the structure of triiron dodecacarbonyl, $Fe_3(CO)_{12}$, had not yet been determined satisfactorily, its Mössbauer spectrum[3] showed that two different kinds of iron atoms are present in the molecule. A number of structures were consistent with the data, and as Wertheim[4] pointed out, the structure could not be proved from the Mössbauer spectrum alone. Later, as a consequence of a Mössbauer study of $Fe_3(CO)_{11}H$ by Erickson and Fairhall[5] and an X-ray study by Dahl and Blount[6], the probable structure of $Fe_3(CO)_{12}$ emerged as a triangular array of iron atoms corresponding to the structure of diiron enneacarbonyl in which one of the bridging carbonyls was replaced by a *cis*-octahedral $Fe(CO)_4$ group; this structure has recently been confirmed by Wei and Dahl.[7] Following the work of Erickson and Fairhall, it has been assumed that the outer lines of the $Fe_3(CO)_{12}$ spectrum arise from the carbonyl-bridged $Fe_2(CO)_8$ moiety, and the central line is due to the essentially octahedral $Fe(CO)_4$ group. This assignment has not been fully demonstrated, nor has there been an adequate explanation of the increase in the quadrupole splitting over that observed in the parent $Fe_2(CO)_9$.

During the past decade, a number of mixed-metal carbonyls with metal–metal bonds have been prepared. Among these is a series of triangular group VIIb diiron dodecacarbonyl anions whose proposed structures are like that of $Fe_3(CO)_{12}$ in which the unique iron atom is replaced by a group VIIb atom. Examination of the Mössbauer spectra of this series afforded an opportunity

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(1) Taken in part from a dissertation submitted by M. W. L. to Florida State University in partial fulfillment of the requirements for the Ph.D. degree.

(2) Oak Ridge Associated Universities Research Participant.

(3) R. H. Herber, W. R. Kingston, and G. K. Wertheim, *Inorg. Chem.*, **2**, 154 (1963).

(4) G. K. Wertheim, "Mössbauer Effect: Principles and Applications," Academic Press, New York, N. Y., 1964, pp 96–98.

(5) N. E. Erickson and A. W. Fairhall, *Inorg. Chem.*, **4**, 1320 (1965).

(6) L. F. Dahl and J. F. Blount, *ibid.*, **4**, 1373 (1965).

(7) C. H. Wei and L. F. Dahl, *J. Amer. Chem. Soc.*, **91**, 1351 (1969).

to establish the validity of the line assignment in the $Fe_3(CO)_{12}$ spectrum and to investigate further the effect of substitution of a bridging carbonyl in $Fe_2(CO)_9$ by a *cis*-octahedral $M(CO)_4$ group on the quadrupole splitting.

The structure of the linear $Mn_2Fe(CO)_{14}$, prepared by Schubert and Sheline,[8] was determined by Agron and coworkers,[9] and the Mössbauer spectrum of this compound afforded an opportunity to gain some insight into the nature of metal–metal bonds in nonbridged polynuclear carbonyls.

Experimental Section

The Mössbauer spectra were obtained on an electromechanical constant-acceleration spectrometer built and operated at the USAEC Savannah River Laboratory, Aiken, S. C. The radiation source consisted of 5 mCi of ^{57}Co diffused into a thin copper disk and was obtained from the New England Nuclear Corp., Boston, Mass. 02118. The transmission spectra were obtained using a Reuter-Stokes RSG-30A krypton–methane-filled proportional counter and associated components to limit detection to only the resonant 14.37-keV γ ray. The transmitted radiation was registered in a RIDL Model 34-12B 400 channel analyzer operated in the multiscaler mode and in synchronization with the velocity-modulated radiation source. The spectrometer was velocity calibrated with the National Bureau of Standards Standard Reference Material 725, a single crystal of sodium nitroprusside, $Na_2Fe(CN)_5NO \cdot 2H_2O$.[10] The linearity of the transducer was checked by measurement of the error signal as described by Kankeleit.[11] The average velocity increment was 0.0215 mm/sec per channel. As an additional check, the Mössbauer spectra of $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ were repeated so that the measurements obtained in this work could be compared with those of other workers; such a comparison is shown in Table I.

TABLE I

MÖSSBAUER DATA[a] OF SOME POLYNUCLEAR IRON CARBONYLS

Compound	78°K		298°K	
	δ	Δ	δ	Δ
$Fe_2(CO)_9$	0.43	0.42	0.33	0.37
Ref 17	0.42	0.42	0.32	0.37
Ref 3	0.36	0.54	0.33	0.37
$Fe_3(CO)_{12}$ (bridged irons)	0.39	1.13	0.29	0.94
Ref 16	0.37	1.13	...	...
$Fe_3(CO)_{12}$ (unique iron)	0.33	0.15	0.24	0.20
Ref 16	0.31	0.13	...	...
$Mn_2Fe(CO)_{14}$	0.34	0.43	0.24	0.37
$MnFe_2(CO)_{12}^-$	0.34	0.91	...	...
$TcFe_2(CO)_{12}^-$	0.34	0.91	...	...
$ReFe_2(CO)_{12}^-$	0.35	0.89	...	...

[a] Isomer shifts, δ, are reported in mm/sec relative to the sodium nitroprusside spectrum; quadrupole splittings, Δ, are given in mm/sec. The value used for the quadrupole splitting in the sodium nitroprusside spectrum was 1.7048 mm/sec reported by R. W. Grant, R. M. Housley, and U. Gonser, *Phys. Rev.*, **178,** 523 (1969). Velocity error limits are estimated to be within ±0.01 mm/sec.

Thin disk-shaped absorbers were prepared by packing polycrystalline specimens into a 0.5-in. hole punched into computer data card stock and covering with thin (*ca.* 0.25 mil) Mylar film. In order to reduce thickness broadening and to minimize scattering, especially in the rhenium-containing specimens, the absorber thickness was not greater than 50 mg/cm². Room-temperature absorbers were also covered with 1-mil aluminum foil to prevent photochemical decomposition. The low-temperature spectra were obtained using a cryostat with Mylar windows. The absorber was convection cooled with helium gas that was in thermal contact with liquid nitrogen. The absorber temperature was checked with a platinum resistance thermometer.

The spectra were collected by accumulating counts, 3.5–7.3 million counts/channel, until a difference of about 10^5 counts/channel was obtained between the nonresonant region and the strongest resonant absorption; by this method, the counting error was always less than the absorption. The spectral data were computer fitted to Lorentzian peaks by a least-squares fitting program.

Triiron dodecacarbonyl as obtained from Alfa Inorganics, Beverly, Mass. 01915, was sublimed by the procedure of King and Stone.[12]

All other polynuclear iron carbonyls used in this work were prepared by photochemical methods.[9,13–15]

Several absorbers were checked for possible decomposition during collection of the Mössbauer spectra by examination of their infrared spectra and/or examination for paramagnetism using a Foner vibrating magnetometer; no evidence of decomposition was found.

Results

Most of the compounds studied show only very weak absorptions at room temperature due to lattice dynamics; the absorptions at liquid nitrogen temperature are considerably stronger as can be seen in Figure 1, which shows the spectra of a $Mn_2Fe(CO)_{14}$ absorber at the two temperatures. Therefore, only the low-temperature spectra are discussed.

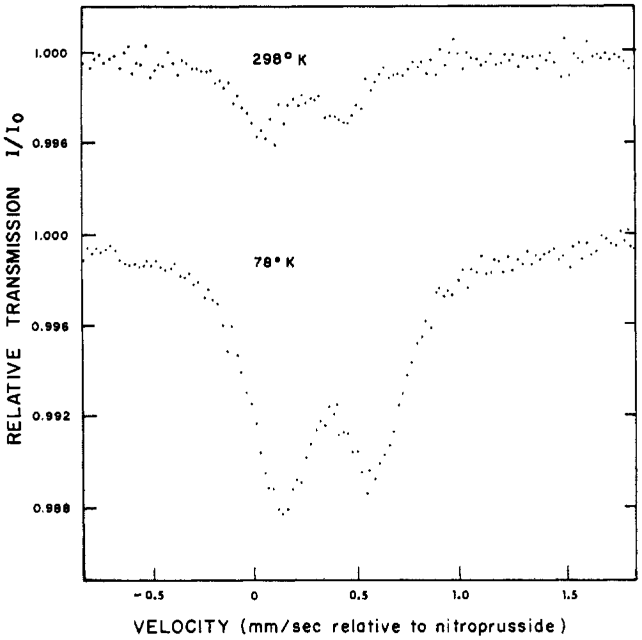

Figure 1.—Mössbauer spectra of $Mn_2Fe(CO)_{14}$.

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[9] P. A. Agron, R. D. Ellison, and H. A. Levy, *Acta Crystallogr.*, **23,** 1079 (1967).

[10] J. J. Spijkerman, F. C. Ruegg, and J. R. DeVoe, "Mössbauer Effect Methodology," Vol. I, I. J. Gruverman, Ed., Plenum Press, New York, N. Y., 1965, p 115. See also NBS Miscellaneous Publication No. 260-13. See R. H. Herber, "Applications of the Mössbauer Effect in Chemistry and Solid State Physics," International Atomic Energy Agency, Vienna, 1966, p 122, for data corrected to the sodium nitroprusside velocity scale.

[11] E. Kankeleit, "Mössbauer Effect Methodology," Vol. I, I. J. Gruverman, Ed., Plenum Press, New York, N. Y., 1965, p 61.

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[13] G. O. Evans, J. P. Hargaden, and R. K. Sheline, *Chem. Commun.*, 186 (1967).

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$Mn_2Fe(CO)_{14}$.—This compound consists of a planar iron tetracarbonyl moiety inserted between two axial manganese pentacarbonyl groups.[9] The structure[9] contains two crystallographically distinct molecules of required C_{2h}-2/mm symmetry giving a molecular geometry that ideally conforms to D_{4h}-4/m2/m2/m symmetry. The two molecules show slightly different Fe–Mn distances, whose mean value is 2.815 Å. In each site the iron atom is in a *trans*-disubstituted octahedral environment, and as a result of this noncubic field, quadrupole splitting was expected in the Mössbauer spectrum. For one of the crystallographic sites the Mn–Fe–Mn direction is a twofold rotation axis, demanding that one of the principal axes of the field gradient tensor (FGT) coincides with the Mn–Fe bonds as well. For both molecules the iron site has approximately D_{4h} symmetry,[9] and it is thus reasonable to assume that the z axis of the FGT lies along the Fe–Mn bond. The room and liquid nitrogen temperature spectra of this compound are shown in Figure 1. The low-temperature spectrum is a simple two-line pattern showing that both sites have essentially the same quadrupole splitting. The usual behavior of the Mössbauer spectra of iron carbonyls with a change in temperature is an increase in both the isomer shift and quadrupole splitting as the temperature is decreased; this behavior is shown by the lines of the $Mn_2Fe(CO)_{14}$ spectra shown in Figure 1. The quadrupole splitting and isomer shift measurements of these spectra fall within the empirical limits suggested by Farmery and coworkers[16] for six-coordinate neutral iron carbonyls; the measured values are tabulated in Table I.

$Fe_2(CO)_9$.—The Mössbauer spectra of this compound were repeated to establish the validity of the measurements obtained by comparison with values reported by other workers.[3,17] The data from these measurements, along with those of other workers, are shown in Table I. Advances in instrumentation and source preparation have made possible much more reliable Mössbauer measurements in recent years, which accounts for the discrepancies observed with earlier data.

$Fe_3(CO)_{12}$.—The Mössbauer spectra of this substance were also remeasured primarily as a check on the reliability of the spectrometer. However, the room-temperature spectrum of this compound clearly shows a broad central absorption consisting of two very closely spaced peaks. The quadrupole splitting of these peaks was estimated to be at least 0.20 mm/sec. The splitting at liquid nitrogen temperature is estimated to be about 0.15 mm/sec. Farmery and coworkers recently observed similar splittings for this compound.[16] This splitting clearly eliminates the possibility of structures in which one of the iron atoms is in a cubic environment, such as the linear structure recently proposed by Lewis and Drickamer.[18] Such splitting is in accord with the triangular structure determined by Wei and Dahl.[7]

$(C_2H_5)_4NMFe_2(CO)_{12}$ Series (M = Mn, Tc, Re).—The Mössbauer spectra of these compounds at 78°K are shown in Figure 2. The distinctive feature of these spectra is that the quadrupole splittings and isomer shifts are essentially unaffected by the atomic number of the group VIIb metal in the apical position of the anion. Furthermore, the isomer shifts and quadrupole splittings of this series are very similar to those of the outer pair of lines in the $Fe_3(CO)_{12}$ spectrum; this confirms the assumed line assignments in the $Fe_3(CO)_{12}$ Mössbauer spectrum. Only small amounts of the technetium diiron dodecacarbonyl salt were available and the low line intensities in its spectrum are due in part to the thin absorber used, but the intensities are also reduced by bremsstrahlung from the technetium β particles. There is also some reduction in absorption intensities in the rhenium compound due to the scattering of the low-energy γ radiation by rhenium atoms.

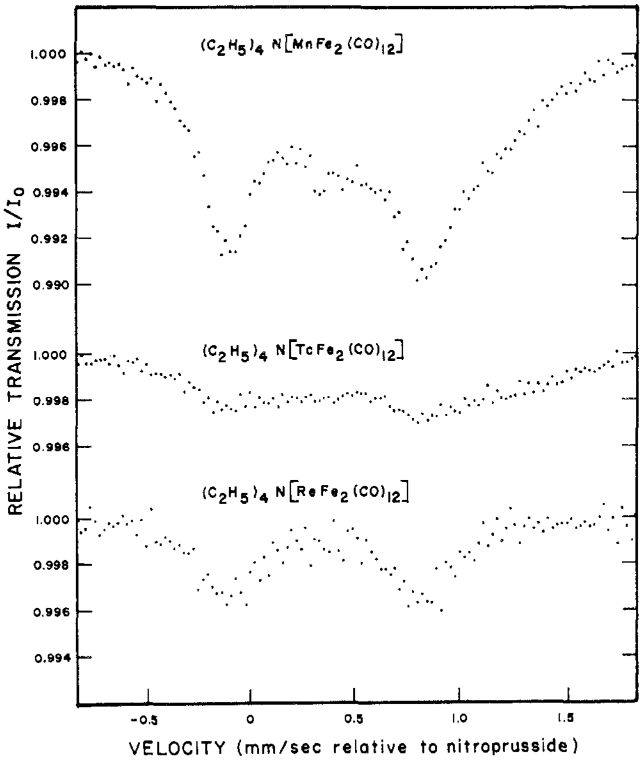

Figure 2.—Mössbauer spectra of $(C_2H_5)N[MFe_2(CO)_{12}]$ series at liquid nitrogen temperature.

Discussion

The isomer shifts of the compounds studied are all very similar; this may be taken to mean that the valence state of the iron is essentially the same in all of these complexes. A detailed discussion of the small differences in isomer shifts does not seem advisable because of the many factors which contribute to the isomer shift in covalent iron complexes. However, there are several interesting aspects in the behavior of the isomer shifts of these compounds. The isomer shifts of $Mn_2Fe(CO)_{14}$ and the unique iron atom in

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(16) K. Farmery, M. Kilner, R. Greatrex, and N. N. Greenwood, *J. Chem. Soc., A*, 2339 (1969).

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(18) G. K. Lewis, Jr., and H. G. Drickamer, *J. Chem. Phys.*, **49**, 3782 (1968).

$Fe_3(CO)_{12}$ are almost identical at both temperatures. In both molecules the iron atom is in an essentially octahedral environment of four terminal carbonyls and two metal–metal bonds, but in one case, the metal–metal bonds are *trans*, and in the other they are *cis*. Farmery and coworkers[16] observed that the isomer shifts in iron carbonyls having the same charge and coordination number are very similar. The isomer shifts in the triangular anions are about 0.05 mm/sec smaller than that of the bridged iron atoms in $Fe_3(CO)_{12}$. This is the same reduction observed by Farmery and coworkers[16] between neutral and singly charged anionic species of the same structure. This is additional evidence for the presence of the bridged $Fe_2(CO)_8$ structure in the series of triangular anions. Finally, the constancy of the isomer shifts in the series of triangular anions indicates that the bonding of the bridged iron atoms, in the $Fe_2(CO)_8$ moiety, is quite independent of the atomic number of the metal in the apical $M(CO)_4$ group; this is further supported by the similarity of values calculated for the Fe–M overlap integrals listed in Table III.

The quadrupole splitting, however, is quite different for the linear and the triangular trimetallic compounds. Although point charge and crystal field calculations have been useful for high-spin compounds of iron,[19] they do not give reasonable results for the iron carbonyls. In $Fe(CO)_5$, for example, the electric field gradient has been shown to be positive.[20] Since the Fe–C distances for the axial carbonyls are shorter than for the equatorial carbonyls, a point charge model will give an electric field gradient with a negative sign. Therefore, this approach is unsatisfactory. A simple crystal field model gives a value much too large for the electric field gradient as pointed out previously by Brown and coworkers,[21] who explained the quadrupole splitting using molecular orbital calculations of this compound.[22] On the basis of an MO description of the bonding, the quadrupole splitting is explained as being due to different populations of the metal orbitals.[21,23–25] For ^{57}Fe coupling constants an additional complication arises from the fact that the coupling constant for a $3d_0$ electron in atomic iron is not yet known. The large electric field gradient in ferrocene[26] and the isoelectronic cobaltocenium ion[24,27] provide a means of estimating its value.[28] We obtain a value of 3.90 mm/sec for the quadrupole splitting of a single $3d_{z^2}$ electron. This compares well with the observed quadrupole splitting of 3.70 mm/sec in $Fe[SiF_6]\cdot 6H_2O$,[29] where the ground-state orbital wave function is d_{z^2} (see ref 30 for details). For the trimetallic complexes studied, MO calculations have not been done, and it is not very likely that they would give reliable enough results at the present time to account for the small differences in these compounds. Empirical charge distribution estimates are, therefore, especially important to understand the metal–metal and metal–carbon bonding in these systems.

$Mn_2Fe(CO)_{14}$.—The environment of the iron atom in this linear molecule was described above. The d-electron configuration is $(t_{2g})^6(e_g)^2$ in a crystal field model, and the e_g electrons would be allocated to the $3d_{z^2}$ orbital to form the metal–metal bond; this would predict a quadrupole splitting much larger than is observed. In an MO model, the contributions to the electric field gradient may be discussed separately for the σ and π orbitals. On the basis of the similarity of the Mn and Fe atomic orbitals, it is reasonable to assume that the electrons forming the Mn–Fe bond are almost equally shared. The orbital electron population in the $3d_{x^2-y^2}$ orbital would be lower because of the polarity of the Fe–C bond. We thus expect the contribution to the electric field gradient from the σ electrons to have a negative sign.[30] For the π electrons, a similar argument holds: the $3d_{xy}$ orbital extends mostly in the plane of the four equatorial carbonyl groups, and the effect of the metal–carbonyl π bonding is to lower the population of the metal orbitals.[22] The remaining $3d_{xz}$ and $3d_{yz}$ orbitals would be equivalent to the $3d_{xy}$ in a true octahedral environment, but in our case, these orbitals are less affected by π bonding because they are in the region of the metal–metal bonds where no empty orbitals are available. Thus, we expect a higher population in the $3d_{xz}$ and $3d_{yz}$ orbitals than in the $3d_{xy}$ orbital, which results in a small contribution, with a negative sign, to the electric field gradient. Our argument shows that the contributions of the σ and π electrons are of the same sign, and the small quadrupole splitting observed corresponds to a total population difference of only about 0.11 electron. The metal orbital population in metal–carbon σ bonds for terminal carbonyls must, therefore, be almost as high as in a metal–metal bond. This conclusion is further supported by the small quadrupole couplings found in $Mn_2(CO)_{10}$[31] and $Re_2(CO)_{10}$[32] and by a recent MO calculation on $Fe(CO)_5$ by Schreiner and Brown.[22]

$Fe_3(CO)_{12}$.—Similarly the unique iron atom in $Fe_3(CO)_{12}$ is in an octahedral environment but with *cis* disubstitution. It is known that *cis* disubstitution produces less asymmetry in the charge distribution than does *trans* disubstitution.[33] Thus, the value found for the quadrupole splitting in $Mn_2Fe(CO)_{14}$

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should serve as an upper limit for the quadrupole splitting for the unique iron atom in $Fe_3(CO)_{12}$; this is borne out by the small splitting observed in this spectrum.

$MFe_2(CO)_{12}^-$ Series.—The trimetallic triangular complexes studied, along with $Fe_3(CO)_{12}$, are structurally related to $Fe_2(CO)_9$ by the substitution of a bridged carbonyl with a $M(CO)_4$ group. The environment of each of the two equivalent iron atoms in these complexes can, therefore, be described in terms of an octahedron with two major distortions along the threefold and fourfold axes (see Figure 3). The total electric field gradient tensor at the iron nucleus can then be written as a sum of two axially symmetric tensors, whose major axes, Z_{C_3} and Z_{C_4}, are along the threefold and fourfold axes, respectively, and a residual part due to additional distortions of the molecule. This residual part is assumed to be small and is neglected. The same concept has been used to explain the quadrupole coupling in the structurally similar $Co_2(CO)_8$[25] where the asymmetry parameter, η, is known and was used along with the coupling constant to obtain values for q_{C_3}, q_{C_4}, and the angle ϕ between the Z axis of the total electric field gradient and the trigonal axis (see Figure 3). The analysis given in ref 25 will be used to understand the quadrupole splitting in the triangular complexes studied here: (1) it is assumed that the electric field gradient due to the trigonal distortion is almost the same for all members of the series and is equal to the total electric field gradient in $Fe_2(CO)_9$ and thus is positive. This has some justification because it was shown[25] that the field gradient with z axis along the Co–Co direction in $Co_2(CO)_8$ was in reasonable agreement with the quadrupole splitting in $Fe_2(CO)_9$. (2) The contribution to the electric field gradient due to the tetragonal distortion arises from the higher metal electron population in the metal–metal bond compared with metal–carbon bonds for bridging carbonyls and is therefore negative. Table II shows the ratio of the quadrupole splittings of $Fe_2(CO)_9$ and the compounds studied. Since q_{C_3} and q_{C_4} are opposite in sign, the z axis of the total electric field gradient tensor will form an angle greater than 54° 44′ with the threefold axis, as shown in Figure 3 (*cf.* ref 25). In $Co_2(CO)_8$, the ratios of q_{C_3}/q_{C_4} are −0.315 and −0.484 for the two crystallographically independent sites. The observed quadrupole coupling constants, however, were almost equal (within 3–6%) to the value of q_{C_4}, resulting from the tetragonal distortion. Moreover, the data showed that the total coupling constant was very insensitive to q_{C_3} as long as the ratio $q_{C_3}/q_{C_4} \leq 0.5$.

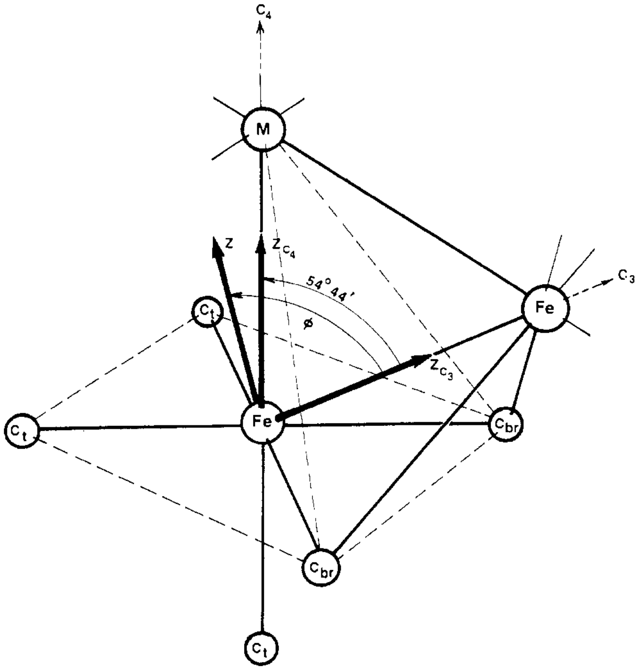

Figure 3.—Environment of one iron atom in substituted $Fe_2(CO)_9$ complexes. C_t and C_{br} indicate terminal and bridging carbonyl groups. The z-axis of the field gradient tensor lies in the same plane as Z_{C_4} and Z_{C_3}.

Since the ratios given in Table II are very similar to those of $Co_2(CO)_8$, it seems reasonable to assume that $q_{C_4} \simeq q_{\text{total}}$ in these compounds.

TABLE II

QUADRUPOLE SPLITTING RATIOS

	$Fe_3(CO)_{12}$	$MnFe_2(CO)_{12}^-$	$TcFe_2(CO)_{12}^-$	$ReFe_2(CO)_{12}^-$
$q_{Fe_2(CO)_9}/q_{\text{total}}$	0.367	0.455	0.458	0.466

A discussion of the bonding in these compounds and in $Fe_2(CO)_9$ is needed for a better understanding of the observed electric field gradients. In $Fe_2(CO)_9$, the σ electrons do not contribute to the field gradient in a first approximation: In an octahedron, the contributions to the electric field gradient from the d orbitals belonging to the e_g representation cancel each other. A trigonal distortion does not split the e levels, and therefore they must have the same population in $Fe_2(CO)_9$ and do not contribute to the electric field gradient. This means that no information about the difference in σ donation for terminal and bridging carbonyls can be obtained from $Fe_2(CO)_9$ alone. The π-bonding t_{2g} orbitals of iron are occupied by only five electrons. In order to explain the diamagnetism of the compound a metal–metal bond was proposed along the threefold axis of the molecule.[34,35] The overlap integral calculated from Richardson's[36] functions (see Table III) shows that the interaction of the $3d_{z^2}$ orbitals is fairly strong and can indeed explain the diamagnetism of this compound (Fe–Fe distance 2.46 Å[37]). The major contribution to the electric field gradient at the iron nucleus then arises from the lack of 3d electrons in the antibonding $3d_{z^2}$ orbital. This is confirmed by the positive sign of the field gradient which has been observed experimentally.[17] Its relatively small value (see Table I) indicates a strong delocalization of the t_{2g}

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TABLE III

METAL–METAL σ BOND OVERLAP INTEGRALS[a]

	Bond length, Å			
	2.40	2.50	2.60	2.70
Fe(3d)–Fe(3d)	0.0775	0.0725	0.0670	0.0612
Fe(3d)–Mn(3d)	0.0824	0.0781	0.0731	0.0675
Fe(3d)–Tc(4d)	0.0822	0.0804	0.0775	0.0737
Fe(3d)–Re(5d)	0.0836	0.0835	0.0821	0.0797

[a] Calculated using the ONE-ELECTRON IV program written by P. O'D. Offenhartz, *J. Chem. Educ.*, **44,** 604 (1967), and available from the Quantum Chemistry Program Exchange, Indiana University, Bloomington, Ind. The coefficients and exponents for the Tc(4d) and Re(5d) Slater-type orbitals were obtained by extrapolation of the data of H. Basch and H. B. Gray, *Theoret. Chim. Acta*, **4,** 367 (1966).

electrons due to π bonding. Kettle[38] showed that it is convenient to group the π-bonding orbitals into two orthogonal sets: a "radial" set consisting of those orbitals which, when viewed along the threefold axis, point toward this axis, and a "tangential" set orthogonal to the radial set. The overlap integral of the $3d_{z^2}$ orbital of iron vanishes with all of the π-bonding orbitals except the A_1 combination orbital of the radial set. For the bridging carbonyls, however, the radial set forms the σ bonds with the second iron atom. A general feature of all MO calculations on metal carbonyls is that the σ donation and π back-donation is of the same order, so that the net charge on the metal is small. We may then conclude that the population of the $3d_{z^2}$ orbital is not greatly affected by π bonding. The other t_{2g} orbitals are, however, strongly π bonding and have correspondingly low metal populations. The observed electric field gradient shows that the population difference between the $3d_{z^2}$ orbital and the other t_{2g} orbitals is only about 0.11 electron compared with a difference of 1.0 electron obtained from a crystal field model neglecting π bonding.

As mentioned above, information about the relative σ donation by bridging and terminal carbonyls cannot be obtained from the electric field gradient of $Fe_2(CO)_9$ alone. In the triangular systems studied here, however, the threefold symmetry is destroyed and an additional tetragonal distortion arises at the iron site. The major contribution to the field gradient, q_{C_4}, due to the replacement of a bridging carbonyl group by the metal tetracarbonyl group arises from the higher σ donation of the metal compared with a bridging carbonyl. Table I shows that the replacement of a bridging carbonyl gives rise to much higher field gradients than the *trans* disubstitution of terminal carbonyls. Due to the similarity of the metal orbitals, the observed field gradients should be quite insensitive to the metal which replaces the bridging carbonyl group. This is supported by the values of the overlap integrals listed in Table III. The experimental values of the quadrupole splittings also support this conclusion. The similarity should be especially pronounced for the different members in a group of the periodic table, as is observed. The quadrupole splitting for $Fe_3(CO)_{12}$ is about 20% higher than for the $MFe(CO)_{12}^-$ salts (M = Mn, Tc, Re) and it does not seem advisable to try to explain this difference at the present time. Clearly, our model gives a simplified description of the compounds studied. It has been found[25,32] that even in neutral metal carbonyl complexes, appreciable lattice contributions exist due to additional distortions of the molecules. The crystal structures of the $MFe_2(CO)_{12}^-$ salts have not yet been determined, and even if these structures were known, only a qualitative discussion of the lattice effects would be possible at the present time. Nevertheless, the data can be used to make semiempirical estimates of the relative σ donations of the terminal and bridging carbonyls. The mean value of the population difference for the σ electrons is 0.266. If the terminal and bridging carbonyls donated equally, the population difference in the triangular compounds would be about half the value for the linear $Mn_2Fe(CO)_{14}$, namely, 0.05 electron. The much higher value observed indicates that each of the bridging carbonyls donates $^1/_2(0.266 - 0.05)$ electron, or about 0.11 electron less than a terminal carbonyl. It should be emphasized that this difference cannot be much higher than the stated amount. In our model, the total quadrupole splitting observed is attributed to the replacement of a bridging carbonyl, thus the values obtained should give an upper limit for the σ-population difference at the iron site.

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[38] S. F. A. Kettle, *Inorg. Chem.*, **4,** 1662 (1965).