

Organometallic Electrochemistry. XVI.¹ Electric Charge Distribution in Organometallic Compounds.

Olefin-Iron Tetracarbonyls

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Abstract: Mössbauer, ir, uv-visible, esr, and electrochemical studies on a series of trigonal bipyramidal iron compounds have yielded definitive information concerning the transmission of electrical charge to and through the metal atom before and after one-electron reduction. For the neutral compound in solution, infrared results suggest the olefin antibonding orbitals lie in the trigonal plane, as evidenced by evaluation of C≡O force constants using the C-K force field approximation method ($k_1 > k_2$). Upon reduction to the radical anions, these species exhibit large shifts to longer wavelength for all CO stretching modes, with $\Delta k_1 > \Delta k_2$. ESR spectra demonstrate high localization of unpaired spin density in an orbital predominantly ligand in character. Such observations are consistent with a radical of the ligand ($>C=C<$), stabilized markedly by coordination to the $Fe(CO)_4$ moiety, transmitting electrical charge to and through Fe by a σ or π mechanism. Clear differentiation between these modes is achieved by the observation that reduction to the radical anion, monitored by Mössbauer spectroscopy, leads to an increase in isomer shift and a decrease in quadrupole splitting.

In a previous publication¹ it was shown that, based on a comparison of CO stretching force constants in neutral and reduced substituted octahedral group VI metal carbonyls, the transmission of electrical charge to and through the metal atom took place mainly by a σ mechanism. As a logical extension of that study we have investigated the nature and mechanism of electronic charge distribution in systems of various bonding schemes and geometries. This paper, then, is concerned with the results of such studies on a series of trigonal bipyramidal olefin-iron tetracarbonyls.

By virtue of its low-lying degenerate pair of empty antibonding orbitals, the carbonyl group may accept a drift of electron density from metal d orbitals of correct symmetry, thus alleviating an otherwise unfavorable situation where the metal atom has accumulated a high negative charge from the σ donation of electron pairs by ligands. Since the CO stretching frequency is sensitive to the electron population in its antibonding orbitals,³ as well as the nature of the $M \rightarrow CO$ bond,⁴ infrared CO force constant analyses have provided a good deal of insight into such systems. Previous studies in this area⁵⁻²³ have focused on the change in CO stretching

frequencies and subsequent force constant comparisons in various series where the substituted ligand is the controlled variable. Inherent in such investigations, however, is the inability to control the anisotropic effects surely introduced by ligand alteration. To overcome this inherent drawback in carbonyl force constant analyses it seemed necessary to devise a method which modifies the electron density in the molecule while keeping geometry and ligand fixed. Reduction of the parent substituted carbonyl compound to the radical anion results in occupation of the lowest previously unoccupied molecular orbital without drastically changing the ligand, symmetry, or bonding scheme of the molecule. Carbonyl force constant analysis before and after reduction then affords one the opportunity, without introducing hazardous variables, of examining the nature and mechanism of molecular electron distribution.

As a system amenable to the above-mentioned technique, the olefin-iron tetracarbonyls provide another major advantage in that the CO force constant results may be studied along with an additional sensitive probe, the Mössbauer effect. Doppler-induced γ -ray resonance absorption experiments previously undertaken on iron organometallic compounds have centered attention on the variation of the two basic Mössbauer parameters, the isomer shift and quadrupole splitting observed as one varies the substituted ligand.²⁴ In attempting to correlate these parameters with electronic structure, however, one becomes plagued, as in the case of carbonyl force constant analyses, with uncontrollable anisotropies introduced by ligand variation. Monitoring the reduction process leading to the radical anion overcomes this difficulty.

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Experimental Section

Electrochemical. The electrochemical work and preparation of infrared, esr, and Mössbauer samples were performed in a Vacuum Atmospheres Dry Lab-Dry Train employing an argon atmosphere controlled to not more than 1 ppm of water vapor and oxygen.

The electrochemical equipment and methodology employed for the group VIb diacetylanils has been described in detail in the paper previously cited.¹ $E_{1/2}$ values were taken relative to a $\text{Ag}|\text{Ag}^+$ ($10^{-3} M$) reference solution with 1,2-dimethoxyethane as solvent and with tetrabutylammonium perchlorate as supporting electrolyte. The group VIb diacetylanils each displayed two polarographic reductive waves (chromium, -1.92 and -2.28 V; molybdenum, -1.80 and -2.25 V; tungsten, -1.68 and -2.16 V). All steps were electrochemically and chemically reversible. Electrochemical reversibility was established by triangular voltammetric sweeps; chemical reversibility was determined by controlled potential electrolyses as previously described. All steps involved one-electron reduction processes as determined by exhaustive controlled potential electrolysis. Thus reduction at the first wave resulted in the radical anion, and subsequent reduction of this species at the second wave gave the dianion of the parent compound.

The olefin-iron tetracarboxyls also displayed electrochemically reversible one-electron/molecule reductive processes in the voltage region from -1.80 to -2.20 V relative to the $\text{Ag}|\text{Ag}^+$ ($10^{-3} M$) reference couple. Controlled potential electrolyses carried out on the iron species gave the radical anion. Although this method resulted in a medium and concentration of radical anion species suitable to esr studies, it was found that the vacuum line preparation *via* chemical reduction techniques described below yielded solutions of the radical anion of more suitable concentration for the infrared and Mössbauer experiments.

Electron Spin Resonance. Two methods were employed to investigate the esr spectra of the group VIb diacetylanil-tetracarboxyls and the olefin-iron tetracarboxyls. The first was electrochemical generation of the radical anion, this species being placed in a standard esr quartz tube fitted with a Delmar Teflon needle valve. The esr spectrometer used throughout this study was the Varian E-3 unit with a variable temperature accessory.

The second method employed a vacuum line technique. The solvent, 1,2-dimethoxyethane, was predried over calcium hydride and distilled from lithium aluminum hydride after which it was thoroughly degassed with argon. Using the Vacuum Atmospheres Dry Lab unit 500-ml bulbs were charged with Na|K eutectic alloy. These flasks, one of which contained the solvent prepared as described above, were then transferred to a vacuum line. After bulb-to-bulb distillation and thorough degassing, the solvent displayed the familiar blue color of the solvated electron at room temperature.

The esr samples were then prepared as follows. A specially constructed tube, having a side arm and quartz esr tube attached, was transferred to the drybox. For low-temperature esr work the quartz esr tube was fitted with a quartz plate to minimize power losses. Graded seals were employed for all Pyrex glass to quartz connections. Clean potassium metal was then placed in a side arm and the tube was charged with 2 mg of neutral sample. After transferring the tube to the vacuum line, a potassium mirror was deposited and solvent was bulb-to-bulb distilled over the sample. The tube containing frozen solvent, sample, potassium mirror, and esr tube was then sealed from the upper portion. Dissolution of the sample and subsequent contact of this solution with the potassium mirror generated the radical anion species whose esr properties were then investigated.

Where necessary, esr spectra were simulated using a program similar to SESR described by Stone and Maki²⁶ with suitable modifications being made to permit use on Virginia Polytechnic Institute's Computing Center IBM 360/65-50 with associated Calcomp plotter.

Infrared. For the group VIb diacetylaniltetracarboxyls, the neutral, radical anion, and dianion spectra were taken in 1,2-dimethoxyethane at a concentration of $2.0 \times 10^{-2} M$ in the presence of supporting electrolyte. Infrared spectra throughout this study were recorded on a Perkin-Elmer Model 621 double beam instrument. The cell in the reference beam contained only solvent and supporting electrolyte thus removing these components from the observed spectra. The cells (Barnes Engineering) employed Teflon spacers (0.1 mm), gaskets, and "O" rings to achieve a well-sealed unit. A needle plate, tightly fitted with suitable serum

caps, was employed to facilitate the syringing of samples within the drybox. The windows employed were of the Irtran-2 type.

For the olefin-iron tetracarboxyls a modification of the method used to generate esr samples was employed. The radical anion was generated in concentrations of approximately $2.0 \times 10^{-2} M$ using a suitable bulb and potassium mirror vacuum line techniques. After transferring the radical anion from the vacuum line to the drybox, the sample was withdrawn and syringed into the infrared cell. The reference cell for these runs contained only 1,2-dimethoxyethane.

The infrared data were analyzed using a nonlinear least-squares method described by Wentworth²⁸ as applied to the Cotton-Kraihanzel force field matrices²⁷. After expansion of the secular equations in a Taylor series successive iterations were performed until the process had gone to convergence. The entire least-squares analysis was coded in FORTRAN IV for the IBM 360/65-50 for use at the Virginia Polytechnic Institute Computing Center.

Mössbauer. The Mössbauer samples were prepared in the following manner. Approximately 200 mg of olefin-iron tetracarboxyl was placed in a 150-ml round-bottom flask equipped with a long neck, side arm, and ground glass joint. After introducing clean potassium metal into the side arm (drybox), the flask was transferred to the vacuum line and evacuated. A potassium mirror was deposited over the neck of the bulb and 20 ml of 1,2-dimethoxyethane was bulb-to-bulb distilled into the flask. The reaction vessel was then sealed and removed from the vacuum line and transferred to the drybox. After approximately 45 min of reaction time (solution and potassium mirror), the solution containing both neutral molecule and radical anion was transferred to a second flask and the solvent stripped. The solid residue was then encapsulated by heat sealing it between two 1.5-in. square trilaminated sheets (polyethylene-mylar-aluminum) provided by Sun Chemical Co. The resultant packet was removed from the drybox and transferred immediately to a tail dewar filled with liquid nitrogen.

The Mössbauer spectra were obtained at liquid nitrogen temperature by use of the tail dewar. A constant acceleration drive system was employed and the data were collected on a Nuclear Data 512 channel analyzer. The system was calibrated before and after each run using either iron foil or sodium nitroprusside as standards. The drift was found to be less than 2×10^{-3} mm/sec over the course of a run. The source was ⁵⁷Co diffused in platinum as prepared by the NSEC division of ICN and was found to have an activity of approximately 1 mCi.

Data from the multichannel analyzer were read out on punched tapes, and the spectra were analyzed by fitting the peaks to Lorentzian curves using a least-squares routine. Two computer programs were utilized. One was the general least-squares program referred to in the infrared section and was processed on the IBM 360/65-50 system. The second program was a curve simulating program which was written for the PDP 8/I "in-house" computer. This latter program permitted the rapid analysis of complex spectra and a quick comparison of simulated and actual data.

Chemicals. 1,2-Dimethoxyethane (Ansol 121) was prepared as described above. The supporting electrolyte for electrochemical runs, tetrabutylammonium perchlorate (G. F. Smith Chemical Co.), was dried in an Abderhalden drying pistol at the boiling point of xylene and 0.1 mm using P_2O_5 as desiccant. The mercury employed (Eastern Smelting and Refining Co.) was triply distilled and used as obtained.

The molybdenum diacetylaniltetracarboxyl compound was prepared according to the method of Bock and Dieck.²⁸ The corresponding chromium and tungsten complexes were synthesized by the same procedure, and were both found to be stable, crystalline compounds. The dark violet crystals of the chromium complex melted with decomposition over the range 260–265°. The dark green crystals of the tungsten compound behaved similarly, decomposing upon heating to 265°. The olefin-iron tetracarboxyls were prepared by the methods of Weiss, *et al.*²⁹ This series was also expanded by synthesizing the N-phenylmaleimide and N,N-dimethylacrylamide complexes. The N-phenylmaleimide complex crystallized from ethanol as yellow plates which melted with decomposition at 150–151°. The N,N-dimethylacrylamide complex sublimed under vacuum as yellow crystals at 35° and melted without

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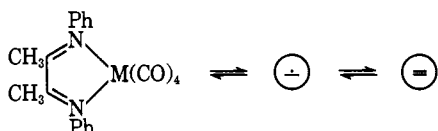
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decomposition at 56°. All compounds analyzed correctly for C, H, and N.

Results and Discussion

Diacetylanil-M(CO)₄ Complexes. As an introduction to the general concept and method employed in the olefin-iron tetracarbonyls, let us consider results obtained on a series of more conventional diacetylanil group VIb tetracarbonyls. These compounds belong to the point group C_{2v}, and closely resemble the general class of L₂M(CO)₄ species in the work previously cited,¹ with the one major and striking exception. Not only do the diacetylanils display clean, electrochemically and chemically reversible reductions to stable radical anions, but an additional electron may be added reversibly to form stable singlet state dianions. Thus, one may monitor the changes in CO stretching frequencies observed in going from neutral molecule to radical anion, and finally to the dianion species.



The radical anions display nearly identical, well-resolved, esr signals consisting of 11 major lines, each of which is split into an additional 11 lines (Figure 1). As indicated for the Mo compound, the total spectral width is 55.6 G, and successful spectrum simulation yields the following probable hyperfine coupling constants (G): $a_N = 5.08$, $a_{H_o} = 5.08$, $a_{H_p} = 5.08$, $a_{CH_3} = 0.48$, and $a_{H_m} = 0.48$. It is noteworthy that in no instance does one observe hyperfine splitting from the group VIb metal atom (Mo, 25% spin $5/2$; Cr, 10% spin $3/2$; and W, 14% spin $1/2$) either in this series of compounds or those previously examined. Upon addition of the second electron per molecule the singlet state dianion is formed as evidenced by the fact that no esr signal was observed even in methyltetrahydrofuran frozen matrices at -196° .

As one might expect, long electronic relaxation times for the radical anion species resulted in severely broadened nmr lines making them undetectable by conventional methods. The nmr spectra for the completely reduced dianions are, however, clearly observable, and the results from these experiments along with the esr experiments may be conveniently compared as follows. For the radical anion one may relate the observed hyperfine splitting, a_H , for the aromatic protons to the unpaired spin density on the adjacent carbon atom by reference to the McConnell equation³⁰

$$a_H = Q_{CH}^H \rho_C$$

where ρ_C is the unpaired spin density on the atomic carbon atom and Q_{CH}^H is a semiempirical constant with an average value of -23 G. From this relationship the unpaired spin density at the *ortho* and *para* positions of the complexed anil radical anion is about 22% and most likely positive in sign.

As the amount of charge residing on an aromatic carbon is altered, one would surely expect a variation in the chemical shift observed in the nmr spectrum due to changes in the amount of shielding at the adjacent proton. Another linear expression relating charge

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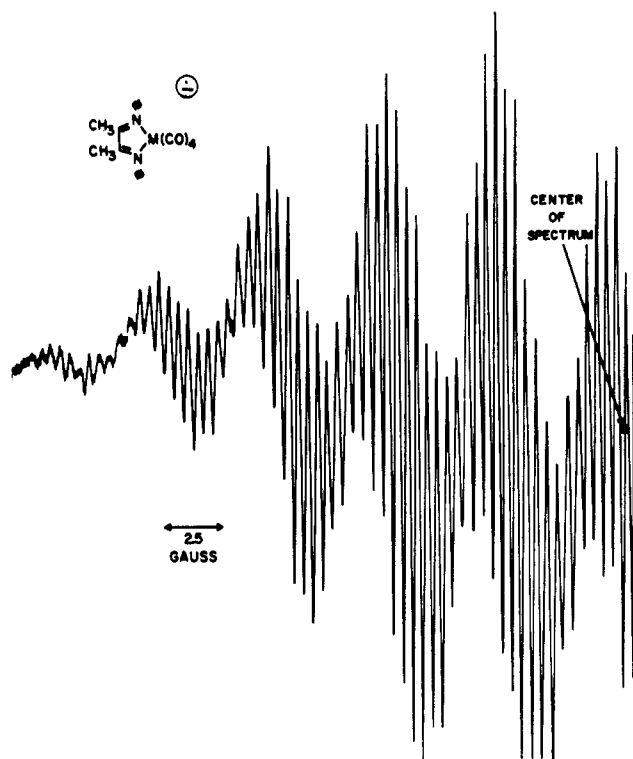


Figure 1. Half spectrum of diacetylanil-Mo(CO)₄ radical anion.

density and chemical shift has been established³¹⁻³³ for aromatic systems, and this is given by

$$\Delta\delta_r = -Kq_r$$

where $\Delta\delta_r$ is the charge-induced chemical shift, q_r is the excess charge at the trigonally hybridized position, and K is a constant which is approximately 10 ppm per unit charge. For the dianion species of the anil complexes the *ortho* and *para* protons are shifted upfield relative to the neutral molecule by only 0.10 ppm. Thus, although approximately 22% unpaired spin density resides on the *ortho* and *para* positions only one-half of 1% excess charge remains on these carbon atoms. These results, then, lead directly to the conclusion that unpaired spin density and excess charge density are two distinctly separate phenomena, and that although unpaired spin density resides chiefly on the anil ligand, the excess charge is spread throughout the M(CO)₄ moiety.

The marked delocalization of excess charge introduced by reduction should yield systems of high stability, and this is, indeed, what is observed, the radical anions and dianions living for up to 3 weeks in sealed ampoules. Since the charge density resides almost entirely on the M(CO)₄ moiety, the variation in CO force constants in going from neutral molecule to radical anion and finally to dianion should be a direct manifestation of the mechanism by which the central metal atom accepts and transmits electrical charge.

On the basis of a group theoretical analysis, the diacetylanil group VIb tetracarbonyls should show four infrared-active carbonyl stretching frequencies resulting from two A₁, one B₁, and one B₂ normal modes. As-

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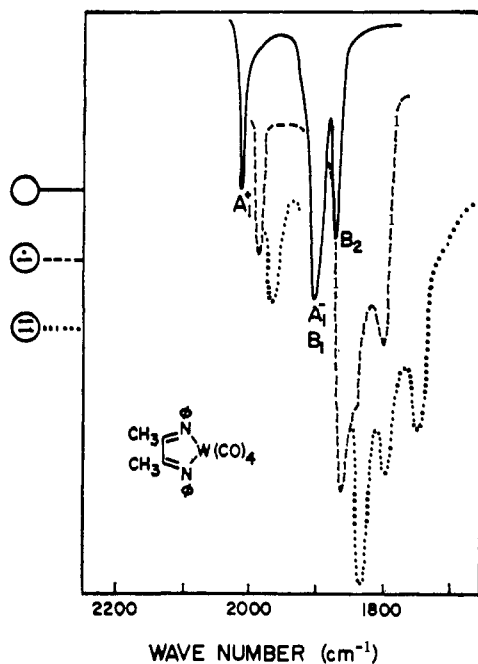


Figure 2. Infrared spectrum of $2 \times 10^{-2} M$ solution of $W(\text{dianil})-(\text{CO})_4$ in 1,2-dimethoxyethane (0.1 M TBAP): \circ = neutral molecule, \ominus = radical anion, $\ominus\ominus$ = dianion.

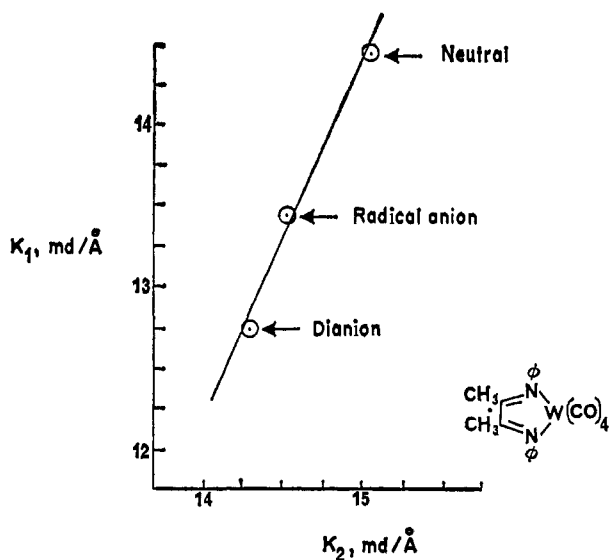


Figure 3. Plot of k_1 vs. k_2 for tungsten-diacetylanil complex.

segment of these modes to the observed frequencies for the general class of $L_2M(\text{CO})_4$ compounds has been made by Cotton and Orgel.^{11,15} Reference to Figure 2 points out the fact that the infrared spectrum for the neutral W compound in the carbonyl stretching region displays but three bands, the low-frequency A_1 mode and the B_1 mode being accidentally degenerate. Upon reduction to the radical anion, however, this degeneracy is lifted as evidenced by the appearance of a shoulder of medium intensity on the low-frequency side of the previously degenerate absorption. In fact, reduction to the dianion completely lifts the degeneracy of the A_1 and B_1 modes as can be seen from Figure 2. Table I lists the absorptions for the W compound, which is representative of the series. Force constants may now be calculated from these assignments and the secular equa-

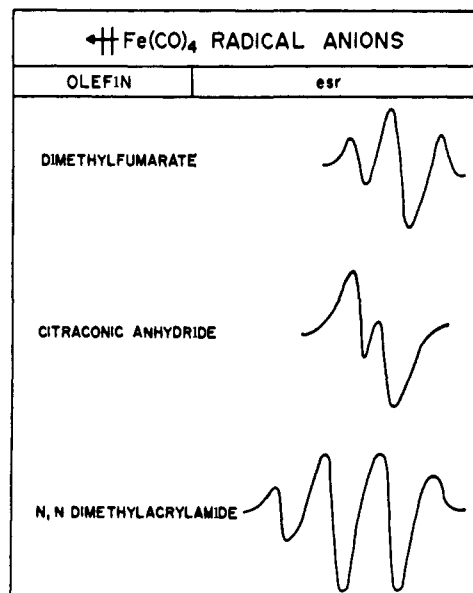


Figure 4. Typical esr spectra of olefin-iron tetracarbonyl radical anions (in 1,2-dimethoxyethane at -55°).

tions as developed by Cotton.⁹ The results given in Table II employ the following notation; a plot of k_1 vs.

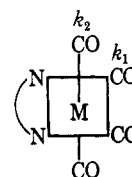
Table I. Infrared Assignments for Diacetylanil- $W(\text{CO})_4$

Assignment	Neutral molecule, cm^{-1}	Radical anion, cm^{-1}	Dianion, cm^{-1}
A_1^+	2004	1972	1950
B_1	1894	1850	1815
A_1^-	1894	1835	1775
B_2	1863	1790	1730

Table II. Force Constants ($\text{mdyn}/\text{\AA}$) for Diacetylanil- $W(\text{CO})_4$

	Neutral molecule	Radical anion	Δk	Dianion	Δk
k_1	14.42	13.41	1.01	12.76	1.66
k_2	15.14	14.53	0.61	14.31	0.83
k_i	0.36	0.40	-0.04	0.45	-0.09

k_2 is given in Figure 3. k_1 is the force constant between C and O atoms of a carbonyl group *trans* to a ligand, k_2 is the force constant between C and O atoms of a carbonyl group *trans* to another carbonyl group and *cis* to a ligand, k_i is the force constant between two interacting carbonyl groups, and $\Delta k = k_{\text{neutral}} - k_{\text{reduced}}$.



These data cannot be explained on the basis of a π -only transmission of charge density. If that mechanism were operative one would predict $\Delta k_2 > \Delta k_1$, whereas the data clearly indicate $\Delta k_1 > \Delta k_2$. Only a directional σ mechanism accommodates the observed data. For the

complete argument leading to this conclusion one is referred to the first paper treating this subject.¹

Olefin-Fe(CO)₄ Complexes. ESR Results. Figure 4 and Table III summarize the esr results obtained on the

Table III. ESR Spectral Data. Olefin-Iron Tetracarbonyl Radical Anions

Complexed ligand	No. of lines	a_H , G
1. Citraconic anhydride	2	5.1
2. Dimethyl fumarate	3	5.0
3. Dimethyl maleate	3	5.0
4. Maleic anhydride	3	5.2
5. N-Phenylmaleimide	3	5.2
6. Acrylamide (K salt)	4	4.9
7. N,N-Dimethylacrylamide	4	4.8
8. Cinnamaldehyde	3	5.0
9. Methyl cinnamate	3	5.0

radical anions of the olefin-iron tetracarbonyl series. Without exception these spectra are characterized by the appearance of olefinic proton hyperfine splitting; hyperfine structure from other nuclei, either monolefinic protons or nitrogen, is absent in all cases regardless of temperature, modulation amplitude, or concentration. Thus, the citraconic anhydride complex with one olefinic hydrogen displays two lines, the dimethyl fumarate complex with two olefinic protons exhibits three lines, and the acrylamide complex with three olefinic hydrogens yields a four-line spectrum.

The nonidentical hydrogens involved appear to have approximately the same hyperfine coupling constant (5.00 ± 0.20 G). Baizar and Fritsch have studied the esr spectra of some of the radical anions derived from the ligands employed in this series.³⁴ These workers have used flow techniques and electrochemical generation in dimethylformamide to study the transiently stable (average lifetime, 3 sec) radical anions of the fumarate and cinnamate esters. Average olefin hyperfine coupling constants found were 6.7 and 5.5 G, respectively. These are close to the values of 5.1 and 5.0 G determined in this study for the corresponding ester-Fe(CO)₄ complex. In addition the olefin-carbonyl stretching frequency shifts to much longer wavelength upon reduction. These facts lead one to conclude that once again one is dealing with a radical of the ligand stabilized markedly by coordination to the M(CO)₄ moiety, which accepts in large part the excess charge introduced by addition of the electron. Thus, in contrast to the instability of the radical anions studied by Baizar and Fritsch, the Fe(CO)₄ complexed radical anions remained unchanged after 1 week in sealed ampoules, and lived for about 5 min after dilution, in air, with acetone.

At room temperature the proton hyperfine structure is not well resolved for the olefin-iron tetracarbonyl radical anions, but resolution increased markedly when the spectra were recorded at -55° , an apparent consequence of spin-lattice relaxation effects. These radical anions are light yellow-brown in color both at room temperature and -55° with two remarkable exceptions. While the maleic anhydride and N-phenylmaleimide radical anion complexes are light yellow-brown at room temperature, both solutions of these

(34) M. Baizar and J. Fritsch, personal communications.

radical anions turn dark red when cooled to -55° . Such a marked thermochromic effect (an apparent 100-m μ shift in electronic spectral band) is not to be expected from just ion pairing phenomena. The uv-visible spectra of these species and the thermochromic effect will be the subject of a future publication.

Infrared Results. The olefin-iron tetracarbonyls, being equatorially substituted, belong to point group C_{2v}, and thus one predicts again four infrared-active carbonyl stretching frequencies resulting from two A₁ modes, a B₂ mode, and a B₁ mode. In fact, four carbonyl stretching absorptions are observed in the region 2150-1950 cm⁻¹, and the problem now becomes one of assignment of these peaks to their representative modes. However, before one can undertake this task the basic geometry of the ligand orbitals must be fixed.

There are two fundamental aspects to be considered in making the assignments at hand. The first relates to the critical importance of the ligand's ability to withdraw large amounts of electron density through its antibonding orbitals. Substitution of electron withdrawing groups on the ligand and the subsequent effect this substitution has on the ligand's ability to withdraw electron density from the metal to the ligand is a key factor in the existence of these complexes; this observation has been well documented.^{29, 35-37} The second aspect is concerned with the geometry of the ligand antibonding orbitals relative to the trigonal plane of the molecule. In the following sections it will be shown that these orbital axes do, in fact, lie in the trigonal plane and not perpendicular to it.

Assignment of the four normal modes must be based on a knowledge of the orbital interactions of ligand, metal, and carbonyl groups. Let us consider the first possibility which finds the olefin antibonding orbital axes lying in the planes coincident with the axis connecting the CO(2) groups (see Figures 5 and 6). If the iron atom is dsp³ hybridized, the d_{xy}, d_{yz}, d_{xz}, and d_{x²-y²} orbitals are left doubly occupied and capable, to varying extents, of π bonding to the ligand and carbonyl antibonding orbitals. Thus, for this case, the ligand antibonding orbitals may remove electron density from metal d_{xz} and d_{yz} orbitals which are just those metal d orbitals capable of π bonding to the CO(2) antibonding orbitals (see Figure 6). The CO(1) antibonding orbitals are also capable of interacting in such a manner with the metal d_{xz} and d_{yz} orbitals, but since they are also in a position of appropriate symmetry to remove electron density from metal d_{x²-y²} and d_{xy} orbitals the amount of cooperative interaction between ligand antibonding orbitals and CO(1) groups for this case will be considerably less than cooperative interaction of ligand and CO(2) groups. Since the CO stretching frequency, and thus the CO force constant, is critically sensitive to the electron population in its antibonding orbitals, one would predict *a priori* for this situation CO(2) force constants greater than CO(1) force constants. In line with this prediction one would assign the infrared stretching frequencies as follows (see Figure 5): A₁⁺ > B₁ > A₁⁻ > B₂.

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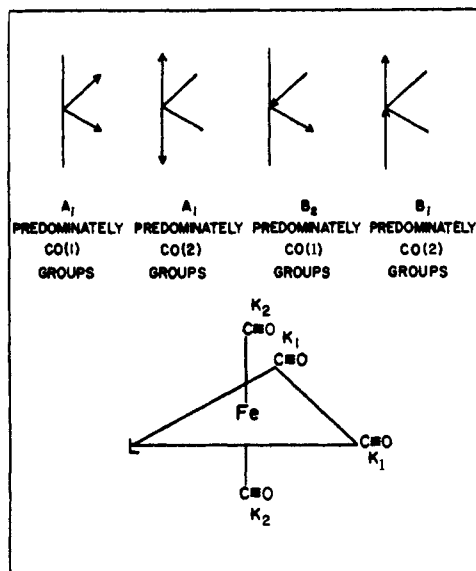


Figure 5. The four ir-active carbonyl stretching modes. The notation for the carbonyl groups and force constants is employed.

The second possibility finds the olefin antibonding orbital axes lying in the trigonal plane. It becomes immediately obvious that for this situation cooperative electron withdrawal between ligand and CO(2) antibonding orbitals is nil (see Figure 6). However, the CO(1) groups should experience considerable relief by electron withdrawal *via* $d_{x^2-y^2}$ and d_{xy} metal orbitals. Thus, for this case one predicts that the CO(1) force constants should be greater than the CO(2) force constants with the corresponding assignment (see Figure 6): $A_1^+ > B_2 > A_1^- > B_1$.

Employing the secular equations as developed by Cotton⁹ and assuming that the axial stretch-stretch interaction constants are approximately twice the equatorial stretch-stretch interaction constants,³⁸ successful convergence with small error can be achieved only for the second case. This result strongly suggests that the ligand antibonding orbital axes lie in the trigonal plane in solution. It should be pointed out that in the solid phase this orientation has indeed been proven as evidenced by single-crystal X-ray studies^{39,40} on the fumaric acid and acrylonitrile derivative.

The observed frequencies, corresponding assignments, and force constants for both neutral and reduced species of the olefin-iron tetracarbonyl series are given in Table IV. Examination of the force constants for the neutral species demonstrates several interesting points in relation to the orientation and ability to withdraw electron density by the ligand antibonding orbitals.

As we have pointed out previously, comparison of force constants between $LM(CO)_x$ and $L'M(CO)_x$ species where L and L' are quite different, is fraught with much danger. However, because of the large force constant changes observed in converting $Fe(CO)_5$ to an olefin-iron tetracarbonyl,

(38) The latter assumption is reasonable both on the grounds of CO orbital interactions, and the fact that the magnitude of these interaction constants is small compared to force constants, and thus small variation in the ratio of equatorial and axial stretch-stretch interaction constants should not affect appreciably the relationship of k_1 to k_2 .

(39) C. Pedone and A. Sirigu, *Inorg. Chem.*, **7**, 2614 (1968).

(40) A. R. Luxmore and M. R. Truter, *Acta Crystallogr.*, **15**, 1117 (1962).

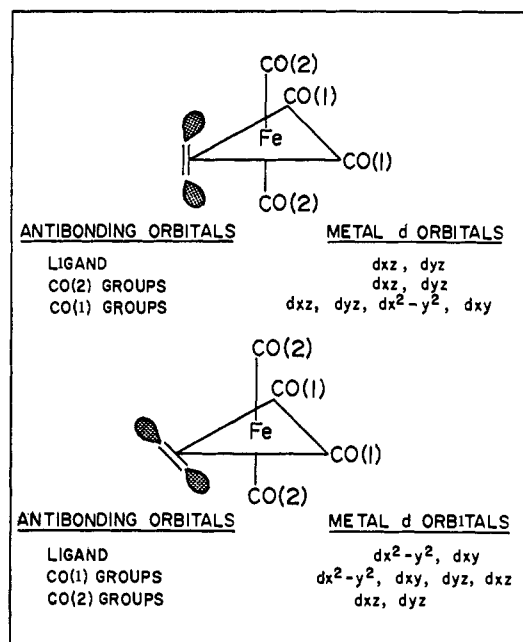


Figure 6. Interactions of olefin and carbonyl antibonding orbitals.

we should like to suggest the following analysis. It is found that in all cases the neutral CO(1) force constants are considerably greater than the neutral CO(2) force constants (17.50 *vs.* 16.00), exactly

Table IVa. Carbonyl Stretching Frequencies (± 2 cm^{-1}) for Olefin-Iron Tetracarbonyls

Compound		Neutral molecule, cm^{-1}	Radical anion, cm^{-1}
Dimethyl fumarate- $Fe(CO)_4$	A_1	2108	1978
	B_2	2043	1915
	A_1	2035	1915
Acrylamide- $Fe(CO)_4$	B_1	2001	1875
	A_1	2100	1980
	B_2	2034	1900
N-Phenylmaleimide- $Fe(CO)_4$	A_1	2012	1900
	B_1	1981	1875
	A_1	2115	1988
Methyl cinnamate- $Fe(CO)_4$	B_2	2060	1930
	A_1	2038	1930
	B_1	2018	1895
Dimethyl maleate- $Fe(CO)_4$	A_1	2098	1920
	B_2	2040	1870
	A_1	2027	1870
Dimethyl fumarate- $Fe(CO)_4$	B_1	1985	1850
	A_1	2103	1982
	B_2	2045	1949
Dimethyl maleate- $Fe(CO)_4$	A_1	2035	1915
	B_1	2001	1882

what one predicts for the second case above. If one compares these force constants for the neutral species with those previously calculated for $Fe(CO)_5$ ($k_1 = 16.95$, $k_2 = 16.55$),³⁷ it is observed that the CO(2) force constants in the substituted species are considerably lower, while CO(1) force constants are markedly higher. This fact seems to be another manifestation of the lack of cooperative electron withdrawal between ligand and CO(2) groups and the existence of a marked degree of electron withdrawal from metal d orbitals shared with CO(1) groups. Substituting the olefin

Table IVb. Carbonyl Force Constants for Neutral Molecules and Radical Anions of Olefin-Iron Tetracarbonyls

Compound	k	Neutral molecule, mdyn/Å	Radical anion, mdyn/Å	Δk , mdyn/Å
Dimethyl fumarate-Fe(CO) ₄	k_1	17.35	14.98	2.37
	k_2	16.05	14.97	1.08
	k_i	0.22	0.29	-0.07
Acrylamide-Fe(CO) ₄	k_1	17.06	14.93	2.13
	k_2	16.14	14.52	1.62
	k_i	0.25	0.25	0.00
N-Phenylmaleimide-Fe(CO) ₄	k_1	17.64	14.98	2.66
	k_2	15.95	14.79	1.66
	k_i	0.14	0.30	-0.16
Methyl cinnamate-Fe(CO) ₄	k_1	17.21	14.00	3.21
	k_2	16.09	14.93	1.16
	k_i	0.24	0.25	-0.01
Dimethyl maleate-Fe(CO) ₄	k_1	17.36	15.38	1.98
	k_2	16.03	15.02	1.01
	k_i	0.20	0.20	0.00

ligand for a CO group in the equatorial position, then, leads to far more effective electron withdrawal by ligand out of the trigonal plane.

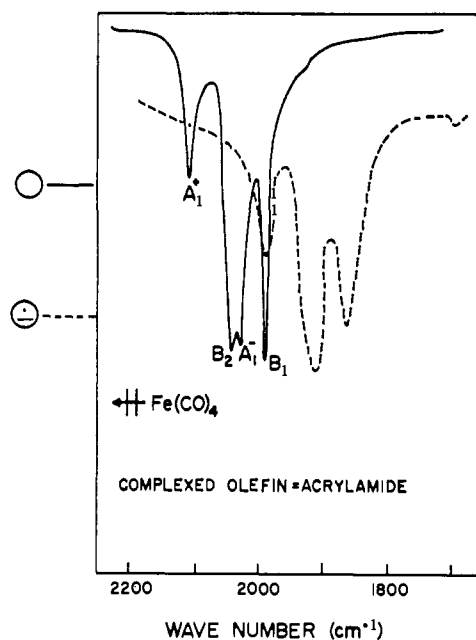


Figure 7. Infrared spectrum of $2 \times 10^{-2} M$ solution of acrylamide-iron tetracarbonyl in 1,2-dimethoxyethane: \circ = neutral molecule, \ominus = radical anion.

An interesting comparison may also be drawn between the olefin-iron tetracarbonyl force constants in general and those calculated for the group VIb substituted tetracarbonyls.^{1,11} The overall force constant average is considerably higher for the iron series than the group VIb series even though the former has four doubly filled metal orbitals capable of π back-bonding, whereas the latter has but three. Apparently, then, the olefin ligands in the iron series are far more effective electron withdrawers than are the ligands (bipyridyl, phosphines, anils, etc.) of the group VIb series previously studied.

Upon one-electron reduction the olefin-iron tetracarbonyls display large shifts to lower frequency for all carbonyl stretching modes, as can be seen from Figures 7 and 8, which are good representatives of the series.

A comparison of neutral and reduced force constants yields the result that $\Delta k_1 > \Delta k_2$ (see Δ column in Table IVb). However, unlike the case of the group VIb tetracarbonyls, this fact alone is not enough to differentiate between a σ and π mechanism of electric charge distri-

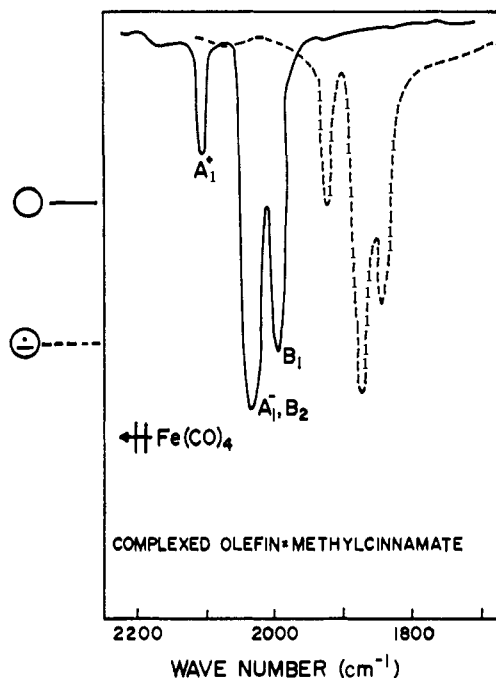


Figure 8. Infrared spectrum of $2 \times 10^{-2} M$ solution of methyl cinnamate-iron tetracarbonyl in 1,2-dimethoxyethane: \circ = neutral molecule, \ominus = radical anion.

bution. That this is the case can be seen from a consideration of the directional character of the metal-to-ligand σ and π bonds for the two series. For the group VIb series the metal-to-ligand σ and π bonds are oriented in such a manner that transmission *via* one or the other pathway will have a differential effect on the CO groups. Unlike this situation the metal-to-ligand σ and π bonds in the iron series are oriented such that transmission *via* either the π or σ system will effect the CO(1) groups more than the CO(2) groups. A π mechanism will result in $\Delta k_1 > \Delta k_2$ for just those reasons given for the fact that $k_1 > k_2$ in the neutral species. But a σ mechanism will result in the same confirmation of experimental facts,

Table V. Mössbauer Parameters (All Measurements Made at -196°)

Compound	IS, ^{a,b} mm/sec		QS, ^b mm/sec	
	Neutral molecule	Radical anion	Neutral molecule	Radical anion
Fe(CO) ₅ ^c	0.201		2.60	
Maleic anhydride-Fe(CO) ₄	0.266	0.28	1.359	0.87
N-Phenylmaleimide-Fe(CO) ₄	0.248	0.37	1.540	0.73
N,N-Dimethylacrylamide-Fe(CO) ₄	0.260	0.30	1.654	1.26
Dimethyl fumarate-Fe(CO) ₄	0.263	0.39	1.563	0.79

^a Relative to sodium nitroprusside. ^b Neutral compounds, ± 0.005 ; radical anions, ± 0.02 . ^c R. L. Collins and R. Petit, *J. Amer. Chem. Soc.*, **85**, 2332 (1963).

since transmission of charge from the ligand to the metal atom *via* the σ framework (predominately through sp^2 hybrid orbitals) with subsequent σ - π configurational interaction or direct interaction with the CO groups will also lead to the prediction that $\Delta k_1 > \Delta k_2$. In providing the key to this dichotomy, Mössbauer spectroscopy yields direct evidence as to which mechanism of electric charge distribution predominates in the iron series.

Mössbauer Results. Iron Mössbauer effect studies yield two parameters of primary importance to the chemist, quadrupole splittings (QS) and isomer shifts (IS). The former arise from the interactions of an asymmetric field gradient with the quadrupole moment of the nucleus. While the ligands which surround the nucleus contribute to this gradient, the principle cause is the nonsymmetric distribution of the valence electrons on the central atom itself. The general expression for the quadrupole splitting for a nucleus such as ⁵⁷Fe (excited state spin $3/2$; ground state spin $1/2$) is given by

$$QS = \frac{1}{2}e^2qQ\left(1 + \frac{1}{3}\eta^2\right)^{1/2}$$

where q is the electric field gradient at the nucleus, Q is the nuclear quadrupole moment, and η is the asymmetry parameter and can be represented by $(V_{xx} - V_{yy})/V_{zz}$, where $V_{\alpha\alpha}$ is the component of the field gradient in the r_α direction. For an axially symmetric field $V_{xx} = V_{yy}$ and $\eta = 0$.

In the case of iron salts the main contribution to this gradient has been considered to be the d electrons since this shell is usually incomplete. Goldanskii^{41,42} has recently pointed out that the contribution of the 4p electrons is not negligible. This latter contribution will be even more pronounced in the case of Fe(0) compounds where both 3d and 4p orbitals are formally considered to be filled. It is especially important in the case of the trigonal bipyramidal compounds of this study where the contributions of the d and p orbitals cannot be clearly differentiated as in the octahedral case.

The second parameter, the isomer shift, is a measure of the difference in electron density found at the nucleus in two compounds. To a first approximation, the IS is a measure of the difference of total s density present at the nucleus, though Goldanskii^{41,42} has indicated that when relativistic corrections are made, p electrons also make finite contributions. The IS can be changed in two distinct manners. The first, and most obvious, is the direct addition or removal of s electron density *via* a change in the outer s orbitals. The second means of

altering the total s density as seen by the nucleus is to add d or p electrons to the system. These electrons act as shields and screen s electron density from the nucleus. In the case of ⁵⁷Fe, as the electron density at the nucleus decreases the IS takes on more positive values.

With the above facts in mind one can examine the bonding picture in the trigonal bipyramidal olefin-iron tetracarbonyls in some detail. Two similar studies have been previously reported.^{43,44} In both cases a linear relationship was found between the QS and the IS where the compound with the most positive IS also had the smallest QS. In the case of those compounds reported by Collins and Petit,⁴³ the relationship is most fortuitous inasmuch as some of the ligands were axially substituted and some were located in the equatorial plane. As pointed out earlier, changing ligands can cause serious perturbations in the overall bonding picture. This would seem to be particularly true for the compounds studied by them where the bonding in the equatorial and axial locations involves vastly different types of orbitals (sp^2 equatorial, dp axial).

The parent compound in this series can be considered to be the trigonal bipyramidal Fe(CO)₅ with an equatorial carbonyl group replaced by an organic moiety. The C-Fe bond lengths have been examined for Fe(CO)₅ in both the solid and gas phase.⁴⁵⁻⁴⁷ While there still exists some controversy as to the exact values for the equatorial and axial bonds, the data³⁹ show that there is considerable increase in the Fe-CO bond lengths for the equatorial carbonyls in going from the pentacarbonyl to the monosubstituted olefin-iron tetracarbonyls, while the axial carbonyl groups remain approximately constant. It should be noted that the Fe-C bond distances can be ordered (olefin Fe-C > equatorial carbonyl Fe-C > axial carbonyl Fe-C). It can clearly be seen here that the changing of even one group can severely disturb the system.

The IS and QS for both neutral and radical olefin-iron tetracarbonyls are listed in Table V with the values for Fe(CO)₅ listed for comparison. A typical spectrum of a radical is shown in Figure 9. Two sets of peaks are clearly visible, those of the radical and a pair belonging to the neutral parent. By referring to Figure 6 the changes in IS and QS in the series Fe(CO)₅ \rightarrow R-Fe(CO)₄ \rightarrow R-Fe(CO)₄ radical anion can readily be explained.

The rationale behind the magnitude and sign of the IS and QS for Fe(CO)₅ has been discussed in some detail.⁴⁸⁻⁵¹ It is sufficient to note two facts. First, the

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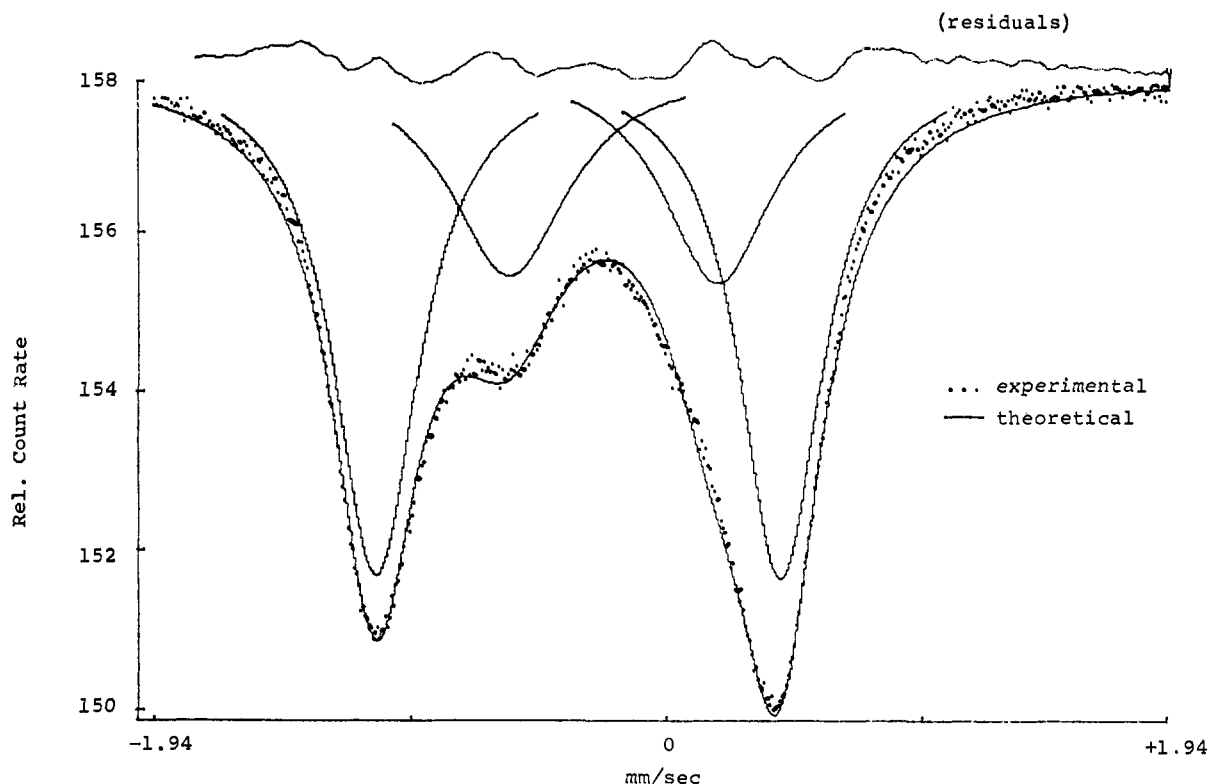


Figure 9. Mössbauer spectra of the neutral molecule and radical anion of dimethyl fumarate-iron tetracarbonyl, showing experimental and calculated spectra and the difference between the two.

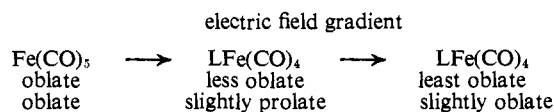
electron density is greater in the equatorial plane than along the axial direction. Second, $V_{zz} = V_{yy}$, which implies that $\eta = 0$. The d orbital asymmetry is reasonably assumed to be negligible. With the formation of the olefin-iron tetracarbonyl profound changes take place. The Fe-CO bond lengths increase and the in-plane OC-Fe-CO bond angles decrease.³⁹ The change in bond angle probably implies addition of d character to the σ framework, while an increase in bond length implies a decrease in strength of both the σ bond and the π back-bonding. All these factors tend to increase the amount of d electron density on iron which implies a positive IS.

The decrease in QS is due to the following factors. First, the olefin has no orbitals which can effectively interact with the axial CO moiety through the d_{zz} and d_{yz} orbitals. Thus, although the olefin serves well as an in-plane electron withdrawer, as evidenced by the infrared studies (see $\text{Fe}(\text{CO})_5$ vs. $\text{LFe}(\text{CO})_4$), it fails to function effectively in this respect along the z axis (Figure 6). The consequence of introducing the olefin is therefore an increase in the electric field gradient in the z direction.

The change in the Mössbauer parameters for the radical anion are now straightforward. When the olefin-iron tetracarbonyl is reduced the electron enters the π antibonding orbitals of the olefin. It is distributed throughout the system *via* the d orbitals of the

metal ($\pi^* - d_{xy}$). Since d orbitals shield the s density from the nucleus a positive IS results. It should be noted that in the radical ion the d_{xy} orbital is the primary means of removing the electron density from the olefin, whereas in the neutral system this orbital contributed electron density to the ligand.

In this case, there is a further decrease in QS. Since the sign of the quadrupole splitting is unknown in these studies, except for $\text{Fe}(\text{CO})_5$, where it is positive (oblate), two possibilities exist, consistent with the observed absolute magnitudes of QS.



We are attempting to solve this dichotomy by Zeeman splitting studies which should give the sign of the quadrupole coupling. The ir data clearly show that the axial carbonyl groups are affected by reduction, but only about half as much as the equatorial groups.

Conclusions. Two quite different systems of the type



have been investigated by the spectral techniques described above—the octahedral $\text{L}_2\text{M}(\text{CO})_4$ complexes involving Cr, Mo, or W, and the formally trigonal bipyramidal $\text{LFe}(\text{CO})_4$ complexes. Of interest has been the mechanism of electron charge transfer to the metal atom, and onto the carbonyl moiety. The conclusions may be exhibited schematically in Figure 10.

In a previous infrared investigation of some bridged iron binuclear complexes,¹ the conclusion was reached that electronic charge was distributed from the ligand to the metal *via* a σ mechanism. Mössbauer studies on the

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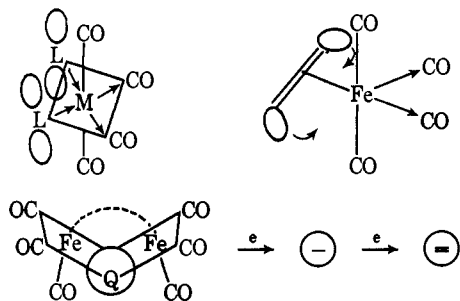


Figure 10.

radical anion are shown in Table VI, in comparison with the neutral material. It is gratifying and totally expected that the changes in direction of isomer shift and magnitude of coupling terms are opposite to those found in the present study. The latter system involves π transmission, while the former involves σ transmission. It appears, then, that in the octahedral complexes, transmission *to* and *through* the metal atom is *via* the σ framework as was reported earlier. In the bipyramidal cases, evidence points to a π transmission to the metal, and in light of the observed changes in carbonyl stretching frequencies, a σ transmission through the metal atom. In both cases it is not yet known how this effect expresses itself in weaker CO stretching force constants. A pure σ argument^{5,2} or one involving σ, π

Table VI. Octahedral Mössbauer Parameters (All Measurements Made at -196°)

Q	Charge	IS, ^{a,b} mm/sec	QS, ^b mm/sec
SCH ₃	○	0.30	0.86
	⊖	0.28	1.62
	○	0.25	0.65
P(CH ₃) ₂	⊖	0.19	1.29
	⊕	0.10	1.53
As(CH ₃) ₂	○	0.28	0.81
	⊖	0.18	1.86

^a Relative to sodium nitroprusside. ^b Neutral compounds, ± 0.005 ; radical anions and dianion, ± 0.02 .

configuration interaction will equally fit the observed facts.

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π Complexation in Ion-Pair Bonding. Tetra(1,4-epoxybutane)disodium(I) Tetramethylbis-1,4-dihydro-1,4-naphthylenedialuminate, $[\text{Na}(\text{C}_4\text{H}_8\text{O})_2]_2[\text{Al}(\text{CH}_3)_2\text{C}_{10}\text{H}_8]_2$, a Novel Organoaluminate Structure^{1,2}

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Abstract: The crystal structure of tetra(1,4-epoxybutane)disodium(I) tetramethylbis-1,4-dihydro-1,4-naphthylenedialuminate, $[\text{Na}(\text{C}_4\text{H}_8\text{O})_2]_2[\text{Al}(\text{CH}_3)_2\text{C}_{10}\text{H}_8]_2$, has been determined from three-dimensional X-ray data measured by counter methods. The compound crystallizes in the space group $C_{2h}^5-P2_1/c$ with cell dimensions $a = 9.175$ (3) Å, $b = 17.356$ (6) Å, $c = 13.112$ (5) Å, and $\beta = 97.98$ (1)°. The calculated density for two $[\text{Na}(\text{C}_4\text{H}_8\text{O})_2]_2[\text{Al}(\text{CH}_3)_2\text{C}_{10}\text{H}_8]_2$ molecules per unit cell is 1.13 g cm^{-3} ; unfortunately, no precise measurement of the density of this compound could be made owing to the reactivity of the compound with the liquids used. Three-dimensional least-squares refinement yielded a conventional R factor of 7.5% for 1103 observed reflections. The compound exists as a centrosymmetric, contact ion-pair complex with two $\text{Na}(\text{C}_4\text{H}_8\text{O})_2^+$ cations complexed to the dimeric dianion. Two 1,4-dihydro-1,4-naphthylene groups are fused into the dianion *via* the two dimethylaluminate species. The aluminum-naphthylenic carbon bond distances of 2.056 (10) and 2.074 (10) Å are significantly longer than the aluminum-methyl carbon bond distances of 1.982 (11) and 1.990 (12) Å. The long Al-C bond lengths are interpreted in terms of electron-deficient Al-C bonding due to the partial delocalization of the formal negative charge of the aluminum atoms onto the carbon atoms of the naphthylenic rings.

Lehmkuhl has reported that 2 mol of Na, 1 mol of naphthalene, and 2 mol of triethylaluminum react in tetrahydrofuran (THF) and other low boiling point

ethers to yield $\text{Na}[\text{C}_{10}\text{H}_8\text{Al}(\text{C}_2\text{H}_5)_2] \cdot \text{THF}$.³⁻⁶ He has

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