

where the  $u_i$ 's are spin orbitals,  $\pi_i$ , multiplied by the appropriate spin function. The result for  $D$  is listed in Table II.

McLachlan<sup>2</sup> reduced his limited CI treatment to the expression

$$D = 1.184\langle\lambda_1(1)\lambda_3(2)|(r_{12}^2 - 3z_{12}^2)r_{12}^{-6}|\lambda_1(1)\lambda_3(2)\rangle - 0.184\langle\lambda_1(1)\lambda_2(2)|(r_{12}^2 - 3z_{12}^2)r_{12}^{-6}|\lambda_1(1)\lambda_2(2)\rangle \quad (12)$$

Substitution of the correct values for the integrals yields  $D$  which is also listed in Table II.

### Conclusion

For a large number of organic molecules, properties dependent on spin distribution have been calculated for single determinant and spin-projected single determinant wave functions. Projection usually results in better agreement with experiment.<sup>30</sup>

Trimethylenemethane, like the allyl radical, has a central carbon atom with large negative spin density surrounded by peripheral carbons with positive spin. The single determinant unrestricted wave function considerably overestimates the negative central and positive peripheral spin densities in the allyl radical<sup>30</sup> (Table I). In the case of trimethylenemethane, comparison of the spin densities calculated from  $\Psi_T$  with those derived

(30) L. C. Snyder and T. Amos, *J. Chem. Phys.*, **42**, 3670 (1965).

from the hyperfine splitting indicates that the single determinant behaves in the same way, though less drastically. The large negative 1,2 spin correlation in trimethylenemethane would then be expected to result in a low value for  $D$  calculated from the single determinant.<sup>2</sup> Table II shows that this is true if the experimental  $D$  is positive.

$D$  calculated for the projected wave function is positive and agrees well with McLachlan's value and reasonably well with the magnitude of experimental  $D$ . The agreement of  $D$  calculated with  $\Psi_T'$  with the result of McLachlan's limited CI calculation suggests that  $D$  is positive for trimethylenemethane.

Use of the larger theoretical repulsion integrals in the SCF calculation gives an interesting result. The positive peripheral and negative central spin densities of the projected wave function are enhanced (footnotes *a* and *b*, Table I) in the direction of the experimental values. This effect, as expected, decreases  $D$  slightly in the direction of the experimental magnitude (footnotes *a* and *b*, Table II). Perhaps a better estimate of the  $\gamma_{rs}$  for uhf wave functions would improve calculations of this kind on hydrocarbon triplets.

**Acknowledgments.** The author acknowledges helpful discussions with Professors M. Karplus and P. Dowd. The author also thanks Karen Gold for programming the SCF calculations.

## Organometallic Electrochemistry. XIV.<sup>1</sup> The Conversion of Formal $\pi$ Acceptors to $\pi$ Donors

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**Abstract:** Infrared spectral data for a number of octahedral systems of the types  $LM(CO)_6$  ( $M = Cr, Mo,$  and  $W$ ;  $L =$  pyridine and quinoline),  $L_2M(CO)_4$  ( $M = Cr, Mo,$  and  $W$ ;  $L_2 =$  ethylenediamine, (pyridine)<sub>2</sub>, and bipyridyl),  $(LM(CO)_4)_2$  ( $M = Cr, Mo,$  and  $W$ ;  $L = As(CH_3)_2$  and  $P(CH_3)_2$ ), and  $(LFe(CO)_3)_2$  ( $L = SCH_3, P(CH_3)_2$ , and  $As(CH_3)_2$ ) before and after electrochemical reduction are presented. Force constants are calculated using the Cotton-Kraihanzel force field and the results discussed in terms of  $\sigma$  and  $\pi$  bonding.

Because of unique bonding of the carbon monoxide molecule<sup>2,3</sup> in organometallic carbonyl compounds and its sensitivity to changes in electron density in the metal to which it is bonded, the infrared spectroscopy of these molecules in the carbonyl stretching region has been an extremely versatile tool.

The bonding between the carbon and oxygen atoms in a carbon monoxide molecule is comprised of a  $\sigma$ -bonding orbital and a pair of degenerate  $\pi$ -bonding orbitals. In addition, there exists a lone pair in non-bonding orbitals on both the oxygen and carbon atoms, the latter being the donor pair used in forming  $\sigma$  bonds with transition metals. The next lowest unoccupied

molecular orbitals are the doubly degenerate  $\pi$ -anti-bonding orbitals. The formation of the dative bond between the carbon monoxide and the (usually) low valence state metal results in a high charge density on the metal, a situation which is alleviated through the overlap of occupied  $d$  orbitals of correct symmetry on the metal with the  $\pi$ -antibonding orbitals of the carbon monoxide molecule. Occupancy of this antibonding orbital of CO results in a lower formal bond order between the carbon and oxygen atoms, and hence a lower C-O stretching frequency. It has also been shown that a change in  $\sigma$  charge density between the metal and CO directly affects the C-O stretching frequency.<sup>4</sup>

Therefore, in theory, by replacing one or more of the carbonyl groups with other ligands one can ascertain certain properties of these ligands as well as the bonding

(1) For previous papers in this series see R. E. Dessy, *et al.*, *J. Am. Chem. Soc.*, **88**, 453, 460, 467, 471, 5112, 5117, 5121, 5124, 5129, 5132, (1966); **90**, 1995, 2001, 2005 (1968).

(2) E. W. Abel, *Quart. Rev.* (London), **17**, 133 (1963).

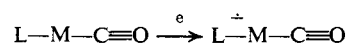
(3) G. Blyholder, *J. Phys. Chem.*, **68**, 2772 (1964).

(4) T. L. Brown and D. J. Darensbourg, *Inorg. Chem.*, **6**, 971 (1967).

schemes of the metal carbonyl moiety by monitoring the change of the carbonyl stretching frequencies as a function of the new ligand. This technique has been applied in numerous cases, and the results have been utilized to calculate changes in bond order of the CO bond,<sup>5</sup> estimate relative weights of hybrid structures,<sup>5</sup> evaluate  $pK_a$ 's,<sup>6-8</sup> predict stoichiometries, determine symmetries, and evaluate donor-acceptor properties of ligands.<sup>5,9</sup> There is general agreement in the cases listed above with the exception of the last. Although little or no disagreement is incurred in assessing the relative order of the donor-acceptor capacities of various ligands, the electronic mechanism by which this order is established has been accorded the full spectrum of explanations.

With the development of a simplified force field method of calculating force constants by Cotton and Kraihanzel,<sup>9,10</sup> and the attention given to making assignments of modes in the CO stretching region,<sup>9,11-17</sup> the force constant calculations were made accessible to nonquantum chemists. There have since been put forth the three possible combinations of  $\pi$  and  $\sigma$  bonding to explain the infrared changes of CO stretches attendant with replacing CO by another ligand. These consist of the pure  $\pi$  effects as essentially embodied in the theories of Cotton,<sup>5,9,11,18-21</sup> the  $\sigma$ -only arguments of Angelici,<sup>6,7</sup> and the more recent  $\sigma$  plus  $\pi$  arguments of Brown and Graham.<sup>4,22,23</sup> All three arguments cannot coexist with an equal degree of validity, and in some instances there are internal inconsistencies in the theories, primarily when trying to apply the theories to different symmetries. They all suffer, however, from the disadvantage that in creating by ligand alterations the changes in the carbonyl stretching frequencies that will be analyzed in terms of the bonding one perforce introduces additional changes such as steric factors, electronegativities, polarizabilities, etc., that cannot presently be separated or compensated for, and which will almost assuredly affect the net bonding scheme so that only a cumulative result is obtained. It was for this reason that the present study was undertaken. The entire premise on which it is based, and for which spectroscopic evidence is offered, is that upon electrochemical reduction of a metal carbonyl compound the electron(s) will occupy the lowest lying molecular orbital in which a vacancy exists without changing the symmetry or bonding scheme of the molecule, so that the final effect

shown by the carbonyl group is purely, or more nearly so than in the case of a ligand change, due to the manner in which the central metal atom distributes and transmits charge density.



## Experimental Section

**Basic Equipment.** Polarographic, triangular voltammetric, and controlled-potential electrolytic experiments were run in a standard H-type cell. The anodic compartment was 35 mm in diameter, 47 mm high, and fitted with a standard taper joint in which was placed a platinum wire sealed in glass which served to make electrical contact with the mercury pool at the bottom of the compartment. The cathodic compartment was 35 mm in diameter, 26 mm high, and fitted with three standard taper joints at the top and a platinum wire sealed in the base. The standard taper joints accommodated the reference, hanging drop, and dropping mercury electrodes while the platinum wire served to make electrical contact with the mercury pool at the bottom of the compartment for controlled-potential electrolysis. A 25-mm medium porosity glass frit separated the two compartments. The reference electrode consisted of two compartments separated by a frit. The upper compartment contained a solution  $10^{-3} M$  in silver perchlorate and  $10^{-1} M$  in tetrabutylammonium perchlorate, and a 20-gauge silver wire in 1,2-dimethoxyethane. The lower portion contained  $10^{-1} M$  tetrabutylammonium perchlorate in 1,2-dimethoxyethane and served as a salt bridge between the Ag|Ag<sup>+</sup> reference solution and the test solution in the cathodic compartment.

The electrolysis cell used in preparing samples for infrared investigation consisted of two concentric compartments connected electrically by a 20-mm medium porosity glass frit. The outer compartment was 45 mm in diameter, 57 mm high, and had a platinum wire pinchsealed into the base to provide electrical contact with the mercury pool. The outer compartment held the test substance. The inner compartment was 25 mm in diameter, 44 mm high, and fitted with a standard taper joint into which was placed the counter electrode. This counter electrode consisted of a platinum wire sealed into glass onto which was spot welded a platinum button 13 mm in diameter. The standard Ag<sup>+</sup>|Ag reference electrode was employed.

Polarograms were recorded using a Metrohm Polarecord E-261 and a Sargent IR compensator (Model A). The capillary used for the dropping mercury electrode had a drop time of 2-3 sec.

Triangular voltammetric data were obtained employing a unit based on standard operational amplifier circuitry.<sup>1</sup> The voltammograms were recorded on a Mosely 2D-2 XY recorder. The hanging drop electrode consisted of a standard capillary attached to a microsyringe head.

Controlled-potential electrolysis was effected using circuits based on standard operational amplifier design<sup>1</sup> and a stirred mercury pool.

Infrared spectra were recorded on a Perkin-Elmer Model 621 double-beam instrument. The cells used were constructed of stainless steel and fitted with a threaded needle valve assembly to which was attached a base portion of a stainless steel syringe tip. The cell windows were of cesium bromide separated by a 0.1-mm amalgamated spacer of lead.

Electron spin resonance spectra were obtained using a Varian E-3 spectrometer. Hyperfine coupling constants were obtained via satisfactory spectrum simulation.

All electrochemical work and preparation of infrared samples were performed in a drybox (Vacuum Atmospheres) in which the water vapor and oxygen contents of the argon atmosphere were controlled at not more than 2 ppm.

**Chemicals.** 1,2-Dimethoxyethane (Ansol 121) was predried over calcium hydride and distilled from sodium-potassium alloy into a receiver in which it was thoroughly degassed with argon. The drying and distillation operations were carried out under a small positive argon pressure.

The 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<sub>2</sub>O<sub>5</sub> as the desiccant.

Triply distilled mercury was used as obtained.

Compounds of systems 28, 29, 36, and 37 were obtained from Dr. W. Hubel, and those of systems 16-20, 23, and 24 from Dr. R. Hayter. Compounds of systems 1-6 and 10-12 were prepared by the method of Strohmeier;<sup>24-28</sup> of systems 7-9 by the method of

- (5) F. A. Cotton, *Inorg. Chem.*, **3**, 702 (1964).
- (6) R. J. Angelici and M. D. Malone, *ibid.*, **6**, 1731 (1967).
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- (11) C. S. Kraihanzel and F. A. Cotton, *ibid.*, **2**, 533 (1963).
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- (13) J. Dalton, I. Paul, J. G. Smith, and F. G. A. Stone, *ibid.*, 1199 (1968).
- (14) M. A. El-Sayed and H. D. Kaesz, *Inorg. Chem.*, **2**, 158 (1963).
- (15) L. Orgel, *ibid.*, **1**, 25 (1962).
- (16) H. Haas and R. Sheline, *J. Chem. Phys.*, **47**, 2996 (1967).
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- (18) F. A. Cotton and F. Zingales, *Inorg. Chem.*, **1**, 145 (1962).
- (19) F. A. Cotton and F. Zingales, *J. Am. Chem. Soc.*, **83**, 351 (1961).
- (20) F. A. Cotton, *Inorg. Chem.*, **3**, 584, (1964).
- (21) F. A. Cotton and R. M. Wing, *ibid.*, **4**, 1328 (1965).
- (22) T. L. Brown and D. J. Darenbourg, *ibid.*, **7**, 959 (1968).
- (23) W. A. G. Graham, *ibid.*, **7**, 315 (1968).

Cotton;<sup>29</sup> of systems 13–15 by the method of Abel;<sup>30</sup> of systems 21, 22, and 26 by the method of King;<sup>31</sup> of systems 30 and 35 by the method of Manuel;<sup>32</sup> of system 13 by the method of Stone;<sup>33</sup> and of systems 32–34 by the method of Bagga.<sup>34</sup>

**Typical Procedure Followed for Determining the Electrochemical Behavior of a Compound.** Test solutions were prepared at  $1\text{--}2 \times 10^{-3} M$  in the H-cell. The following operations were then performed.

(1) A polarographic scan was made from 0.0 vdc to the potential at which the supporting electrolyte began to reduce,  $-3.6$  vdc with reference to the  $\text{Ag}|\text{Ag}^+$  couple.

(2) Triangular voltammetric scans were made of the electrochemically active regions, as determined in operation, to evaluate the electrochemical reversibility of those particular processes.

(3) Controlled-potential electrolysis was then performed with the potential set at a value corresponding to the top of the diffusion current wave as determined in operation 1. The number of electrons per mole of substance was determined at this time by graphical integration of a current vs. time plot of the electrolysis.

(4) A sample was withdrawn from the cell and its esr spectrum recorded.

(5) Another polarographic scan was made to determine the oxidation potentials.

(6) The substance was reoxidized employing the potentials found in operation 5.

(7) Polarography, ultraviolet, and infrared spectroscopy were applied to the regenerated material of operation 6 to determine the extent of chemical reversibility.

**Preparation of Infrared Samples.** (1) The necessary solutions were prepared in the electrochemical cell at a concentration of  $1.0\text{--}2.5 \times 10^{-2} M$ , and a sample of this initial material was withdrawn and its infrared spectrum recorded.

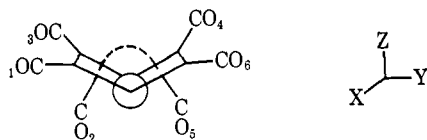
(2) The material was exhaustively electrolyzed at a potential as previously determined from the electrochemical experiments.

(3) Upon completion of electrolysis, a sample was withdrawn and sealed in the infrared cell previously described and its infrared spectrum recorded. All spectra were run in 1,2-dimethoxyethane with tetrabutylammonium perchlorate at  $10^{-1} M$ , and the observed spectra have an estimated precision of  $\pm 2 \text{ cm}^{-1}$  with the exception of those marked as shoulders which have an estimated precision of  $\pm 4 \text{ cm}^{-1}$ . The data obtained for each symmetry class appear in Table I and II ( $w$  = weak,  $m$  = medium,  $s$  = strong,  $vs$  = very strong,  $sh$  = shoulder).

(4) The material was then exhaustively reoxidized and an infrared spectrum of this regenerated material obtained for purposes of comparison with that of the starting material.

**Force Constant Calculations.** The Cotton–Kraihanzel treatment is well documented<sup>11</sup> and is therefore only briefly discussed, with emphasis on the systems 21–24 which involve new matrices.

Point group assignment for  $(\text{LFe}(\text{CO})_5)_2$  species ( $C_{2v}$ ) permits one to predict that five infrared active bands will appear in the carbonyl region,  $\Gamma_5 = 2A_1 + 2B_2 + B_1$ . Internal coordinates based on C–O lengths were chosen, and linear combinations of these formed in such a way that each such combination became a new coordinate—the symmetry coordinate. A force constant matrix was then constructed using the following model



and the normal simplifications and assumptions were made.

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 (25) W. Strohmeier and K. Gerlach, *ibid.*, **15b**, 675 (1960).  
 (26) W. Strohmeier, G. Matthais, and D. von Hobe, *ibid.*, **15b**, 873 (1960).  
 (27) W. Strohmeier and K. Gerlach, *Chem. Ber.*, **93**, 2087 (1960).  
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 (30) E. Abel, M. Bennett, and G. Wilkinson, *J. Chem. Soc.*, 2325 (1959).  
 (31) J. Eisch and R. B. King, "Organometallic Synthesis," Academic Press, New York, N. Y., 1965.  
 (32) T. A. Manuel and T. J. Meyer, *Inorg. Chem.*, **3**, 1049 (1964).  
 (33) F. G. A. Stone and R. B. King, *J. Am. Chem. Soc.*, **82**, 4557 (1960).  
 (34) M. M. Bagga, personal communication.

$$\begin{aligned}
 k_{11} &= k_{33} = k_{44} = k_{66} = k_1; & k_{22} &= k_{55} = k_2 \\
 k_{13} &= k_{31} = k_{46} = k_{64} = k_{12} = k_{21} = \\
 & & k_{32} &= k_{23} = k_{65} = k_{56} = k_{45} = k_{54} = k_c \\
 & & k_{25} &= k_{32} = k_c \\
 k_{42} &= k_{24} = k_{62} = k_{26} = k_{15} = k_{51} = k_{35} = k_{53} = 0 \\
 k_{16} &= k_{61} = k_{34} = k_{43} = 0; & k_{14} &= k_{41} = k_{36} = k_{63} = 0
 \end{aligned}$$

The symmetry coordinates were then used with the force constant matrix to yield the elements of the potential energy matrix ( $F$ ). If coupling between CO groups is entirely nonmechanical, a kinetic energy matrix ( $G$ ) can be constructed and by using the eigenvalue function,  $GF - E = 0$ , the following secular equations are obtained.

$A_1$  modes

$$\begin{aligned}
 u(k_1 + k_c) - \lambda & & 2^{1/2}uk_c & \\
 2^{1/2}uk_c & & u(k_2 + k_c) - \lambda & \\
 & & & = 0
 \end{aligned}$$

$B_2$  modes

$$\begin{aligned}
 u(k_1 + k_c) - \lambda & & 2^{1/2}uk_c & \\
 2^{1/2}uk_c & & u(k_2 - k_c) - \lambda & \\
 & & & = 0
 \end{aligned}$$

$B_1$  mode

$$u(k_1 - k_c) - \lambda = 0$$

$u$  is the reciprocal of the reduced mass of the C–O system;  $\lambda$  is  $(5.889 \times 10^{-2})\nu^2$ , where  $\nu$  is the frequency of the appropriate band in  $\text{cm}^{-1}$ . Expansion and simultaneous solution of these will yield the appropriate force constants.

The data were analyzed using nonlinear least-squares methods. In this approach the secular equations are expanded in a Taylor series in which only the first-order terms are retained. After rearrangement, the problem is reduced to the solution of an over-determined set of equations which are linear in the parameter corrections, which are then simplified to a set of normal simultaneous equations which may then be solved by conventional methods. The corrections are then subtracted from the parameters and another set of corrections is solved for until the process has gone to convergence. Estimates of the standard errors in the parameters are obtained from the final iteration.

In Tables I and II the final force constants have been used to calculate an internally consistent set of frequencies. These are compared with the experimental values. The force constants themselves appear in the Results section of this paper.

## Results

**$\text{ML}(\text{CO})_5$  Systems.** As shown by X-ray crystallography<sup>35–37</sup> and infrared spectroscopy,<sup>9,15</sup> these compounds have  $C_{4v}$  symmetry (if the low local symmetry of 2 is ignored), with the radial CO groups bent slightly out of plane. Therefore, where normally only three fundamentals ( $2A_1 + E$ ) should appear, four are observed. The fourth band is due to the Raman-active  $B_1$  mode which acquires intensity in the infrared due to the above-mentioned axial asymmetry of L. The assignment of the four bands to their respective modes has been made previously on neutral species on both an experimental<sup>9</sup> and theoretical<sup>15</sup> basis.

Typical infrared absorption spectra for the neutral and dianion species derived from  $\text{W}(\text{py})(\text{CO})_5$  and  $\text{W}(\text{quin})(\text{CO})_5$  by electrochemical reduction are shown in Figures 1 and 2. Tabular experimental data for all of the  $\text{ML}(\text{CO})_5$  systems appear in Tables I and II. Using

- (35) S. J. LaPlaca, W. C. Hamilton, and J. A. Ibers, *Inorg. Chem.*, **3**, 1491 (1964).  
 (36) H. Weber and R. F. Bryan, *Chem. Commun.*, 443 (1966).  
 (37) R. F. Bryan, *ibid.*, 355 (1967).

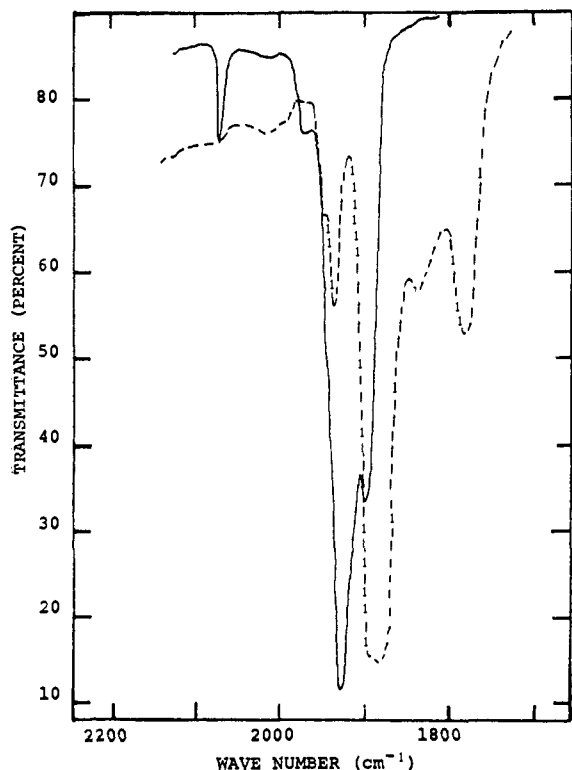


Figure 1. Infrared spectrum of  $2 \times 10^{-2} M$  solution of  $W(py)(CO)_5$  in 1,2-dimethoxyethane (0.1 M TBAP): —, neutral; ---, reduced.

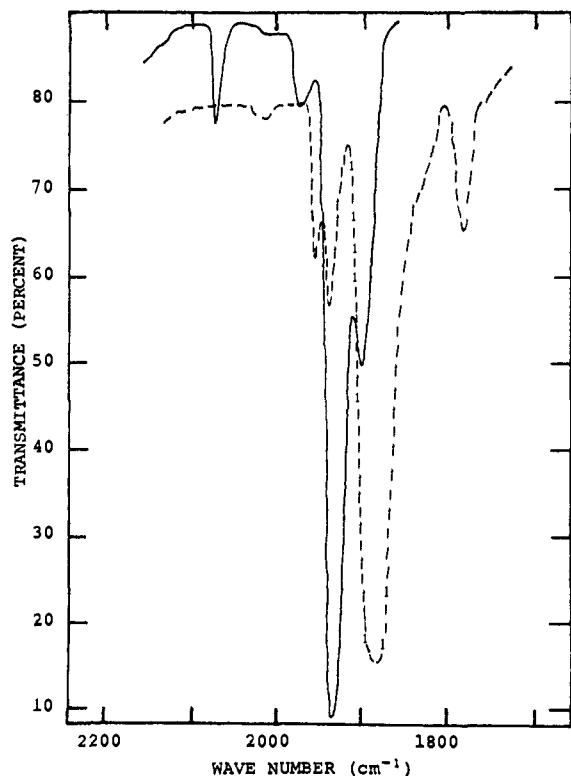


Figure 2. Infrared spectrum of  $2 \times 10^{-2} M$  solution of  $W(quin)(CO)_5$  in 1,2-dimethoxyethane (0.1 M TBAP): —, neutral; ---, reduced.

the assignments and the secular equations developed by Cotton,<sup>9</sup> the force constants which appear in Table III were calculated. The following notation will be used

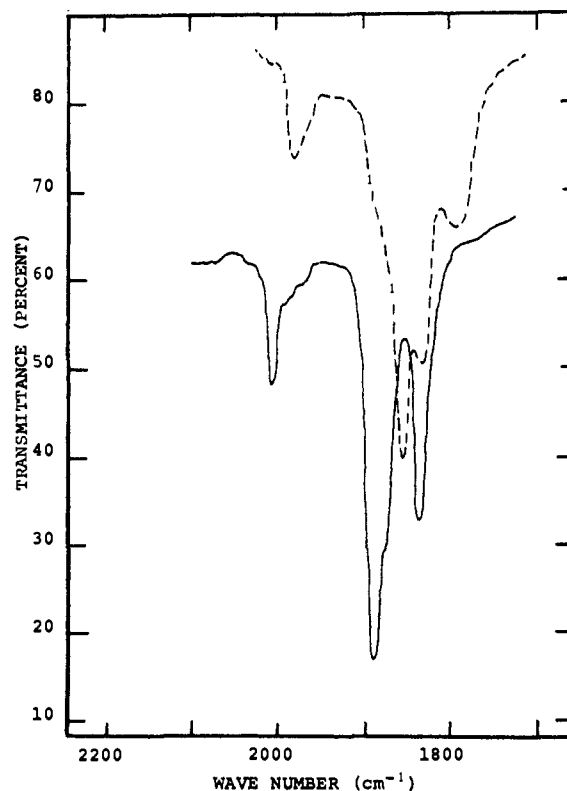
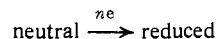


Figure 3. Infrared spectrum of  $2 \times 10^{-2} M$  solution of  $W(bipy)(CO)_4$  in 1,2-dimethoxyethane (0.1 M TBAP): —, neutral; ---, reduced.

on all force constants appearing in this work, with the exception of that used for the binuclear iron compounds:  $k_1$  = force constant between the C and O atoms of a carbonyl group *trans* to a ligand;  $k_2$  = force constant between the C and O atoms of a carbonyl group *trans* to another carbonyl group;  $k_3$  = force constant between two interacting carbonyl groups;  $n$  = number of electrons involved in the process



$$\Delta k = k(\text{neutral}) - k(\text{reduced}).$$

**$ML_2(CO)_4$  Systems.** The symmetry of these systems has been shown by infrared studies<sup>9,15</sup> to be  $C_{2v}$ . Accordingly, four fundamental vibrations are predicted in the carbonyl stretching region ( $2A_1 + B_1 + B_2$ ), and this prediction is borne out experimentally (see Figure 3). The assignment of the bands to their respective modes has been established by Cotton<sup>9</sup> and Orgel.<sup>15</sup> Using these assignments and the secular equations as developed by Cotton, the force constants appearing in Table IV were calculated.

In two instances, the force constants were not or could not be calculated for the reduced species. For the ethylenediamine compounds the infrared spectrum (see Figure 4) of the reduced species is extremely complex. This forbids an assignment in the case of the reduced material and precludes any possibility of a comparison between the neutral and reduced species. As seen from a comparison of the infrared spectra before and after the redox cycle, the reduction of the Mo compound is *clearly reversible*. The chromium and tungsten derivatives do not appear to be electrochemically or chemically reversible, as evidenced by spectrometric and polarographic information.

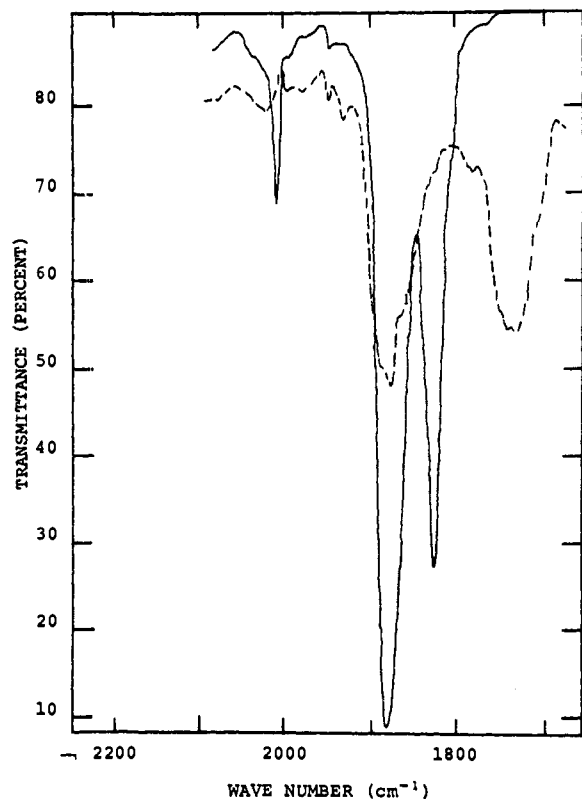


Figure 4. Infrared spectrum of  $2 \times 10^{-2} M$  solution of  $\text{Mo}(\text{en})(\text{CO})_4$  in 1,2-dimethoxyethane (0.1 M TBAP): —, neutral; ---, reduced.

For the bispyridine series similar difficulties were encountered, making analysis of the reduced species impractical. For the chromium compound, there is evidence of slow initial decomposition to  $\text{Cr}(\text{py})(\text{CO})_5$  upon addition of 1,2-dimethoxyethane, and it appears that the redox cycle results in complete conversion to  $\text{Cr}(\text{py})(\text{CO})_6$ . This would support the observation of Cotton<sup>11</sup> concerning the instability of these compounds in solution and his analysis of the decomposition products. For the Mo and W compounds there is, in addition to the  $\text{M}(\text{py})(\text{CO})_6$  formed, evidence that small amounts of  $\text{M}(\text{bipy})(\text{CO})_4$  are also formed. This is postulated on the basis of the similarities of the electron spin resonance signal of  $\text{W}(\text{bipy})(\text{CO})_4$  radical and that shown for  $\text{W}(\text{py})_2(\text{CO})_4$  upon reduction. The infrared spectra of  $\text{Mo}(\text{py})_2(\text{CO})_4$  and  $\text{W}(\text{py})_2(\text{CO})_4$  upon reduction and after the redox cycle appear to be consistent with a mixture of  $\text{Mo}(\text{py})(\text{CO})_5$  and  $\text{Mo}(\text{bipy})(\text{CO})_4$ , and  $\text{W}(\text{py})(\text{CO})_5$  and  $\text{W}(\text{bipy})(\text{CO})_4$ , respectively.

**(ML(CO)<sub>4</sub>)<sub>2</sub> Systems.** By analogy with the crystal structure<sup>38</sup> and the solution infrared spectra<sup>5</sup> given for  $[\text{MnBr}(\text{CO})_4]_2$ , these compounds have symmetry  $D_{2h}$ . They are, therefore, predicted to show four fundamentals in the Co stretching region corresponding to the modes  $B_{1u}$ ,  $B_{2u}$ ,  $2B_{3u}$ . Assuming, however, that there is negligible coupling of the CO stretching modes of the two sides of the molecule, the spectra may be analyzed as that of a molecule having symmetry  $C_{2v}$  with a one-to-one correspondence between the infrared stretching

(38) L. Dahl and C. Wei, *Acta Cryst.*, 16, 611 (1963).

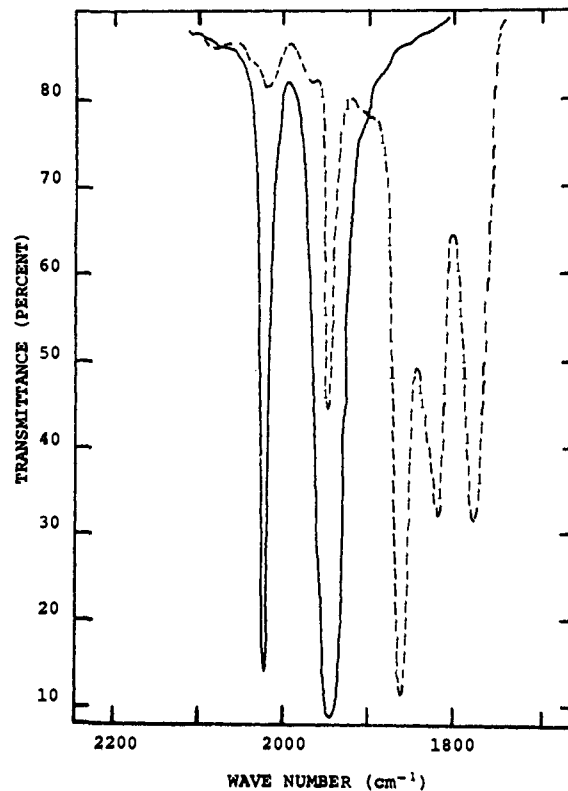


Figure 5. Infrared spectrum of  $2 \times 10^{-2} M$  solution of  $[\text{WAs}(\text{CH}_3)_2(\text{CO})_4]_2$  in 1,2-dimethoxyethane (0.1 M TBAP): —, neutral; ---, reduced.

modes

$D_{2h}$	$C_{2v}$
$B_{1u}$	$B_1$
$B_{2u}$	$B_2$
$2B_{3u}$	$2A$

(Although as found by Cotton<sup>5</sup> and this work the noninteraction assumption does not greatly affect the results, it should not by any means be taken as rigorous since the combination spectra of these compounds can be visibly affected by the metal-metal bond.)

Contrary to the prediction of four bands in the CO stretching region, only two are observed in this work. It has previously been proposed<sup>39</sup> that accidental degeneracy is responsible. This overlap of peaks has also recently been confirmed by Braterman,<sup>40</sup> who, using cyclohexane and high-resolution techniques, resolved the broader of the two bands. Upon reduction, however, this degeneracy is removed in the present examples and the four peaks are well separated and clearly visible (see Figure 5). This has allowed assignment, and the results are presented in Table V.

**[FeL(CO)<sub>3</sub>]<sub>2</sub> Systems.** There is ample evidence from X-ray crystallography<sup>38</sup> and Mössbauer<sup>41</sup> studies to show that these systems have  $C_{2v}$  symmetry. Group theoretical considerations lead to the prediction of five normal vibrational modes for the terminal carbonyls,  $2A_1 + 2B_2 + B_1$ . The normal modes appear schematically in Figure 6. (A vector pointing from the oxygen to a carbon atom,  $\text{C}^-\text{O}$ , represents a vibration whereby the

(39) R. Hayter, *Inorg. Chem.*, 3, 711 (1964).

(40) P. Braterman and D. Thompson, *J. Chem. Soc.*, 1454 (1968).

(41) T. Gibb, R. Greatrex, N. Greenwood, and D. Thompson, *ibid.*, 622 (1968).

Table I. Carbonyl Stretching Frequencies<sup>a,c</sup>

System	Compound	Observed (cm <sup>-1</sup> )		Calculated (cm <sup>-1</sup> )		Assignment		
		Neutral	Reduced	Neutral	Reduced			
LM(CO) <sub>5</sub> Compounds (C <sub>4v</sub> )								
1	Cr(py)(CO) <sub>5</sub>	2070 w	1938 w	2069	1939	A <sub>1</sub>		
		1984 w	1911 s	1981	1905	B <sub>1</sub>		
		1936 vs	1886 vs	1940	1888	E		
		1900 s	1780 m	1892	1778	A <sub>1</sub>		
		2078 w	1945 w	2078	1949	A <sub>1</sub>		
2	Mo(py)(CO) <sub>5</sub>	1984 m	1932 s	1984	1917	B <sub>1</sub>		
		1940 vs	1892 vs	1940	1902	E		
		1901 s	1784 m	1900	1782	B <sub>1</sub>		
		2073 w	1950 w	2074	1956	A <sub>1</sub>		
		1975 w	1935 m	1975	1915	B <sub>1</sub>		
3	W(py)(CO) <sub>5</sub>	1930 vs	1880 vs	1930	1895	E		
		1900 s	1782 m	1900	1776	A <sub>1</sub>		
		2072 w	1938 w	2072	1940	A <sub>1</sub>		
		1985 w	1914 m	1983	1907	B <sub>1</sub>		
		1940 vs	1886 vs	1942	1891	E		
4	Cr(quin)(CO) <sub>5</sub>	1904 m	1790 m	1898	1778	A <sub>1</sub>		
		2077 w	1948 w	2077	1953	A <sub>1</sub>		
		1986 w	1932 m	1984	1916	B <sub>1</sub>		
		1938 vs	1886 vs	1944	1898	E		
		1900 m	1783 m	1893	1779	A <sub>1</sub>		
5	Mo(quin)(CO) <sub>5</sub>	2074 w	1955 w	2074	1961	A <sub>1</sub>		
		1980 w	1938 m	1979	1918	B <sub>1</sub>		
		1935 vs	1884 vs	1936	1898	E		
		1900 m	1782 m	1897	1777	A <sub>1</sub>		
		ML <sub>2</sub> (CO) <sub>5</sub> Compounds (C <sub>2v</sub> )						
7	Cr(en)(CO) <sub>4</sub>	2000 w		2002		A <sub>1</sub>		
		1870 vs		1868		B <sub>1</sub>		
		1860 s, sh		1856		A <sub>1</sub>		
		1823 s		1824		B <sub>2</sub>		
		2005 w		2007		A <sub>1</sub>		
8	Mo(en)(CO) <sub>4</sub>	1880 vs		1877		B <sub>1</sub>		
		1865 s, sh		1859		A <sub>1</sub>		
		1825 s		1827		B <sub>2</sub>		
		2000 w		2004		A <sub>1</sub>		
		1864 vs		1867		B <sub>1</sub>		
9	W(en)(CO) <sub>4</sub>	1850 s, sh		1849		A <sub>1</sub>		
		1818		1816		B <sub>2</sub>		
		2009 w		2014		A <sub>1</sub>		
		1884 vs		1885		B <sub>1</sub>		
		1875 s, sh		1871		A <sub>1</sub>		
10	Cr(py) <sub>2</sub> (CO) <sub>4</sub>	1840 s		1840		B <sub>2</sub>		
		2014 w		2012		A <sub>1</sub>		
		1895 vs		1885		B <sub>1</sub>		
		1882 s, sh		1877		A <sub>1</sub>		
		1843 s		1847		B <sub>2</sub>		
11	Mo(py) <sub>2</sub> (CO) <sub>4</sub>	2004 w		2010		A <sub>1</sub>		
		1878 vs		1887		B <sub>1</sub>		
		1859 s, sh		1863		A <sub>1</sub>		
		1837 s		1831		B <sub>2</sub>		
		2007 w	1987 w	2011	1989	A <sub>1</sub>		
12	W(py) <sub>2</sub> (CO) <sub>4</sub>	1895 vs	1870 vs	1889	1866	B <sub>1</sub>		
		1880 s, sh	1843 s	1868	1836	A <sub>1</sub>		
		1833 s	1800 m	1837	1803	B <sub>2</sub>		
		2010 w	1980 w	2014	1981	A <sub>1</sub>		
		1887 vs	1867 vs	1882	1865	B <sub>1</sub>		
13	Cr(bipy)(CO) <sub>4</sub>	1880 s, sh	1835 s	1870	1830	A <sub>1</sub>		
		1836 s	1796 m	1839	1789	B <sub>2</sub>		
		2008 w	1978 w	2012	1980	A <sub>1</sub>		
		1889 vs	1856 vw	1884	1853	B <sub>1</sub>		
		1880 s, sh	1832 s	1870	1826	A <sub>1</sub>		
14	Mo(bipy)(CO) <sub>4</sub>	1836 s	1790 m	1839	1792	B <sub>2</sub>		
		Binuclear Compounds of Group VI <sup>b</sup>						
		16	(CrPMe <sub>2</sub> - (CO) <sub>4</sub> ) <sub>2</sub>	2012 s	1920 m	2011	1924	A <sub>1</sub>
				1948 vs	1852 vs	1954	1842	B <sub>1</sub>
				1948 vs	1817 s	1955	1802	A <sub>1</sub>
1948 vs	1774 s			1944	1774	B <sub>2</sub>		
2008 vs	1910 m			2006	1928	A <sub>1</sub>		
17	(WPMe <sub>2</sub> - (CO) <sub>4</sub> ) <sub>2</sub>	1945 vs	1860 vs	1950	1859	B <sub>1</sub>		
		1945 vs	1818 s	1953	1798	A <sub>1</sub>		
		1945 vs	1774 s	1942	1774	B <sub>2</sub>		

Table I (Continued)

System	Compound	Observed (cm <sup>-1</sup> )		Calculated (cm <sup>-1</sup> )		Assignment
		Neutral	Reduced	Neutral	Reduced	
18	(MoAsMe <sub>2</sub> - (CO) <sub>4</sub> ) <sub>2</sub>	2028 vs	1947 s	2020	1931	A <sub>1</sub>
		1953 vs	1870 vs	1947	1850	B <sub>1</sub>
		1953 vs	1826 s	1954	1820	A <sub>1</sub>
		1938 s, sh	1783 s	1942	1796	B <sub>2</sub>
19	(WAsMe <sub>2</sub> - (CO) <sub>4</sub> ) <sub>2</sub>	2023 vs	1947 s	2014	1933	A <sub>1</sub>
		1946 vs	1861 vs	1947	1844	B <sub>1</sub>
		1946 vs	1818 vs	1956	1814	A <sub>1</sub>
		1946 vs	1777 s	1945	1788	B <sub>2</sub>
20	(CrAsMe <sub>2</sub> - (CO) <sub>3</sub> ) <sub>2</sub>	2060 w	2009 w			A <sub>1</sub>
		1985 w	1915 w			A <sub>1</sub>
		1947 vs	1887 vs			E
		1930 vs, sh	1858 vs, sh			E
Binuclear Fe Compounds (C <sub>2v</sub> )						
21	<i>trans</i> -(FeSMe- (CO) <sub>3</sub> ) <sub>2</sub>	2075 vs	2025 m	2075	2016	A <sub>1</sub>
		2075 vs	2010 m	2075	2018	B <sub>2</sub>
		2040 vs	1968 vs	2040	1969	B <sub>1</sub>
		1993 vs	1938 vs	1993	1937	A <sub>1</sub>
		1993 vs	1920 vs	1993	1921	B <sub>2</sub>
22	<i>cis</i> -(FeSMe- (CO) <sub>3</sub> ) <sub>2</sub>	2072 vs	2027 m	2072	2015	A <sub>1</sub>
		2072 vs	2004 m	2071	2016	B <sub>2</sub>
		2038 vs	1972 vs	2037	1973	B <sub>1</sub>
		1990 vs	1940 vs	1990	1938	A <sub>1</sub>
		1990 vs	1925 vs	1990	1927	B <sub>2</sub>
23	(FePMe <sub>2</sub> - (CO) <sub>3</sub> ) <sub>2</sub>	2044 vs	1909 w	2044	1909	A <sub>1</sub>
		2044 s	1909 w, sh	2044	1909	B <sub>2</sub>
		2008 vs	1879 vs	2008	1879	B <sub>1</sub>
		1960 vs	1810 vs	1960	1810	A <sub>1</sub>
		1960 vs	1800 vs	1960	1800	B <sub>2</sub>
24	(FeAsMe <sub>2</sub> - (CO) <sub>3</sub> ) <sub>2</sub>	2035 s	1910 w	2035	1910	A <sub>1</sub>
		2035 vs	1910 w	2035	1910	B <sub>2</sub>
		2001 vs	1880 vs	2001	1880	B <sub>1</sub>
		1963 vs	1816 vs	1963	1816	A <sub>1</sub>
		1863 vs	1805 vs	1963	1805	B <sub>2</sub>

<sup>a</sup> bipy = 2,2'-bipyridyl; en = ethylenediamine; py = pyridine; quin = quinoline. <sup>b</sup> Symmetry C<sub>2v</sub> for systems 16–19; C<sub>4v</sub> for system 20. <sup>c</sup> All spectra run in dimethoxyethane with tetrabutylammonium perchlorate.

carbon-to-oxygen distance is shortened, whereas a vector pointing in the opposite direction, C=O, represents a lengthening of that bond.) The highest frequency mode is predicted<sup>17</sup> to be the A<sub>1</sub> mode involving all six carbonyl groups (1) and the B<sub>2</sub> (3) to be the next highest. The relative energies of the remaining modes cannot be as easily predicted. Therefore, all remaining combinations of assignments are tried and the correctness of the assignment judged on the basis of the calculated force constants. Using the *trans*-(FeSCH<sub>3</sub>(CO)<sub>3</sub>)<sub>2</sub> system (see Figure 7) as an example, Table VI is constructed. Using these assignments and the equations developed in the Experimental Section, the force constants corresponding to each of these assignments were calculated and the results are given in Table VII for the two cases that converged in both the neutral and radical anion. Assignments 3–6 are eliminated immediately since this entire study is predicted on the assumption that the structure of the molecules does not change grossly following electrochemical reduction, and, therefore, the same assignments of bands should apply to both neutral and reduced species. Neutral assignments 3–6 did not converge. On the basis of the calculated force constants assignments 1 and 2 cannot be as readily discriminated between. However, when it is considered that the intensity of a particular band is proportional to the square of the vectorial sum of the local dipoles, assignment 2 seems the more likely. A weaker

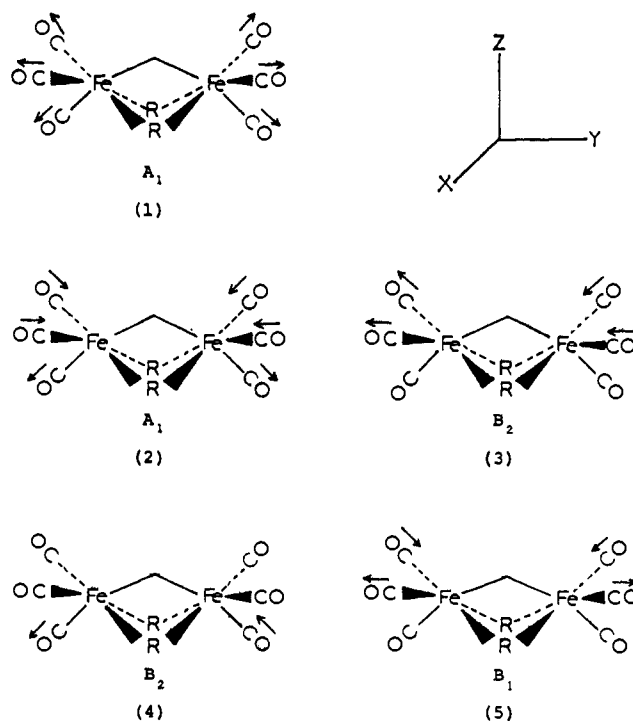


Figure 6. Normal vibrational modes of carbonyl groups in [FeR(CO)<sub>3</sub>]<sub>2</sub>.

**Table II.** Carbonyl Stretching Frequencies of Some Fe Compounds of Low Symmetry<sup>a</sup>

System	Compound	Poss sym	Predicted CO normal modes	Observed, cm <sup>-1</sup>	
				Neutral	Reduced
26	C <sub>8</sub> H <sub>8</sub> Fe(CO) <sub>3</sub>	C <sub>1</sub> C <sub>s</sub> C <sub>2v</sub>	3A 2A' + A'' A + E	2050 vs	1960 w
				1985 vs	1945 w, sh
				1975 s, sh	1927 vs 1910 m, sh 1881 m 1846 vs 1830 s, sh
27	C <sub>2</sub> (CN) <sub>4</sub> C <sub>8</sub> H <sub>8</sub> Fe(CO) <sub>3</sub>	C <sub>s</sub>	2A' + A''	2071 vs	2146 w
				2015 vs	2070 vs
				2007 vs, sh	2056 s 1990 s 1980 s, sh
28	2,4-Diphenyltropone- Fe(CO) <sub>3</sub>	C <sub>1</sub>	3A	2063 s	1925 s
				1998 vs	1895 w, sh
				1740 s	1850 vs 1832 s, sh
29	Fe <sub>2</sub> (CO)(PhC <sub>2</sub> Me) <sub>2</sub>	C <sub>1</sub>	6A	2078 s	2014 s
				2048 vs	1978 vs
				2012 vs	1930 vs
30	(C <sub>4</sub> H <sub>3</sub> S)(C <sub>4</sub> H <sub>3</sub> S)- Fe <sub>2</sub> (CO) <sub>6</sub>	C <sub>1</sub>	6A	1670 m	1909 w, sh 1870 w 1614 w
				2082 m	2020 w
				2048 vs	2008 w
31	(C <sub>8</sub> H <sub>6</sub> S)Fe <sub>2</sub> (CO) <sub>6</sub>	C <sub>1</sub>	6A	2008 vs	1987 w, sh
				2000 s, sh	1974 s 1960 w, sh
					1930 vs 1910 s 1860 m
32	(C <sub>6</sub> H <sub>4</sub> )CH <sub>2</sub> N- (Me)Fe <sub>2</sub> (CO) <sub>6</sub>	C <sub>1</sub>	6A	2080 s	2028 w, sh
				2047 vs	2010 m
				2006 vs	1974 s 1945 m, sh 1926 vs 1910 s, sh
33	(C <sub>6</sub> H <sub>4</sub> )CH <sub>2</sub> (Ph)- Fe <sub>2</sub> (CO) <sub>6</sub>	C <sub>1</sub>	6A	2064 m	2010 m
				2027 vs	1954 vs
				1978 s	1920 s, sh 1916 s 1870 m
34	(C <sub>6</sub> H <sub>4</sub> )CH <sub>2</sub> (tolyl)- Fe <sub>2</sub> (CO) <sub>6</sub>	C <sub>1</sub>	6A	2065 m	2017 s
				2030 vs	1960 vs
				1983 s	1935 s 1918 s 1878 s
35	(C <sub>6</sub> H <sub>4</sub> )NHS- Fe <sub>2</sub> (CO) <sub>6</sub>	C <sub>1</sub>	6A	2065 m	2013 s
				1028 vs	1955 vs
				1983 s	1930 s 1913 s 1874 m
36	Fe <sub>2</sub> (CO) <sub>6</sub> (EtC <sub>2</sub> Et) <sub>3</sub>	C <sub>1</sub>	6A	2040 s	1975 s
				2030 m, sh	1945 s, sh
				1995 vs	1940 vs 1925 vs 1910 w, sh 1855 w
37	Fe <sub>2</sub> (CO) <sub>6</sub> (EtC <sub>2</sub> Et) <sub>3</sub>	C <sub>1</sub>	6A	2066 m	2049 m
				2010 vs	1986 m
				1997 m, sh	1962 m
37	Fe <sub>2</sub> (CO) <sub>6</sub> (PhC <sub>2</sub> Ph) <sub>2</sub>	C <sub>1</sub>	8A	1951 m	1936 m, sh
				1755 m	1923 s 1910 m, sh 1888 vs 1865 vs 1830 m, sh
					2003 m 1050 s, sh 1938 vs 1893 m 1860 w, sh 1810 w

<sup>a</sup> All spectra run in 1,2-dimethoxyethane with tetrabutylammonium perchlorate.



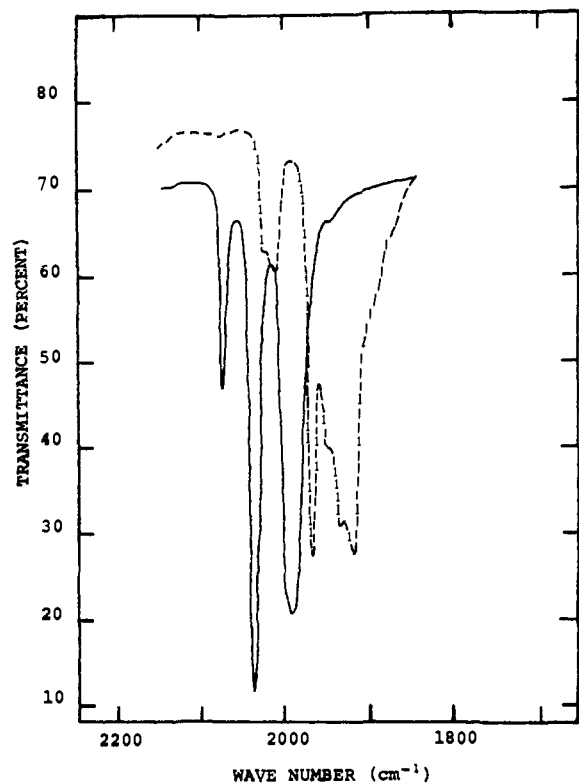


Figure 7. Infrared spectrum of  $2 \times 10^{-2} M$  solution of *trans*- $[\text{FeSCH}_3(\text{CO})_3]_2$  in 1,2-dimethoxyethane (0.1 *M* TBAP): —, neutral; ---, reduced.

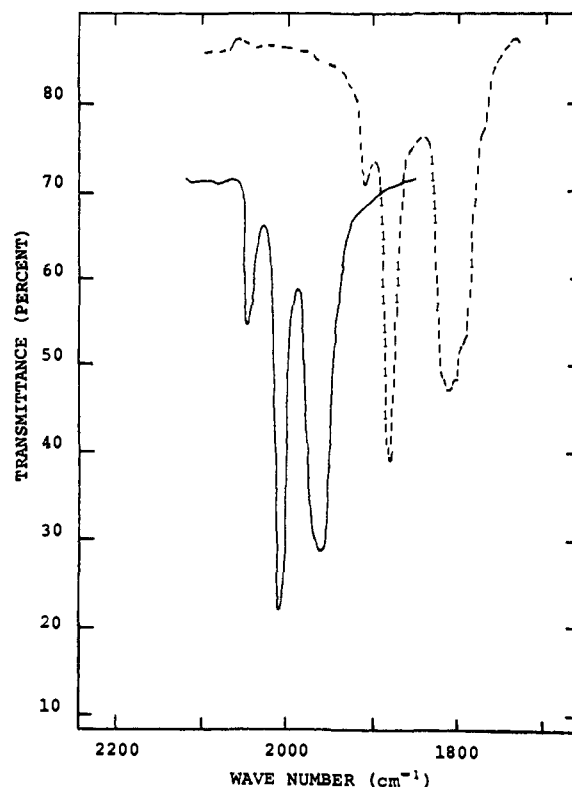


Figure 8. Infrared spectrum of  $2 \times 10^{-2} M$  solution of  $[\text{FeP}(\text{CH}_3)_2(\text{CO})_3]_2$  in 1,2-dimethoxyethane (0.1 *M* TBAP): —, neutral; ---, reduced.

Table III. Force Constants for  $\text{ML}(\text{CO})_5$  Systems

M	$k$	Neutral, mdyn/Å	Reduced, mdyn/Å	$\Delta k$ , mdyn/Å	$n$
L = Pyridine					
Cr	$k_1$	$14.61 \pm 0.09$	$12.80 \pm 0.20$	1.81	2
	$k_2$	$15.84 \pm 0.02$	$14.65 \pm 0.08$	1.19	
Mo	$k_1$	$14.75 \pm 0.09$	$12.84 \pm 0.44$	1.91	2
	$k_2$	$15.89 \pm 0.02$	$14.85 \pm 0.18$	1.04	
W	$k_1$	$14.77 \pm 0.07$	$12.76 \pm 0.71$	2.01	2
	$k_2$	$15.75 \pm 0.02$	$14.80 \pm 0.26$	0.95	
Cr	$k_1$	$14.71 \pm 0.39$	$12.79 \pm 0.23$	1.92	2
	$k_2$	$15.88 \pm 0.10$	$14.69 \pm 0.09$	1.19	
Mo	$k_1$	$14.64 \pm 0.45$	$12.81 \pm 0.54$	1.83	2
	$k_2$	$15.89 \pm 0.11$	$14.82 \pm 0.20$	1.07	
W	$k_1$	$14.70 \pm 0.21$	$12.78 \pm 0.68$	1.92	2
	$k_2$	$15.82 \pm 0.05$	$14.86 \pm 0.25$	0.96	
Cr	$k_1$	$14.71 \pm 0.39$	$12.79 \pm 0.23$	1.92	2
	$k_2$	$15.88 \pm 0.10$	$14.69 \pm 0.09$	1.19	
Mo	$k_1$	$14.64 \pm 0.45$	$12.81 \pm 0.54$	1.83	2
	$k_2$	$15.89 \pm 0.11$	$14.82 \pm 0.20$	1.07	
W	$k_1$	$14.70 \pm 0.21$	$12.78 \pm 0.68$	1.92	2
	$k_2$	$15.82 \pm 0.05$	$14.86 \pm 0.25$	0.96	
Cr	$k_1$	$14.71 \pm 0.39$	$12.79 \pm 0.23$	1.92	2
	$k_2$	$15.88 \pm 0.10$	$14.69 \pm 0.09$	1.19	
Mo	$k_1$	$14.64 \pm 0.45$	$12.81 \pm 0.54$	1.83	2
	$k_2$	$15.89 \pm 0.11$	$14.82 \pm 0.20$	1.07	
W	$k_1$	$14.70 \pm 0.21$	$12.78 \pm 0.68$	1.92	2
	$k_2$	$15.82 \pm 0.05$	$14.86 \pm 0.25$	0.96	

support of assignment 2 lies in the observation<sup>21</sup> that in one case the interaction constant across a metal-to-metal bond is positive; assignment 1 gives a negative value for this quantity. The cases where  $\text{L} = \text{P}(\text{CH}_3)_2$  and  $\text{L} = \text{As}(\text{CH}_3)_2$  are entirely similar although the degeneracy is not lifted as effectively upon reduction (see Figure 8) as in the case where  $\text{L} = \text{SCH}_3$ . The force constants for the entire series are given in Table VIII.

**Iron Systems of Low Symmetry.** No analysis has been carried out on these systems because of their very

Table IV. Force Constants for  $\text{ML}_2(\text{CO})_4$  Systems

M	$k$	Neutral, mdyn/Å	Reduced, mdyn/Å	$\Delta k$ , mdyn/Å	$n$
L <sub>2</sub> = Ethylenediamine					
Cr	$k_1$	$13.87 \pm 0.06$			1
	$k_2$	$14.95 \pm 0.01$			
Mo	$k_1$	$13.87 \pm 0.06$			1
	$k_2$	$15.06 \pm 0.01$			
W	$k_1$	$13.76 \pm 0.07$			1
	$k_2$	$14.95 \pm 0.01$			
Cr	$k_1$	$14.08 \pm 0.08$			1
	$k_2$	$15.17 \pm 0.02$			
Mo	$k_1$	$14.18 \pm 0.02$			1
	$k_2$	$15.20 \pm 0.12$			
W	$k_1$	$13.94 \pm 0.16$			1
	$k_2$	$15.19 \pm 0.03$			
Cr	$k_1$	$14.03 \pm 0.18$	$13.53 \pm 0.11$	0.50	1
	$k_2$	$15.20 \pm 0.03$	$14.86 \pm 0.02$	0.34	
Mo	$k_1$	$14.09 \pm 0.26$	$13.43 \pm 0.07$	0.66	1
	$k_2$	$15.15 \pm 0.03$	$14.80 \pm 0.02$	0.35	
W	$k_1$	$14.07 \pm 0.15$	$13.38 \pm 0.09$	0.69	1
	$k_2$	$15.16 \pm 0.03$	$14.68 \pm 0.02$	0.48	
Cr	$k_1$	$14.03 \pm 0.18$	$13.53 \pm 0.11$	0.50	1
	$k_2$	$15.20 \pm 0.03$	$14.86 \pm 0.02$	0.34	
Mo	$k_1$	$14.09 \pm 0.26$	$13.43 \pm 0.07$	0.66	1
	$k_2$	$15.15 \pm 0.03$	$14.80 \pm 0.02$	0.35	
W	$k_1$	$14.07 \pm 0.15$	$13.38 \pm 0.09$	0.69	1
	$k_2$	$15.16 \pm 0.03$	$14.68 \pm 0.02$	0.48	

low symmetry which leads to an inherent difficulty in making assignments and deriving the necessary equations

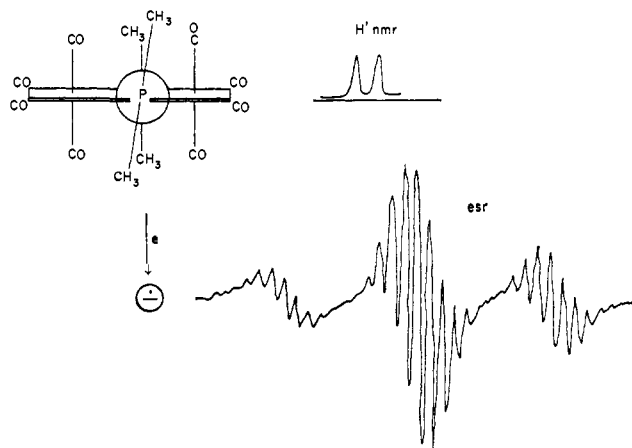


Figure 9.

Table V. Force Constants for  $[ML(CO)_4]_2$  Systems

M	$k$	Neutral, mdyn/Å	Reduced, mdyn/Å	$\Delta k$ , mdyn/Å	$n$
L = P(CH <sub>3</sub> ) <sub>2</sub>					
Cr	$k_1$	15.45 ± 0.01	13.01 ± 0.23	2.44	2
	$k_2$	15.79 ± 0.14	14.24 ± 0.04	1.55	
	$k_i$	0.18 ± 0.05	9.27 ± 0.09	-0.09	
W	$k_1$	15.41 ± 0.13	12.95 ± 0.32	2.46	2
	$k_2$	15.71 ± 0.08	14.43 ± 0.05	1.28	
	$k_i$	0.18 ± 0.05	0.23 ± 0.13	-0.05	
L = As(CH <sub>3</sub> ) <sub>2</sub>					
Mo	$k_1$	15.45 ± 0.14	13.29 ± 0.36	2.16	2
	$k_2$	15.76 ± 0.12	14.35 ± 0.05	1.41	
	$k_i$	0.23 ± 0.06	0.26 ± 0.14	-0.03	
W	$k_1$	15.49 ± 0.17	13.20 ± 0.30	2.29	2
	$k_2$	15.72 ± 0.01	14.31 ± 0.05	1.11	
	$k_i$	0.21 ± 0.07	0.29 ± 0.12	-0.08	

Table VI<sup>a</sup>

Assign. no.	A <sub>1</sub> (1)	A <sub>1</sub> (2)	B <sub>2</sub> (3)	B <sub>2</sub> (4)	B <sub>1</sub> (5)
Neutral					
1, 2	2075	1993	2075	1993	2040
3	2075	1993	2075	2040	1993
4	2075	1993	2075	2040	1993
5	2075	2040	2075	1993	1993
6	2075	2040	2075	1993	1993
Radical Anion					
1	2025	1920	2010	1938	1968
2	2025	1938	2010	1920	1968
3	2025	1920	2010	1968	1938
4	2025	1938	2010	1968	1920
5	2025	1968	2010	1938	1920
6	2025	1968	2010	1920	1938

<sup>a</sup> All values given in cm<sup>-1</sup>.Table VII. Assignment Comparisons in  $(CH_3SFe(CO)_3)_2$ 

Assign. no.	$k$	Neutral, mdyn/Å	Reduced, mdyn/Å
1	$k_1$	17.05 ± 0.00	15.96 ± 0.14
	$k_2$	16.13 ± 0.00	15.18 ± 0.17
	$k_c$	0.00 ± 0.00	-0.14 ± 0.16
	$k_{c'}$	0.24 ± 0.00	0.31 ± 0.08
2	$k_1$	17.05 ± 0.000	15.95 ± 0.01
	$k_2$	16.13 ± 0.000	15.20 ± 0.01
	$k_c$	0.00 ± 0.000	0.17 ± 0.01
	$k_{c'}$	0.24 ± 0.000	0.32 ± 0.01

Table VIII. Force Constants for  $[FeR(CO)_3]_2$  Systems

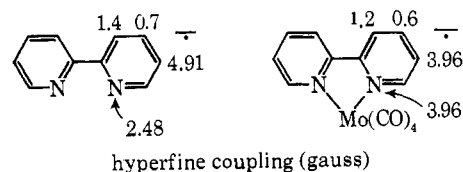
	$k$	Neutral, mdyn/Å	Reduced, mdyn/Å	$\Delta k$ , mdyn/Å	$n$
R = SCH <sub>3</sub>					
<i>trans</i>	$k_1$	17.05 ± 0.00	15.95 ± 0.11	1.10	1
	$k_2$	16.13 ± 0.00	15.20 ± 0.13	0.93	
	$k_c$	0.00 ± 0.00	0.17 ± 0.13	-0.17	
<i>cis</i>	$k_{c'}$	0.24 ± 0.00	0.32 ± 0.06	-0.07	1
	$k_1$	17.01 ± 0.00	15.99 ± 0.20	1.02	
	$k_2$	16.08 ± 0.00	15.22 ± 0.24	0.86	
	$k_c$	0.00 ± 0.00	0.10 ± 0.22	-0.10	
	$k_{c'}$	0.24 ± 0.00	0.28 ± 0.12	-0.04	
R = P(CH <sub>3</sub> ) <sub>2</sub>					
	$k_1$	16.53 ± 0.00	14.46 ± 0.00	2.07	2
	$k_2$	15.61 ± 0.00	13.21 ± 0.00	2.40	
	$k_c$	0.00 ± 0.00	0.08 ± 0.00	-0.08	
	$k_{c'}$	0.25 ± 0.00	0.20 ± 0.00	0.05	
R = As(CH <sub>3</sub> ) <sub>2</sub>					
	$k_1$	16.40 ± 0.00	14.47 ± 0.00	1.93	2
	$k_2$	15.66 ± 0.00	13.29 ± 0.00	2.37	
	$k_c$	0.00 ± 0.00	0.01 ± 0.00	-0.01	
	$k_{c'}$	0.23 ± 0.00	0.20 ± 0.00	0.03	

to calculate the force constants. The absorptions observed in the region 2500–1500<sup>-1</sup> cm<sup>-1</sup> both before and after reduction are tabulated in the Experimental Section along with the number of modes predicted on the basis of an assumed symmetry. No further discussion of these compounds will be given.

## Discussion

The basic premise in this study is that the addition of an electron(s) to the L—M—C≡O system results in an anion in which the added electron(s) are in orbitals having a high degree of ligand π\* character and that the molecule does not severely alter its symmetry in the reduction process. Direct information addressing itself to these questions is not easily obtainable, but several points, which fortunately bear on the most critical areas presented in the following discussion and which support this view, are available.

1. Electron spin resonance (esr) spectra of the radical anions derived from the L<sub>2</sub>M(CO)<sub>4</sub> series (L<sub>2</sub> = bipyridyl) show no evidence of a hyperfine interaction with the core metal atom. In addition, hyperfine coupling constants on the bipyridyl radical anion itself are in good agreement with those observed for the corresponding organometallic radical anion.



hyperfine coupling (gauss)

2. ESR spectra of the bridged bimetallic species,  $(Me_2PCr(CO)_4)_2\cdot^-$ , are consistent with a dihedral angle of 180° between the two basal planes of the shared edge octahedra comprising the structure, all 12 hydrogens being equivalent, giving  $\Delta H_P = 14$  G and  $\Delta H_H = 1.3$  G. The neutral parent has a similar structure as shown by nmr spectra (Figure 9).

If the term ligand in these compounds is defined so as to exclude the attached carbonyl groups, it seems highly probable then that we are dealing with a technique

which alters the ligand bonding characteristics drastically, reduction converting normally  $\pi$ -acceptor ligands into potential  $\pi$ -donor ligands, without altering molecular geometry. The method therefore allows observation of the effect of formal  $\pi$ -acceptor *vs.* formal  $\pi$ -donor ligands on carbonyl stretching frequencies in organometallic complexes without the hazards of actual ligand change.

In considering the infrared results given above, it is seen that in all cases except one  $k_2$  is greater than  $k_1$ , and in going from the neutral to the reduced species  $\Delta k_1$  is greater than  $\Delta k_2$  (Figure 10). In the case of the  $ML_2(CO)_4$  systems, the  $\pi$ -only theory has predicted this behavior with  $\Delta k_1 \cong 2\Delta k_2$ .

The inclusion of  $\sigma$  effects results in the same predicted behavior of the force constants; *i.e.*,  $\Delta k_1$  is greater than  $\Delta k_2$ .<sup>23</sup> The current theories agree that a ligand may exert an inductive effect through the metal-to-ligand  $\sigma$  bond which is rapidly attenuated and results in an increase of electron density on the metal. This increased electron density, postulated to be isotropic in nature, results in a weakening of the metal-to-carbonyl  $\sigma$  bond, thereby decreasing the force constant between the carbon and oxygen atoms of the affected carbonyls. This has been shown quite clearly by Angelici<sup>6</sup> and Graham.<sup>23</sup>

Brown,<sup>22</sup> although considering both  $\sigma$  and  $\pi$  effects, departs from existing theories in evaluating the extent and direction of these two effects. He postulates, on the basis of force constant changes and vibronic effects, that the ligand increases the electron density on the metal, thereby weakening the metal-to-carbonyl  $\sigma$  bond while at the same time increasing the energy of the metal  $d-\pi$  orbitals. This increase in metal  $d-\pi$  orbital energy is, however, compensated for by metal-to-ligand  $\pi$  bonding which serves to decrease the energy of the  $d-\pi$  orbitals. This leads to the conclusion that the lowering of the carbon-to-oxygen force constant upon replacing a carbonyl group by a ligand is primarily a result of  $\sigma$  bond-weakening effects, with very little if any change resulting from altered metal-to-carbonyl  $\pi$  bonding. Implicit in this theory is that these  $\sigma$  effects are directional, *i.e.*, the carbonyl group situated *trans* to the ligand being more affected than one *cis* to the ligand.

In the case of the  $ML_2(CO)_4$  systems there is direct conflict between the data obtained in this work and two of the above theories. The discussion which follows is with reference to the bipyridyl derivatives of the group VI hexacarbonyls which constitute the system for which complete supporting data are available, as described in the opening paragraphs of this section. The  $\pi$ -only theory would predict that  $\Delta k_2 = 2\Delta k_1$ . This is in direct variance with the change,  $\Delta k_1 > \Delta k_2$ , obtained in this work. The method of Graham also fails to predict the experimental observation. Only a directional  $\sigma$  effect remains consistent with the data, for here a decrease in all force constants is predicted with  $\Delta k_1$  greater than  $\Delta k_2$ .

Very much the same considerations apply to the binuclear systems,  $[ML(CO)_4]_2$ , except that here the ligand bridge atoms, P and As, are capable of  $\pi$  bonding with the central metal atom using their empty  $d-\pi$  orbitals. The  $\pi$ -only theory still predicts  $\Delta k_2$  is greater than  $\Delta k_1$ , as does the theory of Graham. Once again, these predictions clearly oppose the observed results, but by

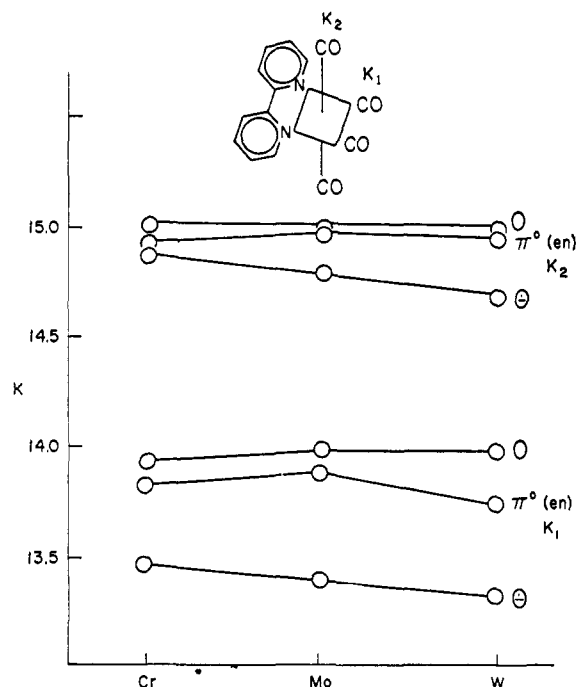


Figure 10.

again invoking a directional  $\sigma$  effect the results can be explained for these systems while retaining consistency with the preceding results.

The iron binuclear complexes represent a departure in behavior from the systems presented above. In contrast to the group VI octahedral systems, these compounds represent a case where  $k_1$  is greater than  $k_2$ . Also in contrast to the systems presented above, the relative change in the force constants for  $[FeP(CH_3)_2(CO)_3]_2$  and  $[FeAs(CH_3)_2(CO)_3]_2$  upon going from neutral to reduced forms gives  $\Delta k_2$  greater than  $\Delta k_1$  (the  $SCH_3$  analog shows a relative change of  $\Delta k_1 \cong \Delta k_2$  for the same process). The first-mentioned fact is due to the rather unique situation wherein  $k_2$  refers to the force constant of the carbonyl group *trans* to the metal-metal bond (see model used in the Experimental Section). As a carbonyl group stretches, increasing the carbon-to-oxygen distance, the  $\pi$  antibonding orbitals of that carbonyl group decrease in energy so that they more nearly match the  $d-\pi$  orbitals of the metal. This results in a drift of electrons onto that carbonyl group. One of the factors controlling this drift of  $\pi$  electrons is the demand for those same electrons made by the group opposite to the stretching carbonyl group. Although the sulfur atom is not noted for its  $\pi$  bonding ability with metal  $d-\pi$  electrons, it is surely better in this respect than a metal-metal bond. This is supported by the results obtained for the P and As analogs, which have substantially *higher* force constants due to their greater  $\pi$  bonding ability relative to the sulfur atom.

At present it is impossible to properly assign the reason for  $\Delta k_2$  being greater than  $\Delta k_1$  for the phosphorus- and arsenic-bridged species. Nmr spectra on  $[(OC)_3FePMe_2]_2$  indicate an obtuse dihedral angle between the basal planes of the shared face octahedra comprising the structure, and two sets of equivalent hydrogens are present. Upon reduction to the radical anion the esr spectrum is consistent with hyperfine interaction with two equivalent phosphorus nuclei and *six* equiva-

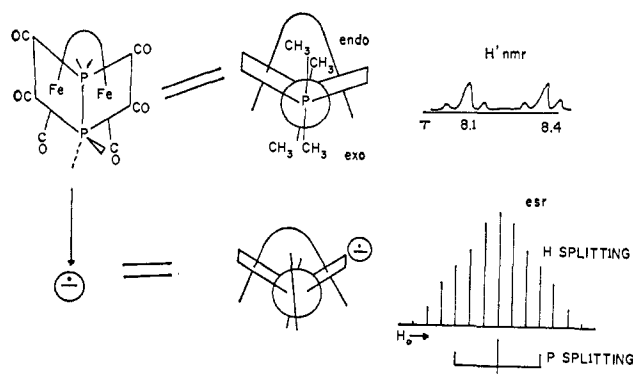
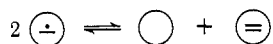


Figure 11.

lent hydrogens. One of the two equivalent sets of hydrogens has a hyperfine coupling constant too low to resolve under the conditions used:  $\Delta H_P = 4.5$  G,  $\Delta H_H = 1.5$  G (Figure 11). Unfortunately, as with the other bridged bimetallic species, which exist in an equilibrium (except systems 21 and 22), the value of the equilibrium constant precludes infrared studies on the



radical anion alone; the system could only be investigated as the dianion, produced by exhaustive electrolysis. Addition of halogen to  $[LFe(CO)_3]_2$  systems is known to lead to a structure with a dihedral angle of  $180^\circ$ , via *trans* addition and rupture of the metal-metal bond. It is not known what electrochemical reduction to the dianion accomplishes. Mössbauer spectroscopy and broad-line nmr techniques are currently being applied to this and similar systems to further investigate geometry. Only then can an analysis of the system be made.

## Conclusions

Based upon the results of this study, it is concluded that the transmission of charge in these systems in which all other factors can be assumed constant occurs primarily by a  $\sigma$  effect. From the fact that both force constants decrease upon electrochemical reduction it is concluded that there is an isotropic inductive effect. There is also a directional  $\sigma$  effect which is quite pronounced, being in all cases examined stronger than the  $\pi$  effect, as is evidenced by the larger change observed in  $k_1$  relative to  $k_2$ . Two possible explanations of these directional qualities are: (1) the polarization theory proposed by Grinberg<sup>42</sup> or (2) a consideration of the  $\sigma$  molecular orbitals which, owing to the symmetry involved, place the carbonyl group *trans* to a ligand in a different molecular orbital from the molecular orbital involving the carbonyl groups *cis* to the ligand.

Although the theories of Cotton and Graham suffice to explain the changes resulting in metal carbonyls due to a change in the  $\pi$  and  $\sigma$  donor-acceptor properties of a ligand, they proved inadequate to explain the transmission of charge density in a molecule with a fixed (assumed)  $\pi$  and  $\sigma$  framework. The theories of Brown have proven adequate to handle both. Since the former theories were not designed to explain the latter phenomenon and are not based on experiments in which this phenomenon is a major factor, there seems to be no reason *a priori* to expect them to be applicable. It should be realized, however, that these factors are present, and they should be taken into consideration.

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## Kinetics and Mechanism of the Iodide Ion Reduction of S,S-Dimethylsulfiminium Perchlorate

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**Abstract:** The kinetics of the reaction  $(CH_3)_2SNH_2^+ + 3I^- + 2H^+ \rightarrow (CH_3)_2S + I_3^- + NH_4^+$  have been measured spectrophotometrically in water and in DMSO-water solvents over the range  $X_{DMSO} = 0-1.00$ . The observed rate law is  $d[I_3^-]/dt = k_1[(CH_3)_2SNH_2^+][H^+][I^-]$ . In aqueous solution at  $25^\circ$  and  $0.120$  M ionic strength,  $k_1 = 0.56 \pm 0.02$  M<sup>-2</sup> sec<sup>-1</sup>,  $\Delta H^\ddagger = 12.2 \pm 0.4$  kcal/mole, and  $\Delta S^\ddagger = -19 \pm 1$  eu. The deuterium solvent isotope effect observed is  $k_{H_2O}/k_{D_2O} = 0.27$ . The reaction is catalyzed by added thiourea, but not by bromide or chloride ions. The mechanism proposed involves nucleophilic displacement at the sulfur center by a soft base nucleophile, iodide ion or thiourea.

The effect of solvent on nucleophilic reactivity has been widely recognized.<sup>1</sup> We have been interested in nucleophilic displacement reactions at sulfur

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centers and the role played by the solvent in modifying the order of nucleophilic reactivity toward these centers. Recent reports have contributed greatly to the over-all understanding of those factors which influence