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Theoretical Study of Structures and Binding Properties of Nickel Tetracarbonyl, Iron Pentacarbonyl, and Diiron and Dicobalt Hexacarbonyl Acetylenes

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For the purposes of testing a theory combining extended Hückel one-electron orbital energies with atom–atom repulsive energies on transition metal coordination compounds, structure and energy levels are calculated for $Ni(CO)_4$ and $Fe(CO)_5$. Carbonyl orientations are calculated for $Fe_2(CO)_6C_2R_2$ and are seen to lie within 6° of the x-ray diffraction values. The stretching of the metal bond in the cobalt analogue, $Co_2(CO)_6C_2H_2$, is traced to a metal antibonding orbital which is empty in the iron case. Furthermore, this orbital is seen to be responsible for the sawhorse structure in the cobalt compound whereas in the iron compound the carbonyl groups on one end rotate 60° and tilt away from the bridging acetylene. The preference for μ as opposed to di-σ acetylene orientations in these complexes is discussed.

I. Introduction

Cluster complexes present stimulating challenges to experimental and theoretical chemists. Some aspects of their richness in structures and bonding variations have been reviewed recently.[1] In this paper diiron and dicobalt hexacarbonyl acetylenes are considered from a theoretical point of view. In each of these the acetylene rests approximately in the μ bridging orientation, perpendicular to the metallic bond. The iron compound has a short metallic bond corresponding to a double bond,[2] and the carbonyl groups are not symmetrically dispersed in a sawhorse arrangement, as in the cobalt analogue; rather, on one end they rotate 60° and bend down. In the cobalt complex the metallic bond is long[3] and is believed to be a single bond.[2] It has been suggested that the difference between carbonyl orientations in these two complexes is related to steric interactions between opposing carbonyl molecules.[2] In this paper the structures are calculated directly from a molecular orbital theory and the differences are traced to electronic orbital energy levels.

The molecular orbital theory used in this paper has not been previously applied to transition metal coordination compounds. For this reason the structures and energy levels for $Ni(CO)_4$ and $Fe(CO)_5$ are calculated, compared with available experimental structural and photoelectron spectroscopic data, and discussed briefly.

The theory has two conceptual steps.[4] First, rigid atoms are superimposed and the electrostatic two-body repulsion energies are calculated with the Hellmann–Feynman force formula. Then the atomic electron charge distributions are allowed to relax. This is accomplished by using molecular orbitals and diagonalizing the Fock matrix in the approximation of superimposed atomic Fock potentials. It would be possible to use these charge density redistributions in the Hellmann–Feynman force formula to calculate the attractive energy component, but it is much more convenient to use the one-electron orbital energies which come from diagonalizing the approximate Fock matrix for the molecule. The procedure provides a physical understanding and justification for the extended Huckel method, which recognizes only the attractive energy component. The forte of this more general theory is that it allows the determination of reasonable bond lengths as well as bond angles, electron orbital energy levels, relative binding energies, probable reaction coordinates, and transition state energy barriers. The utility of the method has been demonstrated in studies of group 4A molecules and solids,[5] first transition series metallic clusters,[6] bonding in some inert gas and chlorine dimers, and argon hydrochloride.[7] More recent studies in the area of catalysis include adsorption, carbon bond cleavage, and dehydrogenation of acetylene and ethylene on iron[8] and nickel[9] surfaces. Details of the calculational procedure are given in the Appendix.

II. $Ni(CO)_4$

It is for the purpose of demonstrating the theoretical procedure that $Ni(CO)_4$ is considered. The molecular orbital description of this d^{10} complex appeared recently,[10] and ref 10 cites numerous earlier discussions. The present calculations produce the tetrahedral structure, which is calculated to be 0.29 eV more stable than the square-planar configuration. The Ni–C distance is calculated to be 1.85 Å compared to 1.84 Å from experiment.[11] The C–O distance is calculated to increase 5% from the free diatomic length, compared to 2% from experiment.[11] This increase is the result of the well-known[12] CO π^* + Ni d mixing. According to the calculations, the decrease in the C–O stretching force constant is 49% compared with the experimental value of 9%.[13] This inaccuracy is due to the overestimation of the increase in the CO bond length. A simple and highly accurate theory is available for determining stretching force constants when bond lengths are known,[14] and it is preferable to these direct calculations.

Shown in Figure 1 are the calculated molecular orbital energy levels compared with a photoelectron spectrum.[15] A relaxation shift[16] is evident in the T_2 and E orbital levels, which are predominantly metallic in character. The CO levels are uniformly 2 eV high in the free state and consequently they are high in the complex. The shifting down of the 5σ levels is evident. Notable is the A symmetry orbital level which shifts to −14 eV. This orbital involves purely metallic 4s interaction. The π levels split only slightly in the calculation. The shoulder at the low-energy side of the π peak in the experimental spectrum may be from further π splitting or from the 5σ A orbital. The 4σ levels split in the same way as 5σ levels and the photoelectron spectrum appears to show corresponding features, although the lowest peak, which corresponds to the 4σ A level, contains a contribution from CO impurities.[15] It appears from the calculation that this peak may not be due solely to impurity but has a 4σ component.

III. $Fe(CO)_5$

Iron pentacarbonyl provides a second test of the theoretical model, and one closer to the iron dimer complex. This D_{3h} d^8 complex has equatorial and axial Fe–C bond lengths of approximately 1.83 and 1.81 Å.[17] Calculations produce 1.86 and 1.87 Å, respectively. In both determinations equatorial and axial distances are close, though in reverse order. An orbital argument has been proposed to explain the observed bond lengths in this and other pentacoordinate compounds.[18] The present calculations reach an opposite conclusion for $Fe(CO)_5$, but the difference in bond lengths is very small. The C–O bond length shows a 5% increase compared to 2% from experiment[11] and the average Fe–C force constant shows a 40% decrease compared to 21% from experiment.[19] Hence,

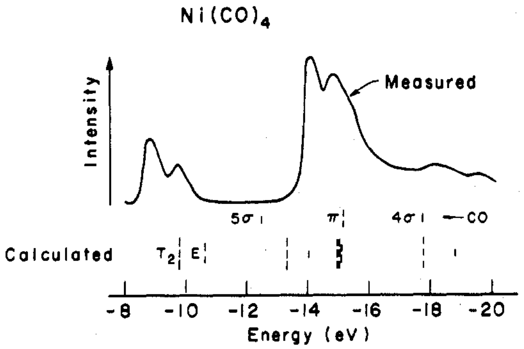

Figure 1. Calculated and observed[15] energy levels for $Ni(CO)_4$. The lowest energy peak in the experimental spectrum may be partially or entirely from CO impurity. Calculated free CO levels are 2 eV too high compared with the work of D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy", Wiley, London, 1970. Were these levels lowered 2 eV by lowering the carbon and oxygen valence atomic orbital ionization energies, then the agreement with experiment would be uniform, within the 1-eV relaxation shift, for all orbitals.

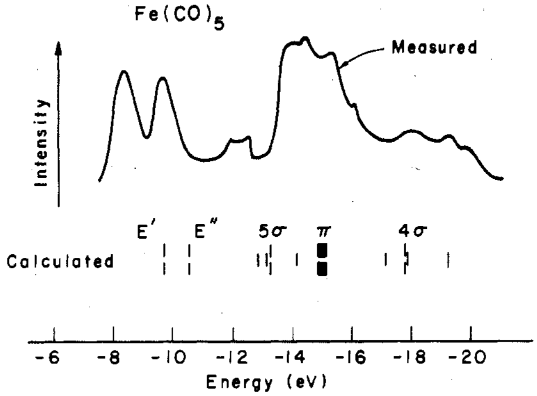

Figure 2. Calculated energy levels for $Fe(CO)_5$ compared to a photoemission spectrum from E. J. Buerends, Ch. Oudshoorn, and A. Oskam, *J. Electron Spectrosc. Relat. Phenom.*, 6, 259 (1975). Note the break in sensitivity at −12 eV.

as in $Ni(CO)_4$, the CO π^* + metal d interaction has been overestimated.

Filled orbital energy levels are shown in Figure 2. The 5σ and 4σ have characteristic low-lying A levels. As for $Ni(CO)_4$, CO π splitting is very small. The photoelectron spectrum of $Fe(CO)_5$, as shown in Figure 2 bears a relation to the calculations similar to that in $Ni(CO)_4$.

IV. $Fe_2(CO)_6C_2R_2$ and $Co_2(CO)_6C_2R_2$

In the calculations on $Fe_2(CO)_6C_2H_2$ the Fe–C and C–O bond lengths calculated for $Fe(CO)_5$ are used. The experimental Fe–Fe length is employed as the calculations tend to overestimate this length. The calculated structure for the iron dimer complex is shown in Figure 3. As may be seen in Table I, the largest error in the calculated CO orientation angle is 6°; however, the geometry was variationally energy optimized in 5° increments. The iron–acetylene distance and acetylene C–C bond stretch[20] are of good accuracy, also to be seen in Table I. A good approximation to the cobalt analogue is to use the iron complex calculation and add two more electrons. This gives the sawhorse geometry in Figure 4. The carbonyl orientations on one end agree within 6° with orientations in the cobalt analogue.

Figure 5 focuses on the Fe–Fe metallic orbitals. The σ_s and σ_s^* orbitals are not shown as they are heavily distributed among lower levels, whose positions are in Figure 6. Hence 4s orbitals contribute nothing to the Fe–Fe bond order. There are five bonding and three antibonding levels filled in the iron

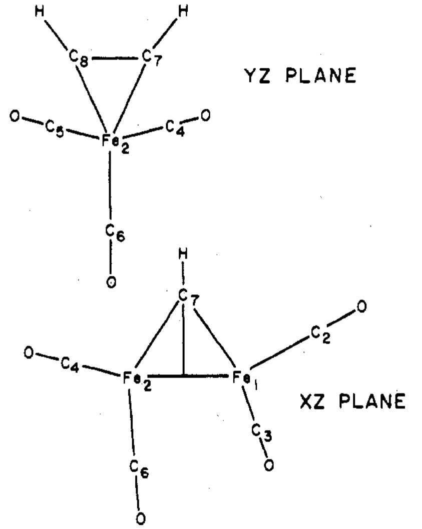

Figure 3. Structure calculated for the iron dimer complex. The orientations of carbonyl groups 1, 2, and 3 were determined in the sawhorse geometry before groups 4, 5, and 6 were adjusted for the lowest molecular energy.

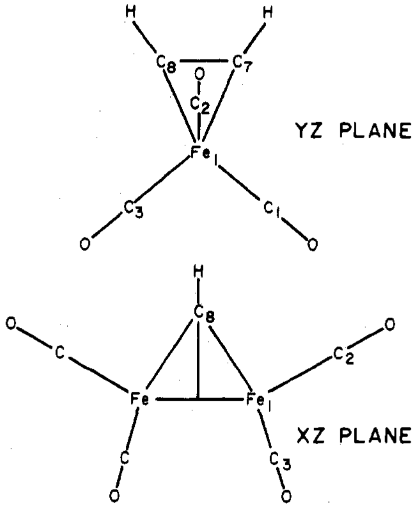

Figure 4. Calculated structure for the iron dimer complex when constrained to the sawhorse geometry. As discussed in the text, this is similar to the geometry for the cobalt analogue.

Table I. Bond Lengths (Å) and Bond Angles (deg) Calculated for $Fe_2(CO)_6C_2H_2$ Compared with Experimental Values for $Fe_2(CO)_6((t\text{-Bu})_2C_2)$ Which Are in Parentheses[d]

Bond	Value, Å	Bond	Value, Å
Fe–Fe	2.316[a] (2.316)	ΔC_7–C_8	0.15 (0.11)
Fe–CO	1.86[b] (1.79)	C–O	1.14[b] (1.15)
Fe–C_7	2.22[c] (2.08)		

Angle	Value, deg	Value for Co analogue, deg
$Fe_1Fe_2C_6$	85 (81.7)	
$Fe_1Fe_2C_4$	134 (135.4)	
$C_4Fe_2C_6$	104 (98.4)	
$C_4Fe_2C_5$	88 (89.0)	
$Fe_2Fe_1C_4$	150 (149.4)	154.2
$Fe_2Fe_1C_3$	100 (104.4)	99.2
$C_3Fe_1C_2$	100 (95.7)	98.0
$C_3Fe_1C_1$	98 (95.9)	103.6

[a] Not optimized. [b] From $Fe(CO)_5$ study. [c] For sawhorse structure. [d] In the calculations the *xy* plane is a mirror-symmetry element. See Figures 2 and 3. The x-ray structure shows small deviations from this symmetry and experimental values are averages of the reported values in ref 2.

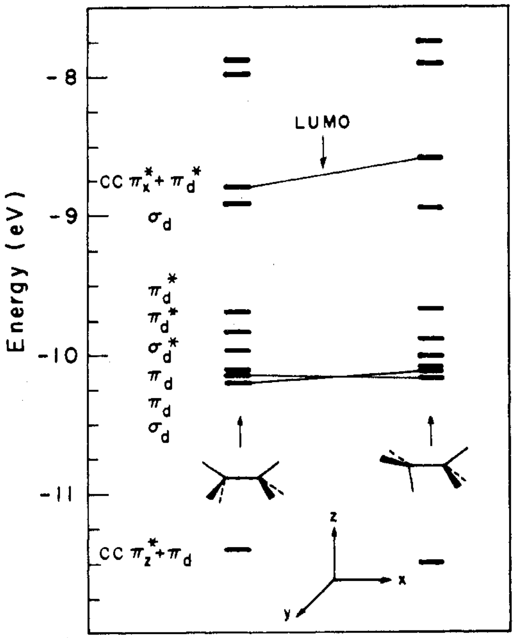

Figure 5. Changes in calculated metallic orbitals in the iron dimer complex on going from the sawhorse to nonsawhorse geometry. The lowest unoccupied molecular orbital (LUMO) for the iron dimer is filled in the cobalt analogue, causing the latter to assume the sawhorse geometry.

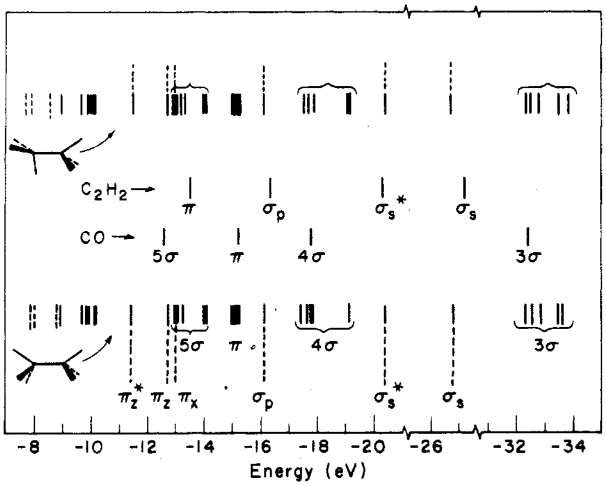

Figure 6. Comparison of all calculated energy levels for the two geometries of the iron dimer complex. Slight changes may be seen and their effects are discussed in the text. Bonding shifts may be seen by comparing calculated free ligand levels with their positions in the complexes.

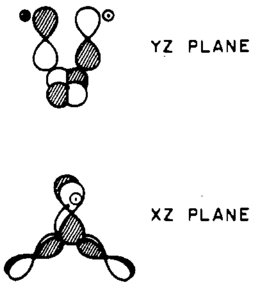

Figure 7. Depiction of the acetylene-metal CO $\pi_z^* + \pi_d$ bonding interaction which causes acetylene substituents to bend up.

complex, as shown in Figure 4. Hence the Fe–Fe bond order is 2, as deduced in ref 2 from consideration of its length. In the cobalt complex there are two additional electrons and these occupy the antibonding level marked LUMO in Figure 5. Hence the Co–Co bond order is 1, as was also deduced in ref 2 on the basis of its length.

The preference of the iron complex for the nonsawhorse structure in Figure 3 may be traced to three sets of orbital energy levels, which are stabilized with respect to the sawhorse structure. The metal bonding set in Figure 5, exclusive of the CC $\pi_z^* + \pi_d$ level, is stabilized by 0.09 eV, and this orbital itself is stabilized by 0.08 eV. The other significant contribution lies in the 3σ set which is stabilized by 0.11 eV. The total stabilization from these orbitals is 0.28 eV which accounts for much of the calculated 0.37-eV energy difference. This 8.5-kcal/mol barrier to rotation is within the range estimated for $Fe(CO)_3$ in various complexes.[2] A steric interpretation for the rotation, as postulated in ref 2, seems to be only a part of the story as the major overlap populations between carbonyl groups on the two ends are positive in both cases, implying weak bonding interactions. In the sawhorse the interaction between groups 1 and 5 and between groups 3 and 6 is 0.0235, giving a total of 0.047. In the other configuration the overlap population between group 6 and groups 1 and 3 is 0.0346, giving a total of 0.069. The rotation may not be a carbonyl group repulsion phenomenon, but partially an attractive phenomenon.

In this model calculation the cobalt complex favors the sawhorse geometry by 2.2 kcal/mol. The relative stability of the CC $\pi_x^* + \pi_d^*$ orbital overcomes the 8.5-kcal/mol destabilization in the lower orbitals. The magnitude of the stabilization is only a rough estimate, but it is clear that this orbital is responsible, when filled, both for the longer Co–Co single bond and for the sawhorse geometry.

In these calculations the acetylenic H–C–C angle is taken as 125°, the calculated value. The angles in the *tert*-butylacetylene complex are experimentally 145°. Using this value for the H–C–C angle produces respective rotational barriers of 10.2 and 0.8 kcal/mol for the iron and cobalt complexes. This shows the above arguments are not qualitatively dependent on this angle. However, it should not be inferred that the carbonyl rotational barrier in the cobalt complex is necessarily as small as 1–2 kcal/mol since calculations with cobalt parameters were not actually performed. One of the larger energy level changes on going to the larger H–C–C angle involves the CC $\pi_z + \pi_d$ orbital, which moves from −11.41 up to −10.80 eV. This is because of the weakening of this bond, whose orbital interactions are shown in Figure 7. It is this interaction which causes the hydrogen atoms and the *tert*-butyl substituents to bend away from the metal, for by bending, the σ bond between the carbon atoms and the substituents is strengthened while the carbon p–metal d σ bonds are formed. This bending is a common occurrence in coordination complexes[1] and has been predicted to occur with chemisorption of acetylene and ethylene on metal surfaces.[8,9]

A final feature of these molecules to be discussed here is the μ acetylene orientation. Theoretical studies using this theoretical method indicate the di-σ orientation is preferred on iron[8] and nickel surfaces. For the sawhorse-structure cobalt complex both the two-body repulsion energy, due predominantly to metal–acetylenic carbon repulsion, and the rising energy of the filled antisymmetric metal orbital, marked A in Figure 8, favor the μ orientation. The stabilization on bending for the bonding orbital, marked S in Figure 8, is insufficient to cause the acetylene to rotate. Shown in Figure 8 are the acetylene–metal orbital interactions responsible for the rising of the A level and the lowering of the S level on rotation. In the A level acetylene π^* + metal π_d^* bonding overlap decreases on bending. In the S level, on bending, an acetylene π^* + metal σ_d bonding interaction forms. Within experimental accuracy,[2,3] the acetylenic CC bond is per-

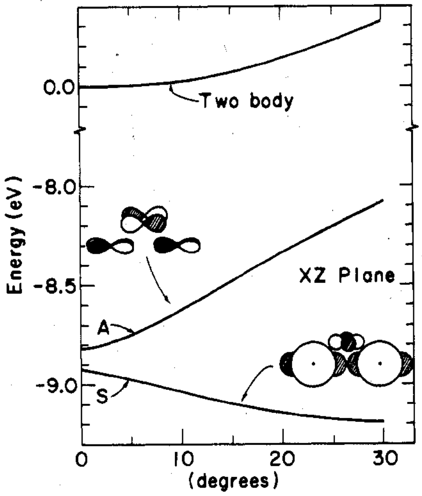

Figure 8. Behavior of antisymmetric metal orbital A, marked LUMO in Figure 5, and symmetric metal orbital on twisting the acetylene ligand. The S orbital is depicted with acetylene somewhat rotated; when actually in the μ orientation there is no acetylene $\pi^* + S$ mixing due to orthogonality. The charge in two-body repulsion, due mostly to carbon-metal interaction, is also shown. Although this figure is based on the sawhorse geometry, the orbital behavior is similar for the nonsawhorse structure.

pendicular to the metal bond in the cobalt complex, in agreement with this analysis. However the iron complex, which has a filled S level only, shows a rotation of a few degrees.[2] Rotation is predicted by Figure 8 and calculations indicate a 30° rotation is most stable, which is an overestimation. Rotation is similarly a result of calculations on the nonsawhorse structure, which is to say the analysis based on Figure 8 is unaffected. The preference for μ or near μ acetylenic orientations in these and many other bimetallic complexes lies in the metal orbital hydridization, which depends on the presence of the other ligands. Metal hydridization in these complexes is quasi-octahedral with the maximum number of metal–ligand bonds only with the μ acetylenic orientation. On a metal surface the situation changes. Iron is difficult to consider in this connection because in calculations acetylene breaks up into CH fragments.[8] However, on a nickel surface two strong σ bonds form, one between each carbon and nickel atom since metal atoms are freer to rehydridize when bonded to other metal atoms than they are when bonded to carbonyl groups. This flexibility is manifest in transition metal cluster studies in ref 6 where three to six atom clusters take on varying nonbulk geometries.

Summary

Calculations of geometries and energy levels in $Ni(CO)_4$ and $Fe(CO)_5$ indicate the one-electron molecular orbital theory in ref 1 can be used for approximate determinations of these properties. Applications of the theory to $Fe_2(CO)_6C_2R_2$ and the cobalt analogue produce an understanding of the metal bond orders and the acetylenic orientations. Carbonyl orientations are calculated within 6° of experiment. The preference of the cobalt complex for the sawhorse geometry lies in a single orbital which is filled with cobalt and empty with iron. However, the preference of the iron complex for the nonsawhorse geometry is related to several orbitals and appears to be an electronic effect. This is not to suggest there is a dichotomy between electronic and steric explanations of structures, for orbital theory can produce nonbonded repulsions and closed-shell attractions.[7] However, in this case closed-shell repulsions, as suggested in ref 2, may not be the whole story, for the carbonyl groups on opposite ends of the iron complex have significant positive overlaps in both structures.

Table II. Parameters Used in the Calculations[a]

Atom	Principal quantum no., Slater exponent, and atomic orbital energy (eV)								
	s			p			d		
H	1	1.2	−13.6						
C	2	1.658	−20.00	2	1.618	−11.26			
O	2	2.246	−28.48	2	2.227	−13.60			
Fe	4	1.600	−7.87	4	0.80	−3.87	3	1.800, 535[b]	−9.0
Ni	4	1.750	−8.25	4	0.86	−3.99	3	2.00, 575[c]	−10.0

[a] Orbital exponents for H and C are based on the work of E. Clementi and D. L. Raimondi, *J. Chem. Phys.*, **38**, 2686 (1963), but are slightly increased. Orbital energies for H, C, and s and p states of Ni are based on the work of W. Lotz, *J. Opt. Soc. Am.*, **60**, 206 (1970), with some slight adjustments. Exponents for Ni and the 4p orbital energy are based on the work of J. W. Richardson, W. C. Nieuwpoort, R. R. Powell, and W. F. Edgell, *J. Chem. Phys.*, **36**, 1057 (1962), and J. W. Richardson, R. R. Powell, and W. C. Nieuwpoort, *ibid.*, **38**, 796 (1963). The same Fe and Ni set of parameters has been used in the cluster study of ref 6; look there for a discussion of parameter choices. [b] Two Slater orbitals with corresponding coefficients 0.6292 and 0.5683. [c] Two Slater orbitals with corresponding coefficients 0.5366 and 0.6678.

Table III. Calculated Structures, Bond Lengths, Harmonic Force Constants (k_e), and Dissociation Energies (D_e)

	State	r_e,[a] Å	k_e,[a] mdyn/Å	D_e,[a] kcal/mol
CO	$X'\Sigma^+$	1.09 (1.128)	20.67 (19.02)	116 (256)
		C–C,[b] Å	C–H,[b] Å	HCC, deg
Acetylene		1.30 (1.204)	1.14 (1.056)	180 (180)

[a] Experimental values in parameters from B. Rosen, "Spectroscopic Data Relative to Diatomic Molecules", Pergamon Press, Oxford, 1970. [b] Experimental values from "Handbook of Chemistry and Physics", C. D. Hodgman, Ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1962.

Because the highest occupied and lowest unoccupied orbitals in the iron complex are close to degeneracy there is reason to consider the effects if the iron complex is a triplet. Of course the orbital procedure may underestimate the splitting of these levels, assuming a singlet ground state. The spin state of the molecule has not been reported. However, if a triplet is assumed and an electron is excited from the highest occupied to the lowest unoccupied orbital, the only qualitative structural change is that the μ acetylene orientation is definitely preferred. In this case the bond order would be 1, corresponding to a single bond. It is conceivable that the $\sigma_s{}^*$ metal bond is not totally occupied, so that the bond order might still be 2. This possibility would probably be excluded by an experimental determination of the spin of the complex. Additional comments on these and other sawhorse dimer complexes will appear elsewhere.[21]

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Appendix

In the one electron orbital procedure diagonal matrix elements are set equal to valence-state ionization energies. Off-diagonal matrix elements are given by 2.25 × (average of diagonal elements) × exp(−0.13r) where r is the internuclear distance. Slater atomic orbitals are used. All parameters used in this paper are given in Table II. The two-body repulsion energies are determined using simple algebraic formulas for Slater orbitals.[22] Since this is not a self-consistent theory, charge transfers are overestimated, but good structures, force constants, and relative binding energies may be calculated despite this. Calculated ligand geometries are in Table III.

References 4–9 tabulate other examples. In polar systems bond energies are, in an absolute sense, not reliable, making careful orbital analyses necessary. For example, the calculated average carbonyl–metal binding energies in $Ni(CO)_4$ and $Fe(CO)_5$ are 51 and 78 kcal/mol, compared to 35 and 28 kcal/mol estimated from experimental considerations.[23]

Registry No. $Ni(CO)_4$, 13463-39-3; $Fe(CO)_5$, 13463-40-6; $Fe_2(CO)_6C_2H_2$, 60209-61-2; $Co_2(CO)_6C_2H_2$, 12264-05-0.

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Vibrational Spectra of the Pentacarbonyl(thiocarbonyl)metal(0) Complexes, $M(CO)_5(CS)$ (M = Cr, W) and *trans*-$W(CO)_4(^{13}CO)(CS)$ (90% ^{13}C Enriched)[1]

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The vibrational spectra of the transition metal thiocarbonyl complexes, $M(CO)_5(CS)$ (M = Cr, W) and *trans*-$W(CO)_4(^{13}CO)(CS)$ (90% ^{13}C enriched), have been studied and assignments are proposed for the fundamental modes on the basis of complete normal coordinate calculations. Many of the interaction constants used in these calculations were transferred directly from earlier work on the corresponding isoelectronic $M(CO)_6$ species. For all three molecules, the average percent error between the observed and calculated frequencies is <1%, thus demonstrating the advantage of such force constant transfers between closely related species, as Jones et al. had predicted. Substitution of CS for CO in going from $M(CO)_6$ to $M(CO)_5(CS)$ has no effect on the equatorial CO and M–C(O) force constants, $f_{CO}{}^{eq}$ and $f_{MC}{}^{eq}$; however, there are significant changes in the corresponding axial force constants, $f_{CO}{}^{ax}$ and $f_{MC}{}^{ax}$, the former increase while the latter decrease. In addition, the M–C(S) force constants, $f_{MC}{}^{s}$, are appreciably larger than any of the M–C(O) force constants. These results are in complete agreement with the stronger metal–carbon bonding found experimentally for metal–C(S) *vs.* metal–C(O) linkages. Also, the weakening of the M–C bonds trans to CS in the $M(CO)_5(CS)$ species is in accord with the chemistry of these molecules and is attributed primarily to the stronger π-acceptor capacity of the CS ligand.

Introduction

Numerous transition metal thiocarbonyls have been synthesized since the initial discovery of this class of complexes 10 years ago.[3,4] Much of the recent interest in these complexes has focused on the comparative bonding properties of the CO and CS ligands.[5] Since vibrational spectra reflect the internal forces and thus the bonding in molecules, we have undertaken a broad study of the complete vibrational spectra of transition metal thiocarbonyls in order to compare the spectra with those of structurally related metal carbonyls. To date, only two such studies have been reported: (a) $(\eta^6\text{-}C_6H_5CO_2Me)Cr(CO)_2(CS)$ and $(\eta^6\text{-}C_6H_5CO_2Me)Cr(CO)_3$;[6] (b) $\eta^5\text{-}C_5H_5Mn(CO)_2(CS)$, $\eta^5\text{-}C_5H_5Mn(CO)(CS)_2$, and $\eta^5\text{-}C_5H_5Mn(CO)_3$.[7] In both cases, detailed vibrational assignments were proposed.

The group 6B metal thiocarbonyl complexes, $M(CO)_5(CS)$, have been reported recently.[8,9] Since extensive normal coordinate calculations have been carried out for the analogous $M(CO)_6$ species,[10] we felt that it would be particularly worthwhile investigating the vibrational spectra of the $M(CO)_5(CS)$ complexes in order to determine the transferability of force constants between these octahedral molecules. According to Jones et al.,[10] many of the interaction constants for the $M(CO)_6$ species should be directly transferable to other metal carbonyls, and this should be particularly true for the $M(CO)_5(CS)$ molecules because of the isoelectronic nature of the CO and CS ligands. Furthermore, because of the larger mass of sulfur relative to oxygen, the CS vibrations will be more highly coupled with the metal–carbon modes than is the case for the CO vibrations. This means that energy factoring of the CS vibrational modes will be a poor approximation and such calculations will lead to force constants which are not reliable measures of CS bond strengths. More complete calculations are essential to obtain such information.

In this paper, we report the results of a vibrational analysis of the spectra of the $Cr(CO)_5(CS)$ and $W(CO)_5(CS)$ molecules and the mono-^{13}CO substituted derivative, *trans*-$W(CO)_4(^{13}CO)(CS)$ (90% ^{13}C enriched). We have attempted to define the valence force constants for both metal thiocarbonyls in order to obtain a quantitative description of the bonding in them. These results are discussed in the light of the known chemistry of the complexes.

Experimental Section

The yellow, crystalline samples (~100 mg) of the metal thiocarbonyls were generous gifts from Professor R. J. Angelici and Mr. B. D. Dombek (Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa 50010) and were prepared by the literature methods indicated: $M(CO)_5(CS)$ (M = Cr, W)[8,9] and *trans*-$W(CO)_4(^{13}CO)(CS)$.[11]

Infrared spectra were recorded on a Perkin-Elmer Model 521 grating spectrophotometer; the sampling conditions employed are given