CO INTENSITIES OF TRANSITION METAL CARBONYL COMPLEXES

INFRARED INTENSITIES OF THE CO STRETCHING MODES OF SOME TRANSITION METAL CARBONYL COMPLEXES

By

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ABSTRACT

The work in this thesis constitutes an additional study of the infrared intensities of the carbonyl stretching absorptions of transition metal carbonyl complexes. CO-intensity data are reported for the following complexes: $Cr(CO)_6$, (Cycloheptatriene)$M(CO)_3$ and (Bicycloheptadiene)$M(CO)_4$ (M = Cr, Mo, W), fac-$Mo(CO)_3[P(C_6H_5)_{3-x}Cl_x]_3$ (x = 1-3), cis-$Mn(CO)_4LBr$ [L = $P(C_6H_5)_3$, $As(C_6H_5)_3$, $Sb(C_6H_5)_3$], π-$RC_5H_4Mn(CO)_3$ (R = H, CH_3), and π-$C_5H_5Mn(CO)_2CS$.

The integrated intensity results are used as a basis for a further investigation of the σ- and π-bonding abilities of the various ligands in these complexes. The first measurement of the infrared intensity of a thiocarbonyl stretching mode in a metal thiocarbonyl complex, π-$C_5H_5Mn(CO)_2CS$, is also reported.

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RESUME

Le contenu de cette thèse est une étude additionnelle des intensités d'absorption par élongation, en spectroscopie infrarouge, des groupes carbonyles des complexes carbonylés des métaux de transition. Les valeurs des intensités CO ont été déterminées pour les complexes suivants: $Cr(CO)_6$, (Cycloheptatriene)$M(CO)_3$ et (Bicycloheptadiene)-$M(CO)_4$ (M = Cr, Mo, W), *fac*-$Mo(CO)_3[P(C_6H_5)_{3-x}Cl_x]_3$ (x = 1-3), *cis*-$Mn(CO)_4LBr$ [L = $P(C_6H_5)_3$, $As(C_6H_5)_3$, $Sb(C_6H_5)_3$], π-$RC_5H_4Mn(CO)_3$ (R = H, CH_3), et π-$C_5H_5Mn(CO)_2CS$.

Les résultats obtenus par intégration des intensités servent de base pour l'étude des possibilités qu'ont les liaisons σ et π de former différents ligands chez ces complexes. La première mesure de l'intensité, en spectroscopie infrarouge, d'un type d'élongation d'un groupement thiocarbonyle du complexe métallique thiocarbonylé, π-$C_5H_5Mn(CO)_2CS$, est également relatée.

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To my parents, Mr. & Mrs. H. T. Johansson,
for their unfailing support
throughout my academic career

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PART I

INTRODUCTION

Chapter 1

INTENSITY OF AN INFRARED ABSORPTION BAND

General

Every distinct infrared absorption band is characterized by the frequency at which maximum absorption occurs and by the integrated absorption intensity. Both band characteristics are related in a fundamental way to the electronic properties of the molecule and consequently provide very useful information concerning molecular properties.[1] However, although absorption frequencies of molecules have been studied extensively, absorption intensities have received comparatively little attention. This apparent lack of interest in absorption intensity studies is due largely to the difficulties and tediousness of the experimental procedures and to the theoretical problems encountered in the interpretation of results. However, now that high resolution infrared spectrophotometers with linear absorbance facilities have become generally available, the practical difficulties, at least, have been minimized. Consequently, as predicted by Brown[1] in 1958 in his review of infrared intensities, much more work has been carried out in recent years.

According to the classical model, a molecule consists of a set of point masses connected to one another by a set of elastic forces. The system is considered to undergo vibrational motion in accordance with the laws of mechanics;[2,3] the 3N-6 vibrational degrees of freedom (3N-5 for a linear molecule) of an N-atom molecule are termed the normal modes.

If the vibrational motion associated with a normal vibration produces a periodic shift in charge distribution and this shift results in a change in molecular dipole moment, the vibration is said to be infrared-active. Since any vibrational motion of the molecule can be resolved as a superposition of the normal vibrations, the frequency at which the absorption occurs is the normal vibration frequency, and the intensity of the absorption is the intensity corresponding to the normal vibration.[1]

Expressions for Band Intensity

The true integrated absorption intensity of an infrared absorption band, A, corresponding to the i th fundamental vibrational transition, is defined as

$$A_i = \int_{band} \alpha_\nu(i)d\nu = \frac{1}{cl}\int_{band} \ln\left(\frac{I_o}{I}\right)_\nu d\nu \qquad (1)$$

where $\alpha_\nu(i)$ is the adsorption coefficient of the band corresponding to the i th normal vibration at frequency ν, I_{o_ν} and I_ν are the incident and transmitted intensities of monochromatic radiation of frequency ν, c is the concentration of solute in moles liter^{-1}, and l is the cell path length in centimeters. Such a definition follows readily from the well-known exponential law of absorption,

$$I_\nu = I_{o_\nu}\, e^{-\alpha_\nu cl} \qquad (2)$$

The absorption intensity is related to the polar properties of a molecule through its direct proportionality to the square of the molecular dipole moment derivative[2]

$$\int_{band} \alpha_\nu(i)d\nu = \frac{N\pi}{3c^2}\left[\left(\frac{\partial\mu}{\partial Q_i}\right)_o\right]^2 \qquad (3)$$

where N is the number of molecules per unit volume of sample, c is the velocity of light and Q_i is the normal co-ordinate for the i^{th} vibration. The vector μ is the molecular dipole moment and $(\partial\mu/\partial Q_i)_o$ is its rate of change with respect to Q_i. The quantity $(\partial\mu/\partial Q_i)_o$, the molecular dipole moment derivative, is evaluated at the molecular equilibrium configuration. This equation expresses the measured intensities in terms of the normal co-ordinates of a molecule. In order to interpret the intensities in terms of bond properties, one must reduce the dipole moment derivatives, $(\partial\mu/\partial Q_i)_o$, to quantities which are characteristic of individual bonds. The difficulties encountered in such an operation are best appreciated by considering the assumptions which are involved.

Equation (3) is derived on the assumption that the molecular dipole moment can be expanded as a Taylor series in terms of nuclear displacements from the equilibrium positions and that all but the first derivatives can be neglected; that is,

$$\mu = \mu_o + \sum_i (\partial\mu/\partial Q_i)_o Q_i + \text{higher terms (negligible)} \qquad (4)$$

This is the assumption of electrical harmonicity. It is true only to a first approximation, since intensities of infrared combination and overtone bands ought to be zero in this approximation. Although this is certainly not the case, it is a fairly reasonable assumption since the intensities of combinations and overtones are usually far less than those of the fundamentals (unless a combination or overtone band gains intensity by resonance from a fundamental of the same symmetry). At any rate, the error involved in the assumption of harmonicity is probably much less than the present experimental errors and those arising from the uncertainty in the normal co-ordinate Q_i.[4,5]

A simpler way of representing Q_i is to express it as a linear combination of molecular symmetry co-ordinates, S_j,[2]

$$Q_i = \sum_j L_{ij}^{-1} S_j \qquad (5)$$

where the coefficients L_{ij} are obtained from the molecular geometry, the masses of the atoms and the potential energy function of the molecule. It is here that the real difficulty arises. Although atomic masses are accurately known and molecular geometries can often be independently determined or estimated fairly accurately, the force field (i.e., the force constants connecting all atoms in the molecule), in terms of which the potential energy function is expressed, constitutes the unknown in a vibrational problem. Unfortunately, force constants are known with precision for very few molecules. Most molecules have more force constants than frequencies, and so their complete potential energy function cannot be determined. The usual procedure is to either assume that some of the force constants can be neglected while some can be carried over from other molecules, or to adopt a model force field which decreases the number of distinct force constants by postulating that some symmetry unrelated force constants have related values (generally a simple proportion). Thus, the major source of uncertainty in the interpretation of infrared absorption bands in terms of bond properties is the form of the force field.[4]

Once a reasonable force field has been deduced, and hence the form of the normal co-ordinates approximated, the next step is to visualize what the resulting $(\partial\mu/\partial Q_i)_0$ mean. Because Q_i is a normal co-ordinate of the molecule, it is conceptually difficult to appreciate the significance of the derivatives $(\partial\mu/\partial Q_i)_0$ and to utilize them. If one could translate the molecular properties into the sum of a set of bond properties, one could reduce the derivatives $(\partial\mu/\partial Q_i)_o$ into those characteristic of individual bonds. In order to accomplish this, two assumptions are necessary:[4,5]

(1) The stretching of a bond by dr produces a change of dipole moment along the bond of $(\partial\mu/\partial r)dr$;

(2) Changes in one bond do not result in changes in another bond.

This means essentially that the total molecular dipole moment change resulting from the simultaneous displacement of several bonds is assumed to be the vector sum of the moments produced by each individual bond. This assumption is quite reasonable for relatively simple molecules and for larger molecules possessing sufficient symmetry.

Now, since the molecular symmetry co-ordinates, S_j, may be expressed as linear combinations of internal bond co-ordinates, R_k,[2]

$$S_j = \sum_k U_{jk} R_k \qquad (6)$$

one can obtain [by utilizing equations (1), (4), (5), and (6)] the desired result: an expression relating the intensity of a normal mode to bond moment derivatives.[4]

$$A_i \propto \left(\frac{\partial\mu}{\partial Q_i}\right)^2 = \left[\sum_j \sum_k L_{ji} U_{jk} \left(\frac{\partial\mu}{\partial R_k}\right) \right]^2 \qquad (7)$$

It follows from equation (7) that one should be able to gain useful information concerning the nature of the bond dipole moment changes upon alteration of bond lengths during a normal stretching vibration by studying the integrated absorption intensity of the normal mode.

Determination of Band Intensity

The expression for the true integrated absorption intensity, A, as cited earlier, is

$$A = \int_{band} \alpha_\nu d\nu = \frac{1}{cl}\int_{band} \ln\left(\frac{I_o}{I}\right)_\nu d\nu \qquad (8)$$

where I_{o_ν} and I_ν are the incident and transmitted intensities of monochromatic radiation of frequency ν, α_ν is the adsorption coefficient for frequency ν, c is the concentration of solute in moles liter^{-1}, and l is the cell path length in centimeters.

Unfortunately, owing to the presence of finite slit widths, the radiation is not monochromatic and the quantity that is actually measured is the apparent integrated absorption intensity, B, given by

$$B = \frac{1}{cl}\int_{band} \ln\left(\frac{T_o}{T}\right)_\nu d\nu \qquad (9)$$

where T_{o_ν} and T_ν are the apparent intensities of the incident and transmitted radiation when the spectrophotometer is set at frequency ν.

The true integrated absorption intensity, A, can be determined essentially in two ways:

(1) by measuring the area under the experimental absorption band and extrapolating the B values so determined as a function of various parameters;[6-9]

(2) by direct calculation from principal band characteristics, such as the peak height and the half-intensity band width, assuming certain functions for the slit and for the shape of the absorption band.[8,10-17]

Direct calculation methods have the advantage that they are generally extremely rapid compared to band-area extrapolations. However, a serious limitation of direct calculation methods lies in the fact that they usually depend on measurements at only a few points on the experimental band while band-area methods involve measurements over the whole of the experimental curve. Assumptions regarding the slit function and the shape of the absorption band are also fundamental to direct calculation methods. Therefore, if a quick crude estimate of intensity is all that is desired, direct calculation methods are sufficient. However, for accurate work, band-area extrapolation procedures are usually the methods of choice. The extent of this discussion, therefore, will be limited to a consideration of this technique.

The first two extrapolation procedures for the determination of true integrated absorption intensities from experimental absorption curves were described by Bourgin[6] and by Wilson and Wells[7] and were applied to gases. The methods involve extrapolations of measurements of band areas made at a series of different concentrations or path lengths to zero concentration or path length and are equally applicable in the case of liquids and solutions.

1. The Bourgin Extrapolation

Bourgin[6] plotted the absorption curve as fractional absorption, $1-(T/T_0)_\nu$, against frequency, ν, in cm^{-1}; the area, A', under the curve is then given by

$$A' = \int_{band}\left[1-\left(\frac{T}{T_0}\right)_\nu\right]d\nu \qquad (10)$$

Since it has been shown that this area is independent of the resolving power, we may write

$$A' = \int_{band}\left[1 - \left(\frac{I}{I_0}\right)_\nu\right]d\nu \tag{11}$$

Substituting in the exponential law of absorption and expanding we get

$$\frac{A'}{cl} = \int_{band}\left[\alpha_\nu - \frac{\alpha_\nu^2}{2!}cl + \frac{\alpha_\nu^3}{3!}(cl)^2 - \dots\right]d\nu \tag{12}$$

or

$$\lim_{cl\to 0}\frac{A'}{cl} = \int_{band}\alpha_\nu d\nu = A \tag{13}$$

Hence, the true integrated absorption intensity may be obtained by plotting A'/cl against cl and extrapolating to cl = 0. Since the area, A', is independent of the resolving power used, the nature of the extrapolation is also independent of the resolving power and is only dependent on the band shape.

2. The Wilson-Wells Extrapolation

Wilson and Wells[7] demonstrated that

$$\lim_{cl\to 0}(A-B) = 0 \tag{14}$$

or in other words

$$\lim_{cl\to 0} B = A \tag{15}$$

Therefore, by extrapolating the apparent integrated absorption intensities taken at a number of concentrations or path lengths to zero concentration or path length, the true integrated absorption intensity is obtained. The method involves the assumption that (i) the incident intensity is constant over the slit width and (ii) the resolving power is constant over the width of the band. The nature of the extrapolation is dependent on the true band shape and on the resolving power used.

3. Ramsay's Methods

Ramsay[8] modified both the Bourgin and the Wilson-Wells procedures by introducing an assumption concerning the form of the absorption curves. He assumed that the true shape of an absorption band could be expressed as a Lorentz function

$$\ln\left(\frac{I_o}{I}\right)_\nu = \frac{a}{(\nu-\nu_o)^2 + b^2} \tag{16}$$

where ν_o is the frequency of the band centre, a and b are constants, and $\nu-\nu_o$ is the interval on either side of the band centre over which the integration is performed. His assumption regarding the slit function was the usual one viz., a triangular slit function.

Ramsay also employed correction factors for the "area under the wings." Although, in principle, the integration of equation (8) should be carried out to an infinite distance on either side of the band maximum, in practice, the area under the absorption curve is measured only to finite limits on either side of the band centre. In the absence of overlapping bands, the limits chosen are those at which the experimental error becomes of the same order of magnitude as the apparent intensity. Ramsay felt, by virtue of his calculations, that the residual unmeasured area could be appreciable, since although the absorption is small, the remaining frequency range is large. For this reason he applied "wing corrections" to all his areas, both calculated and measured. The wing corrections are expressed as a percentage of the measured band area and are available for a series of values of the characteristic band quantity $(\nu-\nu_o)/b$.

a. Extension of the Bourgin Extrapolation

If the shape of the true absorption curve is represented by equation (16) then Bourgin's expression, equation (12), becomes

$$\frac{A'}{cl} = A\left\{1 - \frac{1}{2!}\times\frac{1}{2}\ln\left(\frac{I_o}{I}\right)_{\nu_{max}} + \frac{1}{3!}\times\frac{3.1}{4.2}\left[\ln\left(\frac{I_o}{I}\right)_{\nu_{max}}\right]^2 - \frac{1}{4!}\times\frac{5.3.1}{6.4.2}\left[\ln\left(\frac{I_o}{I}\right)_{\nu_{max}}\right]^3 + \ldots.\right\} \qquad (17)$$

Therefore, the true integrated intensity may be obtained by plotting A'/cl against $\ln(I_o/I)_{\nu_{max}}$ and extrapolating to $\ln(I_o/I)_{\nu_{max}} = 0$.

Alternatively, by defining a quantity, $\emptyset$, such that

$$\emptyset = 1 \Big/ \left\{1 - \frac{1}{2!}\times\frac{1}{2}\ln\left(\frac{I_o}{I}\right)_{\nu_{max}} + \frac{1}{3!}\times\frac{3.1}{4.2}\left[\ln\left(\frac{I_o}{I}\right)_{\nu_{max}}\right]^2 \ldots\right\} \qquad (18)$$

equation (18) can be more conveniently expressed as

$$A = \emptyset.\frac{A'}{cl} \qquad (19)$$

By tabulating values of $\emptyset$ for various values of $\ln(I_o/I)_{\nu_{max}}$, it is then possible to determine the true integrated absorption intensity from a single measurement of the apparent integrated absorption intensity by means of equation (19).

The extrapolations and $\emptyset$ values depend entirely on the assumption of a Lorentzian function for the true band shape, but they are independent of the slit function. Likewise, the wing corrections provided by Ramsay for this method depend mainly on a Lorentzian band; however, they also depend to a very slight extent on the slit function as well.

b. Extension of the Wilson-Wells Extrapolation

Assuming a Lorentzian form for the true band shape, and a triangular slit function, Ramsay calculated, for a fixed value of $s/\Delta\nu^t_{\frac{1}{2}}$ (the ratio of the spectral slit width to the true half-intensity band width), a series of true band shapes for several values of the true peak optical density. He then measured the areas under the corresponding apparent absorption curves and plotted the ratios

$$[\int_{band} \ln(T_0/T)_\nu d\nu] \;/\; [\int_{band} \ln(I_0/I)_\nu d\nu]$$

against the apparent peak optical densities, $\ln(T_0/T)_{\nu_{max}}$. The plots he obtained were very nearly linear and had a slight negative slope, Θ.

It follows that, by tabulating values of Θ for a range of $s/\Delta\nu^t_{\frac{1}{2}}$ between 0.1 and 1.0, the true integrated intensity of an absorption band can be obtained by plotting the apparent integrated absorption intensity measured at several different concentrations or path lengths against the apparent peak optical density and determining the best straight line with intercept A and slope $A\Theta$. Ramsay felt this procedure of determining the intercept, A, was more accurate than the Wilson-Wells extrapolation based on the method of least-squares, since the latter method is dependent on measurements of weak bands where experimental errors are apt to be large.

One advantage of the Θ tabulations is that it is also possible to determine the true integrated absorption intensity from a single measurement of the apparent integrated absorption intensity by means of the relation

$$B = A + A\Theta \ln(T_0/T)_{\nu_{max}} \qquad (20)$$

The θ values, and hence the slopes of the extrapolations, depend on the assumption of a Lorentzian function for the true band shape and on a triangular slit function. The wing corrections provided by Ramsay for this method also depend on these two assumptions.

c. Method for Partially Overlapping Band Systems

Although Ramsay's methods are still valid for overlapping band systems, the slopes of the extrapolations can no longer be calculated. Moreover, Ramsay felt that attempts to fit extrapolation lines by the method of least-squares could result in considerable error unless a large number of observations was carried out.

However, in his studies of isolated absorption bands, Ramsay found that the true integrated absorption intensity of a band differed very little from the apparent quantity, even though the spectral slit width of the spectrophotometer was of the same order as the widths of the absorption bands. He showed that, for a slit width equal to one-half the true width of the absorption band, the true intensity exceeded the apparent intensity by only ~ 2-3%. Apparently the decrease in peak height produced by the finite slit width is roughly compensated by an increase in band width. As a general rule, Ramsay and colleagues[18] found that the true integrated intensity of an isolated absorption band usually exceeded the mean of the apparent intensity determinations (i.e., B values were usually determined at a number of concentrations) by 2%. Since they felt that the uncertainty in the evaluation of the extrapolation slope for overlapping band systems was likely to exceed this considerably, they simply estimated the true intensity by adding 2% to the mean of the apparent intensity values.

4. The Russell-Thompson Extrapolation

Russell and Thompson[9] extrapolated the apparent integrated absorption intensities determined at a number of concentrations or path lengths to zero apparent peak optical density,

$$\lim_{\ln\left(\frac{T_0}{T}\right)_{\nu_{max}} \to 0} B = A \tag{21}$$

as outlined by Ramsay in his extension of the Wilson-Wells technique; however, they evaluated the slope of the extrapolation by the method of least-squares instead of fitting it to Ramsay's predetermined e values (dependent on the assumption of a Lorentzian function for the true band shape and on a triangular slit function), and they omitted Ramsay's wing corrections (also dependent on a Lorentzian function). So, as was the case for the Wilson-Wells extrapolation, the Russell-Thompson technique is independent of any assumption regarding the true band shape, but it is quite sensitive to measurements at dilute concentrations. However, if a fair number of concentrations are measured, the resulting error should not be too serious.

Several studies of integrated intensities by the Russell-Thompson technique[9,20,21] have shown that the extrapolation is essentially linear and that, if performed for several series of measurements made at different slit widths, it converges to a reasonably constant value for the true integrated absorption intensity. An interesting observation is that the slope of the Russell-Thompson extrapolation is larger than that predicted by Ramsay.[9,20,21]

5. Comparison of Methods

The Wilson-Wells extrapolation of B values presents certain advantages over the Bourgin extrapolation of A' values:

(i) the extrapolation of B as a function of cl is approximately linear, especially if the band is wide enough, while that of A' is a shallow curve;

(ii) since A' is independent of the resolving power and B is not, the use of a spectrophotometer with greater resolving power will assist the extrapolation of B but not of A'.

For these two reasons, the Wilson-Wells extrapolation of B values is more precise than the Bourgin extrapolation of A' values. However, an important weakness common to both extrapolation procedures is that they are quite sensitive to measurements at small concentrations or path lengths where experimental errors in determining band areas are apt to be large. In order to obtain satisfactory extrapolations, measurements at a considerable number of concentrations are necessary.

The most serious limitation of the Ramsay procedures is their dependence on a Lorentzian function for the true band shape. Although absolute integrated intensities obtained by Ramsay's methods are dependent on a Lorentzian function only to the extent of the wing correction and the slope of the extrapolation, both of which are fairly small quantities, the Lorentzian dependence may result in significant error, since it has been shown that the assumption of a Lorentzian form for the true band shape of an infrared absorption band is uncertain and often produces unsatisfactory results.[10,19] Since the Wilson-Wells and Russell-Thompson procedures are independent of any assumption regarding the true band shape (i.e., they do not utilize wing corrections in evaluating the area under an absorption band, and they analyse the slopes of the extrapolations by the method of least-squares instead of fitting the slopes to predetermined values dependent on some assumption for the true band shape), it is felt that the Wilson-Wells and Russell-Thompson extrapolations are somewhat more reliable for evaluating the true integrated intensity of an infrared absorption band than the Ramsay procedures.

Also, even though the Wilson-Wells and Russell-Thompson techniques are sensitive to measurements at dilute concentrations, it is expected that any error resulting from using the least-squares technique in evaluating the extrapolation slope (especially if measurements at a considerable number of concentrations are used in the intensity plot) will be less than the error incurred in utilizing Ramsay's e and ϕ values which were determined assuming a Lorentzian function for the true band shape. Likewise, since the procedures for determining Ramsay's wing corrections are quite imprecise,[19] particularly in the case of overlapping bands, any error made in preserving the apparent intensity values in the Wilson-Wells and Russell-Thompson procedures is probably less than that incurred in the Ramsay methods by applying wing corrections.

However, an important advantage of Ramsay's procedures over the Wilson-Wells and Russell-Thompson extrapolations is that it is possible by means of Ramsay's calculated ϕ and e values to estimate the true integrated intensity from a single measurement of the apparent integrated absorption intensity. Therefore, when a quick estimate of the true integrated intensity is required, Ramsay's methods are convenient techniques.

As far as a comparison of the Wilson-Wells and Russell-Thompson procedures is concerned, no advantage of one technique over the other may be demonstrated because of their similarities: (1) the nature of the extrapolations [i.e., apparent integrated intensity as a function of concentration (Wilson-Wells) or apparent peak optical density (Russell-Thompson)] as long as the intensity measurements are taken over a concentration range in which the Beer's-Law plots are linear; (2) freedom from any assumptions regarding the true band shape; (3) analysis of extrapolation slopes by the method of least-squares; and (4) omission of wing corrections. So the two procedures were considered to be equivalent.

BONDING IN METAL CARBONYLS

Molecular Orbital Description of the Bonding

Before considering the infrared intensities of the carbonyl stretching vibrations in metal carbonyl complexes, it is necessary to briefly describe the bonding between a terminal carbonyl group and a transition metal atom and to consider the sensitivity of the M-C-O bond towards replacement of other carbonyl groups in the molecule by different ligands. A molecular orbital description of the bonding between a terminal CO group and a transition-metal atom is presented in several texts;[22-24] a simplified version of the bonding is sufficient for present purposes.

In the carbon monoxide molecule, the bonding is represented by a σ system, consisting of a filled σ-bonding orbital and two σ-nonbonding lone pairs; and a π system, comprised of two mutually perpendicular filled π-bonding orbitals and the corresponding unfilled π^*-antibonding orbitals (Figure 2-1). When co-ordinated to a metal atom, the less electronegative atom of the CO group, carbon, donates lone-pair electron density to a σ-oriented metal orbital. However, since it is apparent from the general chemistry of carbon monoxide that the donor properties of carbon monoxide are very slight (i.e., CO forms a weak complex with BH_3 and no compounds with metals in which there are no d electrons for back bonding), it is believed that additional π bonding makes a significant contribution to the molecular stability. Various

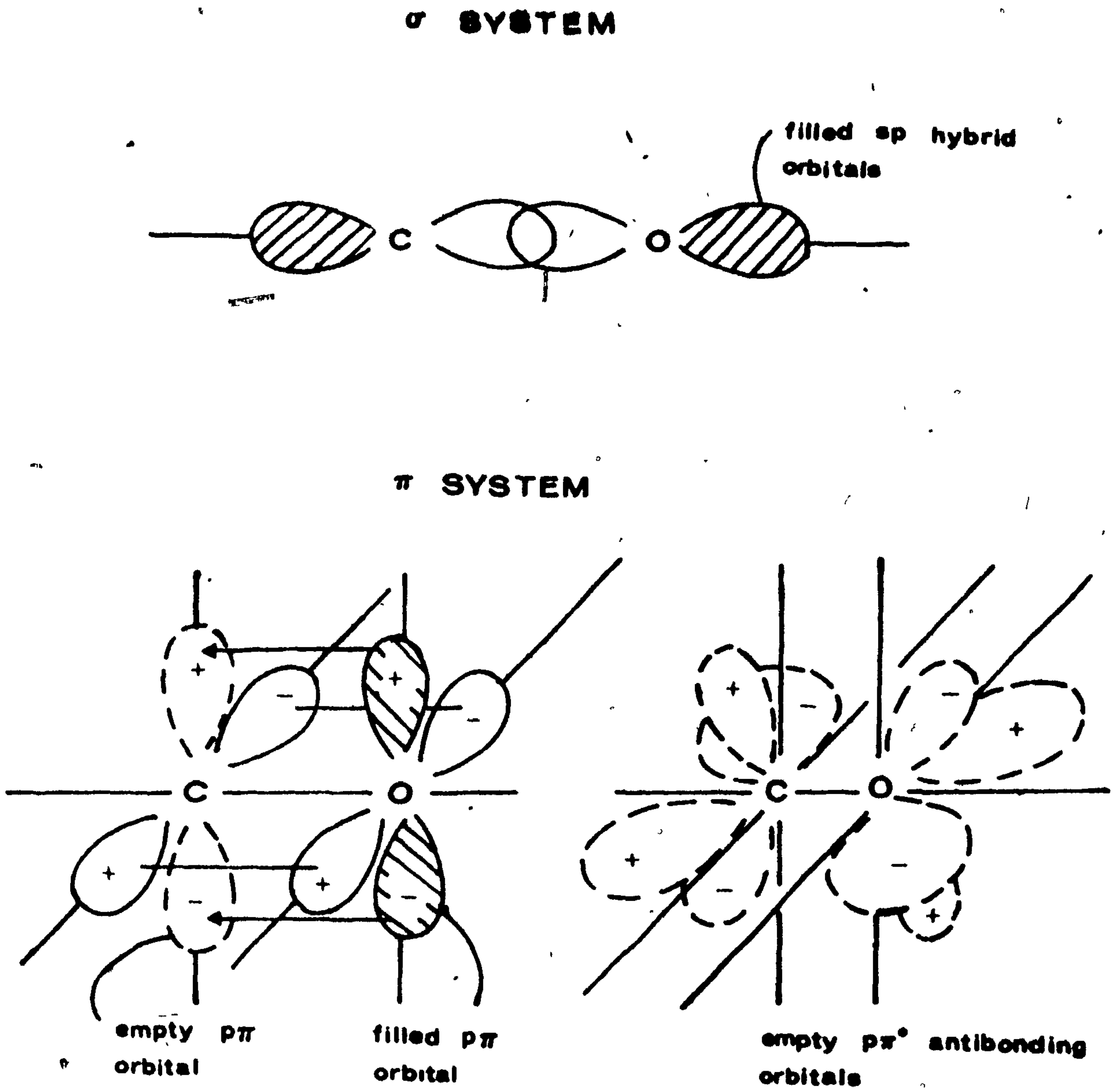

Figure 2-1. Molecular Orbital Description of the Bonding in Carbon Monoxide.*

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[*] F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 3rd ed, Interscience Publishers, Inc., New York, N. Y., 1972, p 685.

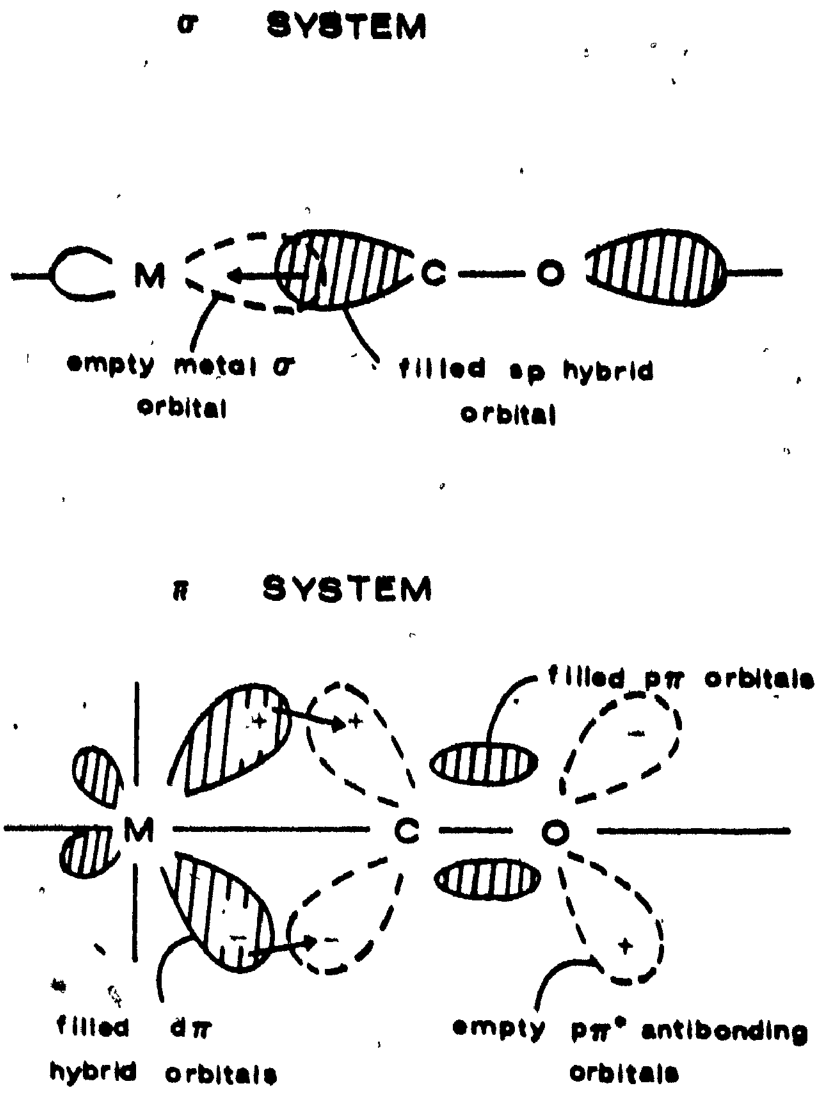

Figure 2-2. Molecular Orbital Description of the Bonding in Transition-Metal Carbonyls.*

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[*] F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 3rd ed, Interscience Publishers, Inc., New York, N. Y., 1972, p 685.

experimental techniques (x-ray crystallography, infrared spectroscopy, etc.,) provide physical evidence for the double bond character of the M-C bond.

To summarize then, the essentials of the bonding between a terminal CO group and a transition-metal atom are:

(1) σ donation from the unshared pair of electrons on carbon to an unfilled σ orbital on the metal;

(2) π back-donation of electrons from the dπ orbitals on the metal to the empty pπ*-antibonding orbitals on the CO group.

Thus, the two components of the metal-carbon bond complement one another in the sense that charge is shifted in opposite directions in the two bond systems. π bonding has the effect of inducing still stronger σ-bond interaction between C and M and vice versa.

A pictoral description of the bonding is presented in Figure 2-2. For present purposes, the M-C-O skeleton will be considered linear because, although small deviations from linearity (rarely more than 5°) often occur, they are not sufficiently large to effect present bonding arguments.[4,25]

Vibrational Stretching Distortion of the CO Bond

Stretching the bond of a co-ordinated CO group will lead to a change in electron density within the M-C-O bonding system. Calculations using Slater atomic orbitals indicate that relatively little change in σ-electron density occurs during a small vibration of carbon monoxide, but that there are quite large changes in the π-electron density.[4,26] It would seem, therefore, that π-bonding effects within a bound vibrating CO group probably predominate.

The relative charge densities on the atoms in a co-ordinated CO group appear to be $^{\delta-}C \rightarrow O^{\delta+}$. Thus, a vibrational stretching distortion most probably leads to a transfer of electron density C→O.[25] If this C→O electron transfer occurs and is located in the π system, then, as the CO bond is stretched, the empty $p\pi^*$ orbitals will be increasingly lowered in energy and will localise more and more on the carbon atom. The expected result would be enhanced M→C dπ-electron donation.[4] The converse of the above argument is also useful, i.e., that M→C dπ-electron donation should enhance C→O pπ-electron transfer.

It would appear then that the flow of electrons C→O in the π system of the CO group during a CO vibrational stretching distortion should serve as an indication of the availability of the metal dπ-electron density. The dipole moment change created by this charge transfer will be reflected in the frequencies and in the intensities of the CO stretching absorptions of metal carbonyl complexes. Hence, the foregoing arguments may be usefully applied to a discussion of the effects of substitution of CO groups in metal carbonyl complexes by other ligands.

If a CO group in a metal carbonyl complex is replaced by a ligand of greater σ-donor but poorer π-acceptor ability, the effective nuclear charge of the metal atom will decrease, providing a greater amount of π-electron density for donation to the π^* orbitals of the remaining CO ligands. The resultant increase in the C→O π-electron transfer during a CO bond stretching vibration and consequent weakening of the CO bond should result in decreased CO-frequencies and enhanced CO-intensities relative to those of the parent complex.

Conversely, replacement of a CO group in a metal carbonyl complex with a highly electronegative group, such as a halogen atom, will lead to an increased effective nuclear charge on the metal atom. This in turn will lead to a decrease in π-electron transfer to the remaining CO groups during a CO bond stretching vibration and hence to a strengthening of the CO bond. The expected result for such a substitution would therefore be increased CO frequencies and decreased CO intensities relative to the parent complex.[4]

The foregoing discussion will be used as a basis for a further investigation of the σ- and π-bonding abilities of various ligands in substituted metal carbonyls, since replacement of a CO group by a ligand of differing σ-donor and π-acceptor ability will be reflected in a change in CO-intensity relative to that of the parent complex.

PART II

EXPERIMENTAL

Chapter 3

PREPARATION METHODS

Physical Measurements

Carbon and hydrogen microanalyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, New York, except for the analysis of fac-tricarbonyltris(chlorodiphenylphosphine)molybdenum(0) which was done by Mr. N. J. Coville in the Department of Chemistry, McGill University, on a model 185 Hewlett·Packard carbon-hydrogen-nitrogen analyzer equipped with a Cahn ratio electrobalance, model G, and a Honeywell recorder. Phosphorus and halogen microanalyses were carried out by Schwarzkopf.

Melting points were taken in unsealed capillaries on a Gallenkamp melting point apparatus design number 889339 and are uncorrected. A Zeiss Opton Nr121133 Abbe refractometer was used for refractive index measurements. Values are reported for the D line of the spectrum of sodium; the temperature of determination was 20°. Infrared spectra were recorded in the metal carbonyl stretching region (2200-1800 cm^{-1}) on a model 337 Perkin Elmer double-beam grating spectrophotometer.

Materials

Alfa Inorganics, Beverly, Massachusetts, was the source of most starting materials: hexacarbonylchromium(0), hexacarbonylmolybdenum(0), hexacarbonyltungsten(0), decacarbonyldimanganese(0), π-cyclopentadienyltricarbonylmanganese(I), π-methylcyclopentadienyltricarbonylmanganese(I), trichlorophosphine, dichlorophenylphosphine, and chlorodiphenylphosphine.

Triphenylphosphine, triphenylarsine, triphenylstibine, cycloheptatriene and bicyclo[2.2.1]heptadiene were obtained from the Aldrich Chemical Company, Milwaukee, Wisconsin. π-Cyclopentadienyldicarbonylthiocarbonylmanganese(I) was generously provided by Mr. A. E. Fenster[27] of the Department of Chemistry, McGill University.

A & C American Chemicals, Ville St-Laurent, Quebec, supplied the common solvents; n-hexane, benzene, methylenechloride, chloroform and carbon tetrachloride. The remaining reagents were purchased from various companies: acetonitrile from Brickman and Company, Montreal, Quebec; mesitylene from the J. T. Baker Chemical Company, Phillipsburg, New Jersey; methylcyclohexane from Eastman Organic Chemicals, Rochester, New York; and bromine and petroleum ether (bp 30-60°) from Anachemia Chemicals, Montreal, Quebec.

Hexacarbonylchromium(0)[$Cr(CO)_6$]

The white, crystalline solid was purified by sublimation (50°/0.1 mm Hg), mp 150-153°; lit.[28a,29] 152-153°, 154-155°, 152-155°, 151-152°.

π-Cyclopentadienylmanganese(I) Complexes

1. π-Cyclopentadienyltricarbonylmanganese(I) [π-$C_5H_5Mn(CO)_3$]

Purification of the yellow crystals was accomplished by sublimation (50°/0.1 mm Hg), mp 73-77°; lit.[28b,30a] 76.8-77.1°, 77°.

2. π-Methylcyclopentadienyltricarbonylmanganese(I) [$(\pi$-$CH_3C_5H_4)Mn(CO)_3$]

The yellow liquid was used as received, $n^{20}D$ 1.5862; lit.[28c,30b] 1.5868. Further purification was deemed unnecessary.

3. π-Cyclopentadienyldicarbonylthiocarbonylmanganese(I) [π-$C_5H_5Mn(CO)_2CS$]

The yellow, crystalline solid was sublimed (45°/0.1 mm Hg) before use, mp 52-54°; lit.[27] 52-53°.

Group VI Metal-Olefin Carbonyls

1. Tricarbonylcycloheptatrienechromium(0) [$C_7H_8Cr(CO)_3$]

$C_7H_8Cr(CO)_3$ was prepared according to King's[31] method by refluxing hexacarbonylchromium(0) (4.4 g, 20 mmol) and excess cycloheptatriene (5 ml, 4.0 g, 44 mmol) in acetonitrile (50 ml). The resulting red crystals were purified by sublimation (100°/0.1 mm Hg), mp 126-128° dec; lit.[28d,31-33] 128-130° dec, 129-130°, after having first sublimed out (70°/0.1 mm Hg) any unreacted hexacarbonylchromium(0).

2. Tetracarbonylbicyclo[2.2.1]hepta-2,5-dienechromium(0) [nor-$C_7H_8Cr(CO)_4$]

nor-$C_7H_8Cr(CO)_4$ was prepared by refluxing hexacarbonylchromium(0) (5.0 g, 23 mmol) and excess bicycloheptadiene (8 ml, 7.3 g, 79 mmol) in methylcyclohexane (40 ml), as described previously in the literature.[28e,34] Purification of the yellow, crystalline product was accomplished by sublimation (80°/0.1 mm Hg), mp 91-93°; lit.[28e,34] 92-93°, after having first sublimed out (60°/0.1 mm Hg) any unreacted hexacarbonylchromium(0).

3. Tricarbonylcycloheptatrienemolybdenum(0) [$C_7H_8Mo(CO)_3$]

The reported procedure[28f,32] for preparing $C_7H_8Mo(CO)_3$ by refluxing hexacarbonylmolybdenum(0) (26.4 g, 0.1 mol) and excess cycloheptatriene (50 ml, 40.3 g, 0.44 mol) in methylcyclohexane (200 ml) was employed. The resulting red crystals were dried (50°/0.1 mm Hg) for 12 hr to remove any unreacted hexacarbonylmolybdenum(0) or other volatile impurities, and were sublimed (100°/0.1 mm Hg) before use, mp 98-102°; lit.[28f,32,35,36] 100.5-101.5°, 100°. <u>Anal.</u> Calcd for $C_{10}H_8O_4Mo$: C, 44.1; H, 3.0; Mo, 35.3. Found: C, 44.4; H, 3.1; Mo, 35.2.

4. <u>Tetracarbonylbicyclo[2.2.1]hepta-2,5-dienemolybdenum(0) [*nor*-$C_7H_8Mo(CO)_4$]</u>

<u>nor</u>-$C_7H_8Mo(CO)_4$ was prepared according to the published methods[28f,34] by refluxing hexacarbonylmolybdenum(0) (26.4 g, 0.2 mol) and excess bicycloheptadiene (40 ml, 36.0 g, 0.4 mol) in methylcyclohexane (200 ml). The resulting yellow crystals were purified by sublimation (100°/0.1 mm Hg), mp 76-78°; lit.[28f,33,34] 77-78°, 76-77°, after having first sublimed out (60°/0.1 mm Hg) any unreacted hexacarbonylmolybdenum(0).

5. <u>*fac*-Tricarbonyltris(acetonitrile)tungsten(0) [$(CH_3CN)_3W(CO)_3$]</u>

The published method[37,38] for preparing $(CH_3CN)_3W(CO)_3$ by refluxing hexacarbonyltungsten(0) (7.0 g, 20 mmol) in actonitrile (50 ml) was used. Purification of the yellow, crystalline product was not attempted; the crude form was adequate for subsequent reaction with the olefins.

6. <u>Tricarbonylcycloheptatrienetungsten(0) [$C_7H_8W(CO)_3$]</u>

$C_7H_8W(CO)_3$ was prepared by refluxing <u>fac</u>-tricarbonyltris(acetonitrile)-tungsten(0) (1.2 g, 3 mmol) and excess cycloheptatriene (2 ml, 1.6 g, 18 mmol) in <u>n</u>-hexane (50 ml) as described previously in the literature.[38] The resulting red crystals were purified by sublimation (100°/0.1 mm Hg), mp 114-118°; lit.[38-41] 115-121° dec, 117-118°, 110°, after having first sublimed out (70°/0.1 mm Hg) any hexacarbonyltungsten(0) present.

7. Tetracarbonylbicyclo[2.2.1]hepta-2,5-dienetungsten(0) [nor-$C_7H_8W(CO)_4$]

The procedure[38] for preparing nor-$C_7H_8W(CO)_4$ was the same as the one used for the preparation of $C_7H_8W(CO)_3$ except that bicycloheptadiene was substituted for the cycloheptatriene. Purification of the yellow, crystalline product was accomplished as outlined above for the cycloheptatriene analogue, mp 88-91°; lit.[38,39] 90-92°.

Molybdenum-Phosphine Carbonyls

1. Tricarbonylmesitylenemolybdenum(0) [[1,3,5-$(CH_3)_3C_6H_3$]$Mo(CO)_3$]

The published method[42,43] for preparing [1,3,5-$(CH_3)_3C_6H_3$]$Mo(CO)_3$ by refluxing hexacarbonylmolybdenum(0) (4.0 g, 0.015 mol) in excess mesitylene (20 ml, 17 g, 0.14 mol) was used. The infrared spectrum of the yellow, crystalline product was identical to that reported previously[43] for [1,3,5-$(CH_3)_3C_6H_3$]$Mo(CO)_3$. No attempt was made to purify the product; the crude form was adequate for subsequent reaction with the phosphines.

2. fac-Tricarbonyltris(trichlorophosphine)molybdenum(0) [fac-$Mo(CO)_3(PCl_3)_3$]

fac-$Mo(CO)_3(PCl_3)_3$ was prepared by heating tricarbonylcycloheptatrienemolybdenum(0) (1.2 g, 0.002 mol) and excess trichlorophosphine (20 ml, 0.23 mol), as described previously in the literature.[44] The resulting yellow crystals were purified by recrystallization from petroleum ether (bp 30-60°), mp 82-85° dec; lit.[44] 85° dec. Anal. Calcd for $C_3P_3O_3Cl_9Mo$: C, 6.1; Cl, 53.9; P, 15.7. Found: C, 6.1; Cl, 53.3; P, 15.6.

3. *fac*-Tricarbonyltris(dichlorophenylphosphine)molybdenum(0)

[*fac*-$\mathrm{Mo(CO)_3[P(C_6H_5)Cl_2]_3}$]

The procedure for preparing *fac*-$\mathrm{Mo(CO)_3[P(C_6H_5)Cl_2]_3}$ was analogous to that of Poilblanc and Bigorgne[45] for preparing *fac*-$\mathrm{Mo(CO)_3P(C_6H_5)_3}$. Tricarbonylmesitylenemolybdenum(0) (0.3 g, 1 mmol) and excess dichlorophenylphosphine (1.0 ml, 1.3 g, 7 mmol) were dissolved in benzene and allowed to stand for 3 hr under nitrogen. The solution was then evaporated to dryness and the residue extracted with petroleum ether (bp 30-60°) (4 x 50 ml), as outlined by Abel, Bennett and Wilkinson.[44] Filtering, concentrating (50 ml) and cooling (-78°) the extract deposited yellow crystals. After filtration, washing with petroleum ether (40 x 25 ml) and drying (25°/0.1 mm Hg), the crystals were identified as *fac*-$\mathrm{Mo(CO)_3[P(C_6H_5)Cl_2]_3}$ by a comparative infrared spectrum,[44] mp 115-117° dec; lit.[44] 106-110° dec.

4. *fac*-Tricarbonyltris(chlorodiphenylphosphine)molybdenum(0)

[*fac*-$\mathrm{Mo(CO)_3[P(C_6H_5)_2Cl]_3}$]

The preparation of *fac*-$\mathrm{Mo(CO)_3[P(C_6H_5)_2Cl]_3}$ was analogous to Poilblanc and Bigorgne's[45] preparation of *fac*-$\mathrm{Mo(CO)_3P(C_6H_5)_3}$. A solution of tricarbonylmestitylenemolybdenum(0) (0.3 g, 1 mmol) and excess chlorodiphenylphosphine (1.0 ml, 1.2 g, 5 mmol) in benzene was allowed to stand for 3 hr under nitrogen, during which time yellow crystals deposited. Filtration, washing with benzene (4 x 20 ml) and drying (25°/0.1 mm Hg)[44] yielded the desired product, mp 155-157° dec; lit.[44] 148° dec. *Anal.* Calcd for $\mathrm{C_{39}H_{30}P_3O_3Cl_3Mo}$: C, 55.7; H, 3.6. Found: C, 55.6; H, 3.4.

Manganese-Mixed-Ligand Carbonyls.

1. Bromopentacarbonylmanganese(I) [$Mn(CO)_5Br$]

$Mn(CO)_5Br$ was prepared by reacting bromine (1.3 ml, 3.7 g, 23 mol) with decacarbonyldimanganese(0) (6.9 g, 18 mol) in carbon tetrachloride (100 ml), as described previously in the literature.[28g,46] The resulting yellow-orange crystals were identified by a comparative infrared spectrum [28g,46] and were purified by sublimation (60°/0.1 mm Hg).

2. *cis*-Bromotetracarbonyl(triphenylphosphine)manganese(I) [*cis*-$Mn(CO)_4[P(C_6H_5)_3]Br$]

cis-$Mn(CO)_4[P(C_6H_5)_3]Br$ was prepared according to Angelici and Basolo's method[47] by reacting bromopentacarbonylmanganese(I) (0.54 g, 2 mmol) and triphenylphosphine (0.53 g, 2 mmol) in chloroform (25 ml) at 40°. The orange-yellow product was recrystallized from *n*-hexane by dissolution at room temperature and recrystallization at dry-ice temperature, mp 130°. The infrared spectrum is identical to that reported previously[47] for *cis*-$Mn(CO)_4[P(C_6H_5)_3]Br$. *Anal.* Calcd for $C_{22}H_{15}PO_4BrMn$: C, 51.9; H, 3.0. Found: C, 52.1; H, 3.0.

3. *cis*-Bromotetracarbonyl(triphenylarsine)manganese(I) [*cis*-$Mn(CO)_4[As(C_6H_5)_3]Br$]

The procedure for preparing and purifying *cis*-$Mn(CO)_4[As(C_6H_5)_3]Br$ was similar to that used for the preparation of *cis*-$Mn(CO)_4[P(C_6H_5)_3]Br$. Identification of the triphenylarsine product (mp 130-134°) was confirmed by a comparative infrared spectrum.[47] *Anal.* Calcd for $C_{22}H_{15}AsO_4BrMn$: C, 47.8; H, 2.7. Found: C, 47.8; H, 3.0.

4. cis-Bromotetracarbonyl(triphenylstibine)manganese(I)

[cis-$Mn(CO)_4[Sb(C_6H_5)_3]Br$]

cis-$Mn(CO)_4[Sb(C_6H_5)_3]Br$ was also prepared and purified according to the method described above for the triphenylphosphine analogue, mp 131-134°. A comparative infrared spectrum[47] was used for identification purposes. Anal. Calcd for $C_{22}H_{15}SbO_4BrMn$: C, 44.0; H, 2.5; Br, 13.3. Found: C, 44.3; H, 2.6; Br, 14.2.

Chapter 4

INTENSITY MEASUREMENTS

Instrumentation

Infrared spectra were recorded on a Perkin-Elmer model 337 double-beam grating spectrophotometer equipped with a 70-min linear frequency scan (4000-1200 cm^{-1}, i.e., a recording rate of 40 cm^{-1} min^{-1}), and a variable slit program (10 settings ranging from narrower than normal for high resolution scans to wide slit operation where high energy is required). The spectral slit width[48] in the metal carbonyl CO stretching region (2200-1800 cm^{-1}) ranged from 3.21 cm^{-1} at 2200 cm^{-1} to 2.55 cm^{-1} at 1800 cm^{-1}; for the manganese thiocarbonyl CS stretching absorption, 1264 cm^{-1}, it was equal to 2.14 cm^{-1} (Appendix B).

A Texas Instruments Servo/Riter II recorder, and later a Sargent-Welch model SRLG recorder, was installed to expand the frequency scale (286 cm^{-1} $inch^{-1}$) of the standard chart paper. As much frequency scale expansion as possible was employed because of the narrowness of the metal carbonyl peaks. On the Texas Instruments recorder, maximum expansion corresponded to a chart paper frequency scale of 5 cm^{-1} $inch^{-1}$; on the Sargent-Welch instrument, it was equivalent to a chart paper frequency scale of 8 cm^{-1} $inch^{-1}$. The carbon monoxide absorption at 2147.08 cm^{-1} and the polystyrene peak at 1601.4 cm^{-1} were used for calibration purposes.[49]

In order to ensure accurate measurements, proper attention to double-beam balancing, zero transmission setting, etc., is essential.

The employment of narrow slit widths is also important in the measurement of the sharp metal carbonyl absorptions.

Optics

Matched, sealed, standard-type liquid cells (1 mm and 0.1 mm path length) with NaCl windows were used for all measurements. International Crystal Laboratories (Irvington, New Jersey) calibrated the 1 mm cells by comparison of the benzene absorption doublet peak at 3.89 microns with that of a known 1 mm cell (previously calibrated against a 0.2 mm cell, the path length of which had been obtained by means of interference fringes between 8 and 13 microns). The 0.1 mm cells were calibrated prior to each set of intensity measurements by means of interference fringes[50] between 4.8 and 5.2 microns; the path lengths were found to be the nominal values (determined by ICL by the interference fringe pattern method from 4.5 to 8 microns) ± 2% (Appendix C).

Sample Preparation

In general, solutions were prepared from individually weighed samples; however, for the three manganese-mixed-ligand carbonyls, volumetric dilution techniques were employed giving results which fitted Beer's-Law plots for the individually prepared samples fairly well.

The solid material was weighed on a Mettler balance accurate to ± 0.1 mg, transferred carefully to a 50-ml volumetric flask and then the solution was diluted accurately to the mark with solvent. Whenever possible, <u>n</u>-hexane was used as solvent because of the optimum resolution of the metal carbonyl absorption spectra in this solvent.[51] However, where low solubility of the complexes in <u>n</u>-hexane precluded its use, methylene chloride (molybdenum-phosphine carbonyls and metal-cycloheptatriene carbonyls) or carbon disulphide [π-cyclopentadienyldicarbonylthiocarbonylmanganese(I)] was substituted. Spectrograde n-hexane, methylene chloride and carbon disulphide were obtained from Fisher Scientific Company, Fair Lawn, New Jersey and were used without further purification.

Recording Procedure

Spectra were recorded as soon as possible after complete dissolution of the sample, usually within 30 min. Decomposition of the samples was minimized by using fresh solutions protected from light by aluminum foil. Generally, decomposition was not extensive enough (usually less than 1%) to affect the intensity results.

Spectra were recorded for at least four, usually five, different concentrations of each sample providing a smooth distribution of bands within the 15 to 65% transmittance range (i.e., $1.89 \geq \ln(T_0/T)_{\nu_{max}} \geq 0.427$). This required sample concentrations ranging from 0.1 to 15.5 mM. The relative error in the integrated intensities is expected to be less than 10% under these conditions.[52] Four individual recordings were taken at each concentration and the average values of $\ln(T_0/T)_{\nu_{max}}$ and of the area for each band at each concentration were used in the intensity calculations.

Area Determination

The area under the absorbance curve

$$\int_{band} \log_{10}(T_0/T)_\nu d\nu \qquad (21)$$

where T_{ν} and T_ν are the apparent intensities of the incident and transmitted radiation when the spectrophotometer is set at frequency ν, was determined by two techniques, depending on which recorder was in use

(Appendix A). The Sargent-Welch instrument presented the spectrum in linear absorbance; this permitted direct evaluation of the integral in (21) by cutting out the band profile and weighing it. Recordings were made on Sargent recorder chart paper catalog No. S-72167 and a Sartorius-Werke model AG balance accurate to ± 0.01 mg was used for the weighings. The paper was calibrated for each spectrum and was found to be quite uniform.

On the Texas Instruments recorder, a linear transmittance spectrum was obtained; here conversion of the experimental absorption band from a linear transmittance to a linear absorbance curve necessarily preceded evaluation of the integral in (21). Readings were taken usually at increments of about 1/7 the true half-intensity band width (Appendix B), providing an equidistantly tabulated function of $\log_{10}(T_0/T)_\nu$ versus ν. Evaluation of the area under the absorbance curve was then accomplished by the application of Simpson's rule. This procedure is quite reliable for reasonably broad bands. However, for very narrow bands, where the increments of the argument values were sometimes greater than $\frac{1}{4}$ the half-intensity band width, the errors encountered were somewhat larger, making the procedure less useful in these cases. A comparison of intensity results for $Cr(CO)_6$ determined by the weighing method and by Simpson's rule (Table 5-1) affords good evidence for the equivalence of the two techniques.

The integration was generally performed over an interval of approximately five times the true half-intensity band width (Appendix B) on either side of the band centre, $\nu_{max} \pm 5\Delta\nu^t_{\frac{1}{2}}$ (i.e., the region from the band centre to the point at which the absorption appeared complete). The area under the solvent background curve was subtracted, but no correction for the area under the wings was applied since the wing corrections provided by Ramsay[8] seemed to be overly large for the sharp CO stretching bands of most substituted metal carbonyls. In order to convert the areas to the naperian base (i.e., to obtain the area under the optical density curve, $\int_{band}\ln(T_o/T)_\nu d\nu$), the results were multiplied by 2.303. Overlapping bands were resolved by extrapolation procedures assuming symmetric band shapes. Such an extrapolation for $C_7H_8Mo(CO)_3$ is illustrated in Figure 4-1.

Treatment of Data

Three methods were employed for the determination of the true integrated absorption intensity

$$A = \frac{1}{cl}\int_{band}\ln\left(\frac{I_o}{I}\right)_\nu d\nu \tag{22}$$

where c is the concentration of solute in moles per liter, l is the cell path length in cm, and I_{o_ν} and I_ν are the incident and transmitted intensities of monochromatic radiation of frequency ν. In the first method, the Wilson-Wells extrapolation,[7] A is obtained by extrapolating measurements of apparent integrated absorption intensity

$$B = \frac{1}{cl}\int_{band}\ln\left(\frac{T_o}{T}\right)_\nu d\nu \tag{23}$$

made at a number of concentrations to zero concentration. The plots for π-$C_5H_5Mn(CO)_2CS$ are shown in Figure 4-2.

The second method used to determine A is the Russell-Thompson extrapolation.[9] In this procedure, A is obtained by plotting B as a function of apparent peak optical density, $\ln(T_o/T)_{\nu_{max}}$ and extrapolating to $\ln(T_o/T)_{\nu_{max}} = 0$. The extrapolations for π-$C_5H_5Mn(CO)_2CS$ are illustrated in Figure 4-3.

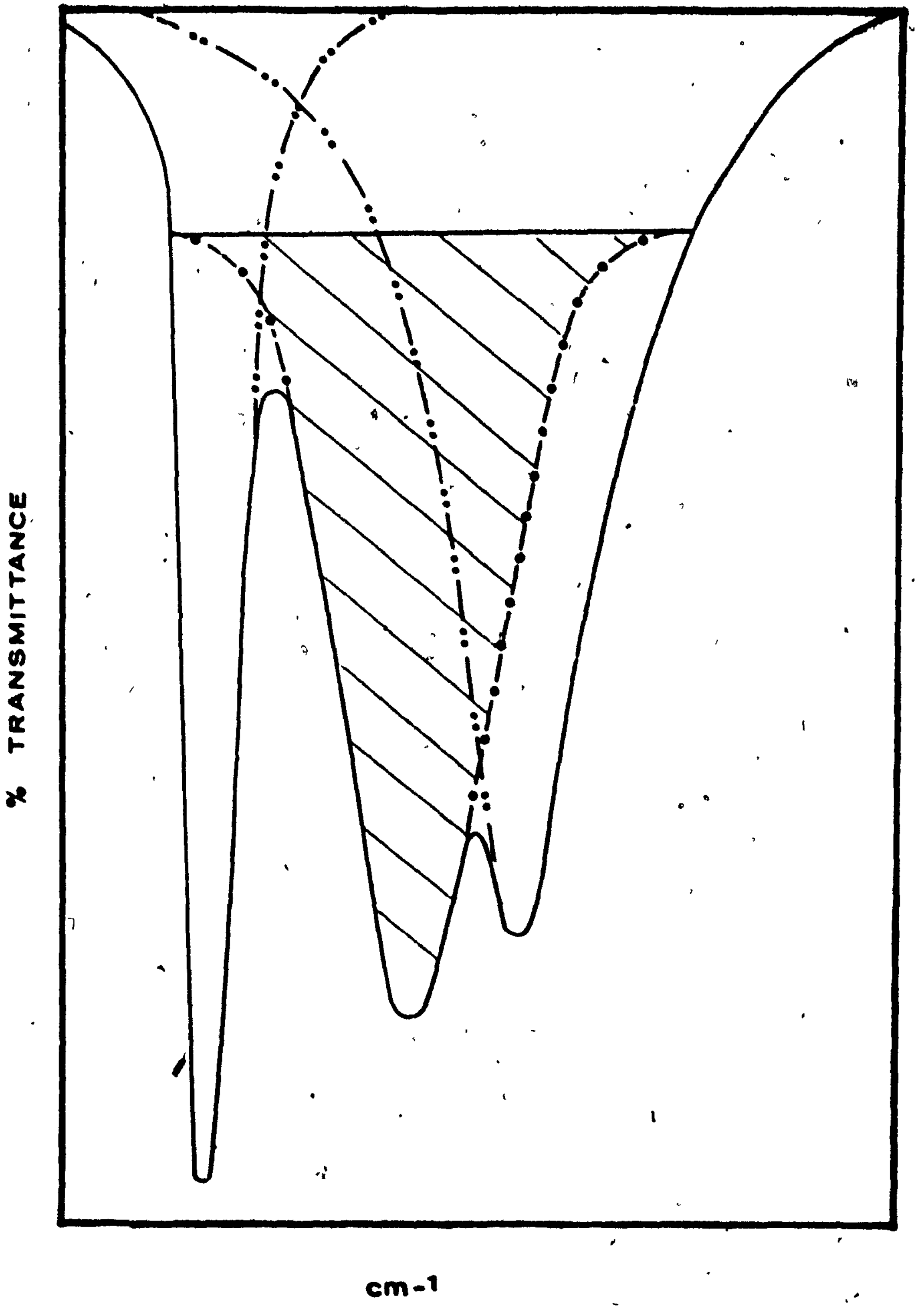

Figure 4-1. Resolution of Overlapping Bands in Spectrum of $C_7H_8Mo(CO)_3$ by Extrapolation Procedures.

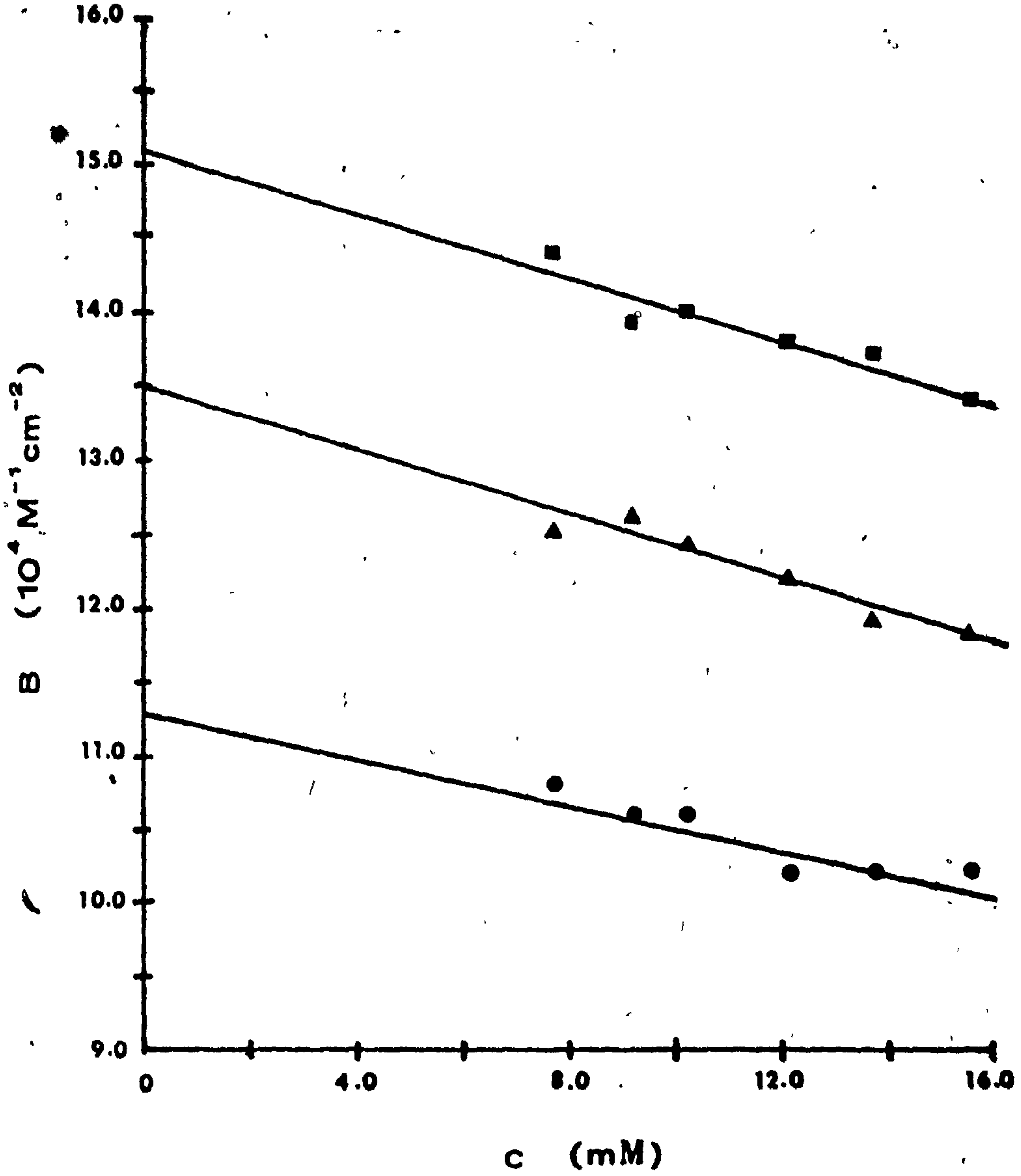

Figure 4-2. Apparent Intensity versus Concentration Plots for the CO and CS Vibrational Modes in the π-$C_5H_5Mn(CO)_2CS$ Complex. CO Modes: ●, A' Vibration; ■, A" Vibration. CS Mode: ▲, A' Vibration.

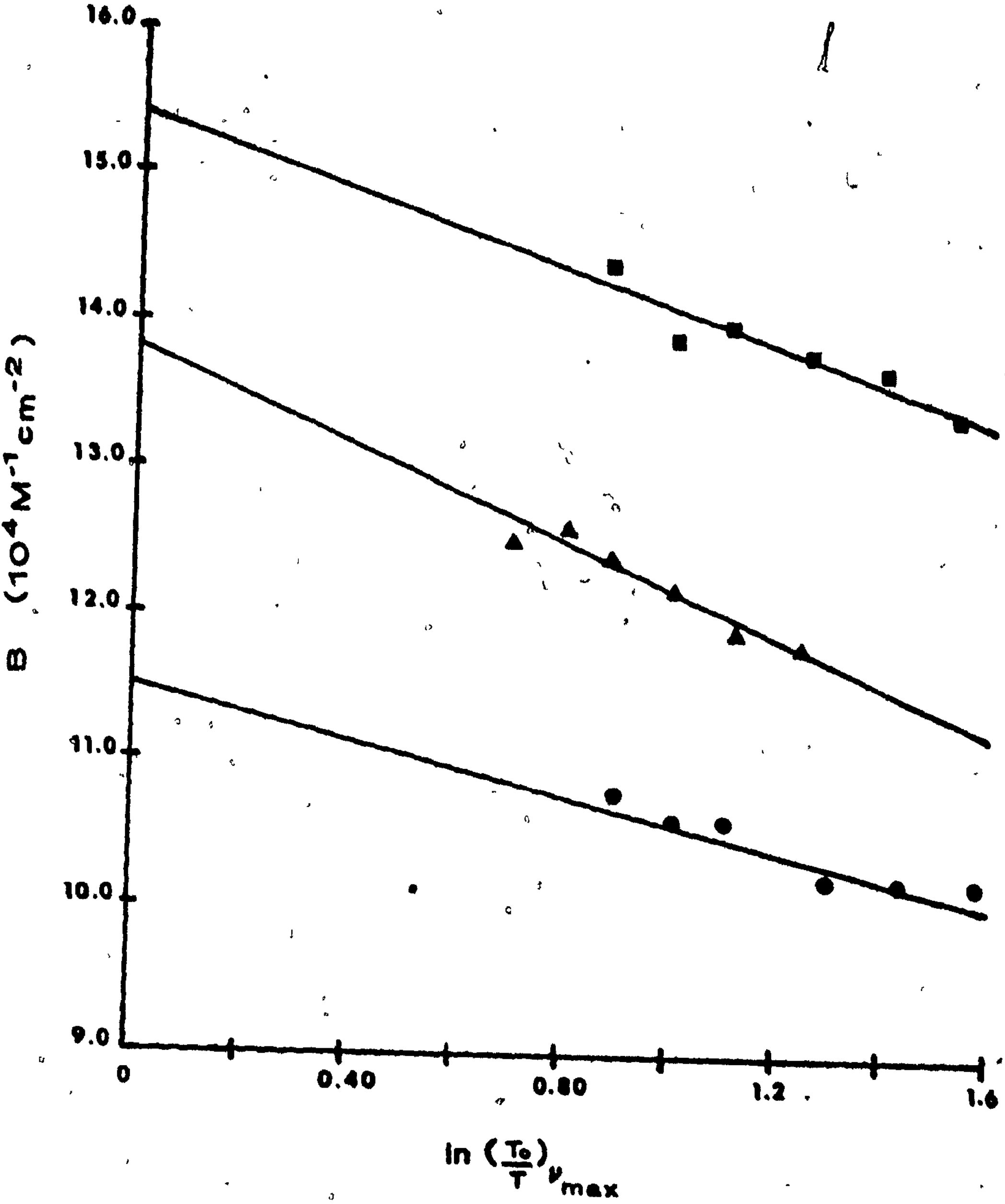

Figure 4-3. Apparent Intensity versus Apparent Peak Optical Density Plots for the CO and CS Vibrational Modes in the π-$C_5H_5Mn(CO)_2CS$ Complex. CO Modes: ●, A' Vibration; ■, A" Vibration. CS Mode: ▲, A' Vibration.

In both extrapolation procedures, the data were analyzed by the method of least-squares using a program written for the IBM 360/65 computer (Appendix A). Since the number of observations was small (usually five), a statistical treatment of data was considered meaningless,[53] and so all points were retained in the analyses and were assigned equal weight. For the most part, negative slopes which generally increased in magnitude with increasing half-intensity-width were obtained by both extrapolation techniques (Appendix B).

The third method used to determine A is the method described by Ramsay and colleagues[8,18] for partially overlapping band systems. In this method, A is determined simply by increasing the mean of the B values by 2% (Appendix A). B values for at least four (usually five) different concentrations were used in the calculation of the mean.

A comparison of intensity results determined by the three methods outlined above (Appendix C) shows that the values obtained by the two extrapolation procedures agree very closely (usually to within 1%); this affords good evidence for the equivalence of the two techniques. However, the extrapolation results tend to be somewhat higher than the results obtained by Ramsay's method (generally about 7% higher). A similar increase in A value (over that predicted by Ramsay on the basis of the assumption of a Lorentz band contour and a triangular slit function) was noted by Russell and Thompson[9] with their extrapolation method.

In conclusion, therefore, it is felt the two extrapolation procedures are the most reliable methods for determining the true integrated intensity of an infrared absorption band. However, an important advantage of Ramsay's method is that it is possible by means of his relation (i.e., $A = 1.2\ B$)

to estimate the true integrated intensity from a single measurement of the apparent integrated absorption intensity. Therefore, when a quick estimate of the true integrated intensity is required, Ramsay's method for overlapping band systems is a convenient technique.

Results

Complete details of the integrated intensity calculations are presented in Appendix C. The tabulated data used in the discussion were extracted from this Appendix.

PART III

DISCUSSION

Chapter 5

INFRARED INTENSITIES IN METAL CARBONYL COMPLEXES

Interpretational Approach

Integrated infrared intensities of the carbonyl stretching absorptions of metal carbonyl compounds and their derivatives were investigated by Noack[54] as far back as 1962; however, the results of relatively few studies have appeared subsequently.[25,55-72] This lack of activity is unfortunate, since the intensities of the CO stretching vibrations of metal carbonyl complexes can provide very useful information concerning the electronic properties of the molecules.

Metal carbonyl CO stretching vibrations are many times more intense than those of free CO (i.e., the intensity of the allowed CO stretching mode in $Cr(CO)_6$, $\sim 65 \times 10^4$ M^{-1} cm^{-2}, is approximately 110 times the value of the fundamental for CO in the gas state, 0.58×10^4 M^{-1} cm^{-2}).[25] Explanations for such intensity enhancement have been given in terms of π-electron transfer from the metal to the CO groups.[25,62] Stretching of a CO bond lowers the energy of the $p\pi^*$ orbitals which act as acceptors for metal $d\pi$-electron density (vide supra, Chapter 2). The dipole moment change created by this charge transfer accounts for the large increase in intensity. Since the effects on the CO intensity due to variations in σ-bonding during a CO stretching vibration are very small,[25] it is assumed that they can be ignored and that the intensity of metal carbonyl CO stretching vibrations is determined solely by π-bonding effects. This assumption appears to be in accord with many of the results which have been published.

Thus, the CO intensity of a metal carbonyl complex can be taken as a measure of the extent of π-bonding present in the molecule. Replacement of one or more of the CO groups in a metal carbonyl complex by other ligands of varying σ-donor and π-acceptor ability should result in a change of π bonding to the remaining CO groups (vide supra, Chapter 2). This should in turn lead to different values for the CO intensities. So, it should be possible to gain an appreciation of the sensitivity of metal carbonyl complexes to substitution by studying the integrated intensities of the CO stretching absorptions of the various molecules.

Unfortunately, it is not clear how a change in π-electron density in a metal carbonyl complex will be distributed among the various CO stretching modes, since both electronic coupling among several CO modes or vibronic contributions to individual CO modes often occur. Thus, a method of analyzing the measured intensity data wherein coupling could be disregarded was described.[4,25] The total integrated CO intensity of any particular metal carbonyl complex is independent both of the angle between any of the symmetry related dipole moment derivatives and the symmetry axis and of any vibrational coupling, provided that the bond moment derivatives of all carbonyl groups in a molecule are identical and that there is only electronic interaction between the carbonyl groups. These requirements are fairly reasonable[4,25] and appear to be quite realistic for most of the metal carbonyls and their derivatives which have been investigated.

Dividing the total absolute integrated CO intensity of a metal carbonyl complex by the number of carbonyl groups present in the molecule affords the integrated intensity per carbonyl group, or specific intensity.[54] Using specific CO-intensity data, it is possible to compare

CO-intensities of metal carbonyl complexes of varying molecular symmetries and with differing numbers of carbonyl groups.[4] In their recent review article on the CO-intensities of metal carbonyl complexes, Kettle and Paul[4] utilized specific CO-intensities in order to reduce the published data (reported using several systems of presentation) to a common basis. In this manner, a ready comparison of existing results could be made.

The work in this thesis constitutes an additional study of the integrated intensities of the carbonyl stretching absorptions of metal carbonyl complexes. The CO-intensities of the individual stretching vibrations as well as the specific CO intensity results for the following series of compounds will be considered: $Cr(CO)_6$, (Cycloheptatriene)$M(CO)_3$ and (Bicycloheptadiene)$M(CO)_4$ (M = Cr, Mo, W), fac-$Mo(CO)_3[P(C_6H_5)_{3-x}Cl_x]_3$ (x = 1-3), cis-$Mn(CO)_4LBr$ [L = $P(C_6H_5)_3$, $As(C_6H_5)_3$, $Sb(C_6H_5)_3$], and π-$RC_5H_4Mn(CO)_3$ (R = H, CH_3) and π-$C_5H_5Mn(CO)_2CS$. The first measurement of the infrared intensity of a thiocarbonyl stretching mode in the metal thiocarbonyl complex, π-$C_5H_5Mn(CO)_2CS$, will also be discussed. The features of Kettle and Paul's report which are pertinent to the research carried out in this thesis will be reviewed at the same time; where applicable, the results of more recent publications will be summarized as well.

Hexacarbonylchromium(0)

The $Cr(CO)_6$ molecule is octahedral (Figure 5-1) and possesses O_h symmetry. Group theory[23] predicts one infrared-active CO stretching mode (T_{1u}) for compounds of this type (Figure 5-2). As expected, the infrared spectrum of $Cr(CO)_6$ displays a single isolated peak in the CO stretching region.

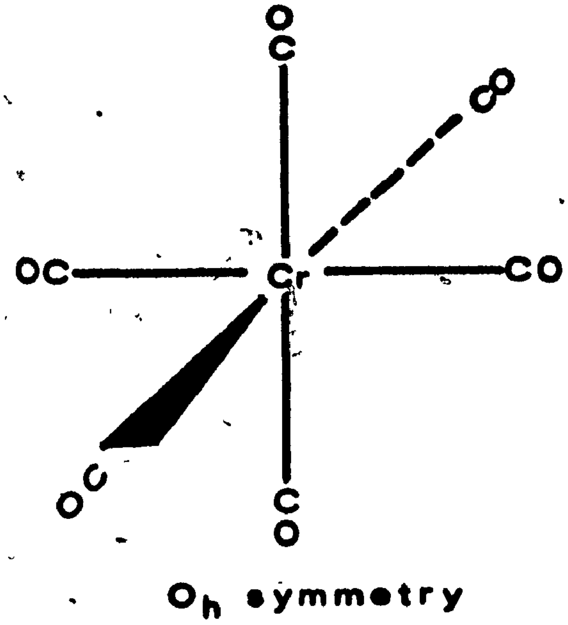

Figure 5-1. Structure of the $Cr(CO)_6$ Molecule.

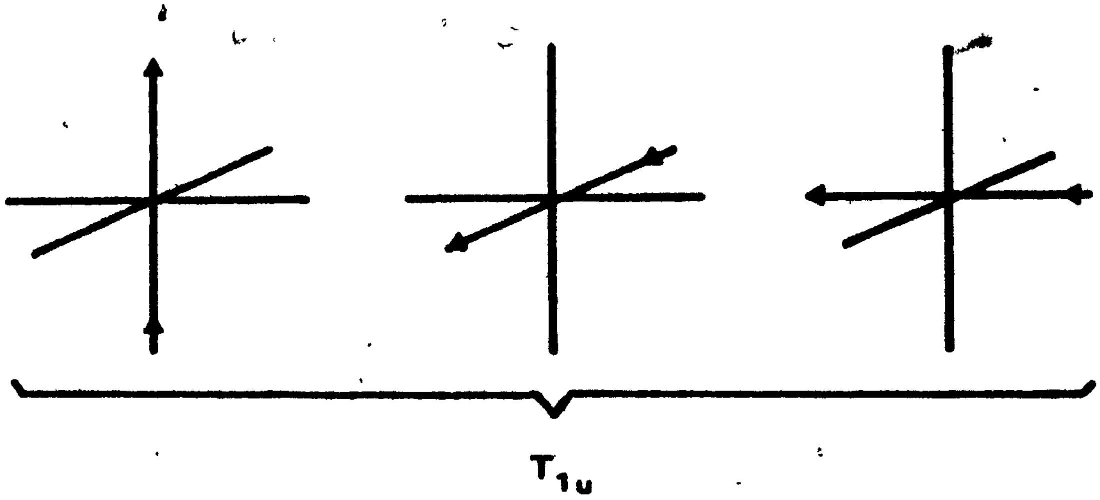

Figure 5-2. Infrared-Active CO Stretching Vibration of the $Cr(CO)_6$ Molecule.

Since single peaks which are essentially free of neighbouring absorptions make convenient standards for comparison of intensity measurement techniques, we measured the integrated intensity of the CO stretching mode of $Cr(CO)_6$ to check the reliability of our measuring techniques (Tables 5-1 and 5-2). The first point that emerges from an examination of the results is that the two integration methods used to measure band area produce almost identical results. Thus, integration of band area by the weighing method and by Simpson's rule are considered to be essentially equivalent procedures.

Second, if our specific CO intensity results are compared with the published values for $Cr(CO)_6$ (Table 5-5), it is evident that our results obtained by Ramsay's method, 4.71 and 4.69 x 10^4 M^{-1} cm^{-2} (integration performed by Simpson's rule and the weighing method, respectively), agree very closely with the reported values measured in the same solvent (*n*-hexane), 4.65[54] and 4.61[60] x 10^4 M^{-1} cm^{-2}. Since Abel and Butler's[60] result was also determined by using one of Ramsay's methods (Noack's[54] value is not corrected for the finite slit width of the spectrophotometer and, as such, is only an apparent intensity and so should tend to be somewhat lower than the corrected results), it is apparent that our technique for determining integrated intensities by Ramsay's method compares well with the Ramsay techniques of other researchers, and so our Ramsay results may be reliably compared with equivalent values in the literature. Also, the specific intensity results obtained by the Wilson-Wells and Russell-Thompson extrapolations (Table 5-2) tend to be somewhat higher than both our Ramsay values and the published results. This is the expected trend because Russell and Thompson[9] noted a similar increase

TABLE 5-1

Infrared Frequency, Half-Intensity Band Width, and Absolute Integrated Absorption Intensity for the CO Stretching Vibration of $Cr(CO)_6$ in *n*-Hexane Solution

			ν_{max}	$\Delta\nu_{\frac{1}{2}}^{t}$*	E,** 10^4 M^{-1} cm^{-2}			
Complex	Integration method	Normal mode	cm^{-1}	cm^{-1}	Ramsay	Wilson-Wells	Russell-Thompson	Mean
$Cr(CO)_6$	Simpson's	T_{1u}	$1986._9$	1.92	28.3 (± 0.6)	29.8 (± 1.9)	29.8 (± 2.0)	29.3 (± 1.5)
$Cr(CO)_6$	Weighing	T_{1u}	$1987._2$	2.00	28.2 (± 0.6)	29.9 (± 1.3)	30.1 (± 1.4)	29.4 (± 1.1)

*These are the true half-intensity band widths computed from the observed values by applying Ramsay's corrections for the finite slit width of the instrument [D. A. Ramsay, J. Am. Chem. Soc., 74, 72 (1952)].

**Defined as $\frac{1}{cl}\int_{band}\log_{10}(\frac{I_0}{I})_\nu d\nu$, where c equals the concentration of solute in M^{-1}, l is the cell path length in cm, and I_{0_ν} and I_ν are the incident and transmitted intensities of monochromatic radiation of frequency ν. Ramsay: E is computed by taking the mean of the observed intensities (defined as $\frac{1}{cl}\int_{band}\log_{10}(\frac{T_0}{T})_\nu d\nu$, where T_{0_ν} and T_ν are the observed intensities of the incident and transmitted radiation when the spectrophotometer is set at frequency ν) obtained at a number of concentrations and increasing it by 2%. The numbers in parentheses are the standard deviations from the mean. Wilson-Wells: E is evaluated by extrapolating the observed intensities taken at several concentrations to zero concentration. The numbers in parentheses are the standard deviations from least-squares analyses of the intensity versus concentration plots. Russell-Thompson: E is determined by extrapolating the observed intensities taken at a number of concentrations to zero apparent peak optical density. The numbers in parentheses are the standard deviations from least-squares analyses of the intensity versus peak optical density plots. Mean: the E value is the mean for the three methods of determination. The numbers in parentheses are the average standard deviations for the three methods.

TABLE 5-2

Specific Intensity for the CO Stretching Vibration of $Cr(CO)_6$

Complex	Integration Method	Solvent	Specific Intensity,* 10^4 M^{-1} cm^{-2} Ramsay	Wilson-Wells	Russell-Thompson	Mean
$Cr(CO)_6$	Simpson's	n-Hexane	4.71 (± 0.10)	4.97 (± 0.31)	4.97 (± 0.34)	4.88 (± 0.25)
	Weighing	n-Hexane	4.69 (± 0.10)	4.93 (± 0.21)	5.01 (± 0.24)	4.90 (± 0.18)

*Denotes the integrated intensity per CO group, $\sum_i K_i/n$, where n is the number of CO groups present in the molecule and K_i represents the integrated intensity of the i^{th} normal mode. A definition of K and descriptions of the methods for obtaining it are provided in Table 5-1.

in integrated intensity with their extrapolation procedure over the value predicted by Ramsay on the basis of the assumption of a Lorents band contour and a triangular slit function. Therefore, it is reasonable to assume that our extrapolation techniques are comparable to other extrapolation techniques.

Group VI Metal-Olefin Carbonyls

Early in the study of the CO intensities of metal carbonyl complexes, Beck and Nitzmann[55] observed that the specific CO intensities of isoelectronic and isostructural series of metal-carbonyls increase steadily from cationic through neutral to anionic species (Table 5-3). The most striking example of this trend is for the series $Mn(CO)_6^+$, $Cr(CO)_6$ and $V(CO)_6^-$ (Table 5-3). Such trends are thought to reflect the greater availability of metal $d\pi$-electron density with increasing negative charge. A considerable body of data supporting Beck and Nitzmann's original observations is now available (Tables 5-3 and 5-4).

Another early observation was that for related species in a given group, an increase in atomic number of the transition metal atom results in an increase in the CO intensities. This observation has also been consistently reported (Tables 5-5 to 5-7) and is in good agreement with π-bonding arguments since one would expect the availability of metal $d\pi$-electron density to increase with the size of the metal atom electron cloud. In the case of $Mn(CO)_6^+$ and $Re(CO)_6^+$ (Table 5-6) and some complexes containing iodo ligands (Table 5-6), however, some anomalous behaviour has been reported.

A comparison of CO-frequency and band-width data for the two series of group VI metal-olefin carbonyls studied in this work shows that there

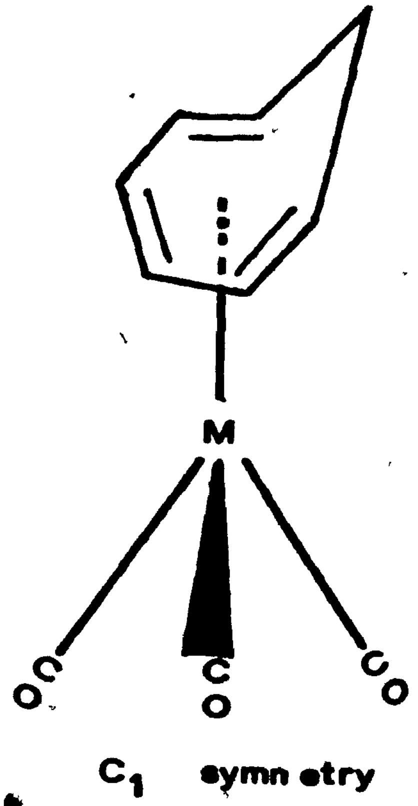

Figure 5-3. Structure of $C_7H_8M(CO)_3$ Molecule (M = Cr, Mo, W).

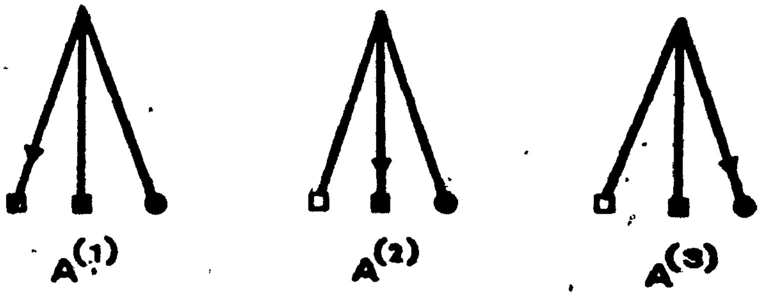

Figure 5-4. Infrared-Active CO Stretching Vibrations of the $C_7H_8M(CO)_3$ Molecule (M = Cr, Mo, W).

TABLE 5-3

Specific Intensities for the CO Stretching Vibrations of Some Isoelectronic and Isostructural Series of Metal-Carbonyls[a]

Complex	Solvent	Specific Intensity[b] $10^4\ M^{-1}\ cm^{-2}$	Reference
$Ni(CO)_4$	Tetrahydrofuran	4.95	c
$Co(CO)_4^-$	Diethyleneglycol diethylether	7.50	c
$Mn(CO)_6^+$	Tetrahydrofuran	2.52	c
$Cr(CO)_6$	Tetrahydrofuran	6.10	c
$V(CO)_6^-$	Tetrahydrofuran	9.47	c
$Mn_2(CO)_{10}$	Tetrahydrofuran	3.85	d
$Cr_2(CO)_{10}^{2-}$	Tetrahydrofuran	4.95	d
$Re(CO)_6^+$	Tetrahydrofuran	2.11	c
$W(CO)_6$	Tetrahydrofuran	7.75	c

[a] S. F. A. Kettle and I. Paul in "Advances in Organometallic Chemistry," Vol. X, F. G. A. Stone and R. West, Ed., Academic Press, Inc., New York, N. Y., 1972, pp 224, 230.

[b] As defined in Table 5-2.

[c] W. Beck and R. E. Nitzmann, Z. Naturforsch., 17B, 577 (1962).

[d] R. M. Wing and D. C. Crocker, Inorg. Chem., 6, 289 (1967).

TABLE 5-4

Specific Intensities of the CO Stretching Vibrations of Some Isoelectronic and Isostructural Series of Metal Carbonyl Complexes[a]

Complex	Solvent	Specific Intensity[b] 10^4 M^{-1} cm^{-2}	Reference
$Mn(CO)_5Cl$	Chloroform	3.06	[illegible]
$Cr(CO)_5Cl^-$	Chloroform	4.47	[illegible]
$Mn(CO)_5Br$	Chloroform	3.76	[illegible]
$Cr(CO)_5Br^-$	Chloroform	4.52	[illegible]
$Mn(CO)_5I$	Chloroform	4.23	[illegible]
$Cr(CO)_5I^-$	Chloroform	6.28	[illegible]
$Re(CO)_5Br$	Chloroform	4.25	[illegible]
$W(CO)_5Br^-$	Chloroform	6.08	[illegible]
$Re(CO)_5I$	Chloroform	4.19	[illegible]
$W(CO)_5I^-$	Chloroform	6.20	[illegible]
cis-$Fe(CO)_4Br_2$	*n*-Hexane	1.84	d
cis-$Mn(CO)_4Br_2^-$	Chloroform	3.47	[illegible]
cis-$Fe(CO)_4I_2$	Chloroform	2.51	[illegible]
cis-$Mn(CO)_4I_2^-$	Chloroform	3.99	[illegible]
$Co(CO)_3NO$	Tetrahydrofuran	4.15	[illegible]
$Fe(CO)_3NO^-$	Diethyleneglycol diethylether	5.16	[illegible]

[a] S. F. A. Kettle and I. Paul in "Advances in Organometallic Chemistry," Vol. X, F. G. A. Stone and R. West, Ed., Academic Press, Inc., New York, N. Y., 1972, pp 224-226.

[b] As defined in Table 5-2.

[c] E. W. Abel and I. S. Butler, *Trans. Faraday Soc.*, 63, 45 (1967).

[d] K. Noack, *Helv. Chim. Acta*, 45, 1847 (1962)

[e] W. Beck and R. E. Nitzmann, *Z. Naturforsch.*, 17b, 577 (1962).

TABLE 5-5

Specific Intensities for the CO Stretching Vibrations of a Series of Group VI Metal-Carbonyls in Various Solvents[a].

	Specific Intensity,[b] 10^4 M^{-1} cm^{-2}				
Complex	*n*-Hexane[c]	*n*-Hexane[d]	Tetrachloro-ethylene[d]	Carbon tetrachloride[e]	Tetrahydro-furan[e]
$Cr(CO)_6$	4.61	4.65	5.09	5.14	6.10
$Mo(CO)_6$	5.39	5.01	5.19		
$W(CO)_6$	5.54	5.53	5.37	6.62	7.75

[a] S. F. A. Kettle and I. Paul in "Advances in Organometallic Chemistry," Vol. X, F. G. A. Stone and R. West, Ed., Academic Press, Inc., New York, N. Y., 1972, p 224.

[b] As defined in Table 5-2.

[c] E. W. Abel and I. S. Butler, *Trans. Faraday Soc.*, *63*, 45 (1967).

[d] K. Noack, *Helv. Chim. Acta*, *45*, 1847 (1962).

[e] W. Beck and R. E. Nitzmann, *Z. Naturforsch.*, *17B*, 577 (1962).

TABLE 5-6

Specific Intensities for the CO Stretching Vibrations of Some Series of Group VI and VII Metal-Carbonyls and Derivatives[a]

Complex	Solvent	Specific Intensity[b] $10^4\ M^{-1}\ cm^{-2}$	Reference
$Mn(CO)_6^+$	Tetrahydrofuran	2.52	c
$Re(CO)_6^+$	Tetrahydrofuran	2.11	c
$Cr(CO)_5P(C_6H_5)_3$	n-Hexane	5.25	d
$Mo(CO)_5P(C_6H_5)_3$	n-Hexane	6.14	d
π-$C_5H_5Mn(CO)_3$	Carbon tetrachloride	4.85	e
π-$C_5H_5Re(CO)_3$	Carbon tetrachloride	5.36	e
$(\pi$-$C_6H_5COC_5H_4)Mn(CO)_3$	Carbon tetrachloride	4.59	e
$(\pi$-$C_6H_5COC_5H_4)Re(CO)_3$	Carbon tetrachloride	5.14	e
$Mn(CO)_5Br$	Chloroform	3.31 (3.76)	d (f)
$Re(CO)_5Br$	Chloroform	4.15 (4.25)	d (f)
$Mn(CO)_5I$	Chloroform	4.23	f
$Re(CO)_5I$	Chloroform	4.19	f
$Cr(CO)_5Cl^-$	Chloroform	4.47	f
$W(CO)_5Cl^-$	Chloroform	6.24	f
$Cr(CO)_5Br^-$	Chloroform	4.52	f
$W(CO)_5Br^-$	Chloroform	6.08	f
$Cr(CO)_5I^-$	Chloroform	6.28	f
$W(CO)_5I^-$	Chloroform	6.20	f

[a] S. F. A. Kettle and I. Paul in "Advances in Organometallic Chemistry," Vol. X, F. G. A. Stone and R. West, Ed., Academic Press, Inc., New York, N. Y., 1972, pp 224, 225, 227.

[b] As defined in Table 5-2

[c] W. Beck and R. E. Nitzmann, <u>Z. Naturforsch.</u>, <u>17B</u>, 577 (1962).

[d] T. L. Brown and D. J. Darensbourg, <u>Inorg. Chem.</u>, <u>6</u>, 971 (1967).

[e] A. N. Nesmeyanov, G. G. Dvoryantseva, Kh. P. Pustyl'nik, Yu. N. Sheinker, N. E. Kolobova, and K. N. Anisinov, <u>Dokl. Akad. Nauk SSSR</u>, <u>174</u>, 368, (1967); <u>Acad. Sci. USSR Chem.</u> <u>174</u>, 457 (1967).

[f] E. W. Abel and I. S. Butler, <u>Trans. Faraday Soc.</u>, <u>63</u>, 45 (1967).

TABLE 5-7

Specific Intensities for the CO Stretching Vibrations of Some Series of Polynuclear Metal-Carbonyls[a]

Complex	Solvent	Specific Intensity[b] $10^4\ M^{-1}\ cm^{-2}$	Reference
$Mn_2(CO)_{10}$	Cyclohexane	2.87	c
$Re_2(CO)_{10}$	Cyclohexane	3.57	c
$Mn_2(CO)_{10}$	Carbon tetrachloride	3.36	d
$ReMn(CO)_{10}$	Carbon tetrachloride	3.44	d
$Re_2(CO)_{10}$	Carbon tetrachloride	3.63	d
π-$C_5H_5MoMn(CO)_8$	Carbon tetrachloride	3.68	d
π-$C_5H_5MoRe(CO)_8$	Carbon tetrachloride	4.08	d
π-$C_5H_5WMn(CO)_8$	Carbon tetrachloride	3.74	d
π-$C_5H_5WRe(CO)_8$	Carbon tetrachloride	4.15	d
π-$C_5H_5MoMn(CO)_8$	Carbon tetrachloride	3.68	d
π-$C_5H_5WMn(CO)_8$	Carbon tetrachloride	3.74	d
π-$C_5H_5MoRe(CO)_8$	Carbon tetrachloride	4.08	d
π-$C_5H_5WRe(CO)_8$	Carbon tetrachloride	4.15	d
$HCr_2(CO)_{10}^-$	Tetrahydrofuran	4.95	c
$HW_2(CO)_{10}^-$	Tetrahydrofuran	6.33	c

[a] S. F. A. Kettle and I. Paul in "Advances in Organometallic Chemistry," Vol. X, F. G. A. Stone and R. West, Ed., Academic Press, Inc., New York, N. Y., 1972, p 230.

[b] As defined in Table 5-2.

[c] R. M. Wing and D. C. Crocker, Inorg. Chem., 6, 289 (1967).

[d] A. N. Nesmeyanov, G. G. Dvoryantseva, Yu. N. Sheinker, N. E. Kolobova, and K. N. Anisimov, Dokl. Akad. Nauk SSSR, 169, 843 (1966); Acad. Sci. USSR Chem., 169, 751 (1966).

is little change in either variable in going from chromium to tungsten (Tables 5-8 and 5-9). Because of this, a study of the CO-intensities of the two series of compounds was undertaken to see whether the expected increase in CO-intensity with increasing size of the metal atom would occur or whether the two series of metal-olefin carbonyls would be further exceptions to the general trend.

Owing to the incomplete delocalisation of the π-electron system in cycloheptatriene, free rotation about the metal-ring axis does not occur[32] (i.e., cycloheptatriene-metal complexes have the ring fixed with respect to the carbonyl groups). The structure of the $C_7H_8M(CO)_3$ (M = Cr, Mo, W) molecules is a piano-stool type arrangement (Figure 5-3), with the exact disposition of the carbonyl groups relative to the ring as yet undecided. The symmetry is C_1 for which group theory predicts three infrared-active CO stretching modes (3A). Each carbonyl group should give rise to a symmetric A stretching mode of reasonable intensity (Figure 5-4). As expected, infrared spectra exhibiting three well-resolved bands of comparable intensity were obtained.

Molecules of the type nor-$C_7H_8M(CO)_4$ (M = Cr, Mo, W) have an octahedral structure (Figure 5-5) and possess formal C_{2v} symmetry. Four infrared-active CO stretching modes ($2A_1 + B_1 + B_2$) would be expected for such an arrangement. The trans pair of carbonyls should produce a weak $A_1^{(2)}$ mode (which may be more intense than anticipated because of coupling with the other A_1 mode) and a strong antisymmetric B_1 stretching mode, while the other two carbonyls should give rise to a symmetric $A_1^{(1)}$ mode and to an antisymmetric B_2 stretching mode of comparable intensity (Figure 5-6).

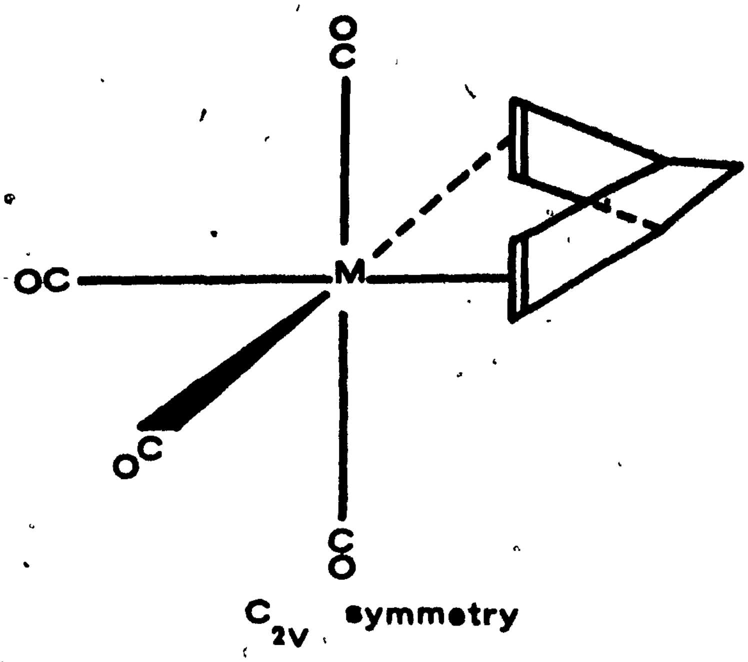

Figure 5-5. Structure of the nor-$C_7H_8M(CO)_4$ Molecule [M = Cr, Mo, W].

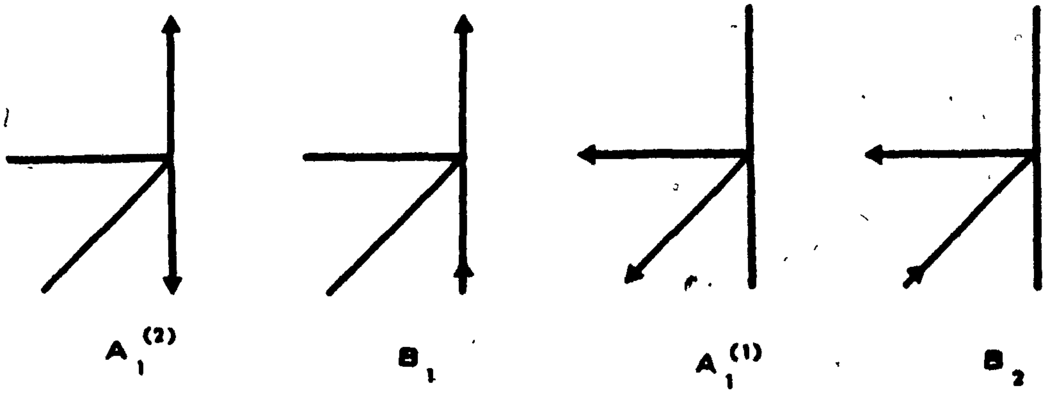

Figure 5-6. Infrared-Active CO Stretching Vibrations of the nor-$C_7H_8M(CO)_4$ Molecule [M = Cr, Mo, W].

The spectrum of nor-$C_7H_8Cr(CO)_4$ does display four well-resolved bands in the CO stretching region as expected; however, the spectra of the molybdenum and tungsten analogues exhibit only three distinct peaks. It is likely that the strong middle band in the spectra of these two compounds actually consists of two coincident absorptions. The CO-intensity data for the series (Table 5-9) help to corroborate this view; it is clear that the intensity of the strong middle band of both the molybdenum and tungsten complexes is comparable to the sum of the intensities of the two middle bands of the chromium complex.

Probable assignments of the four peaks in the nor-$C_7H_8Cr(CO)_4$ spectrum in order of decreasing frequency are $A_1^{(2)}$, $A_1^{(1)}$, B_1, and B_2, respectively (Table 5-9). The highest frequency band is readily assigned to the $A_1^{(2)}$ mode since the local dipoles of the $A_1^{(2)}$ mode have their similar poles facing one another and hence there should be some cancellation giving rise to a weak absorption. The assignment of the B_1 mode to the absorption at 1944 cm^{-1} is supported by the CO-intensity data; the B_1 mode should give rise to the most intense band and the 1944 cm^{-1} absorption is in fact the most intense. The two remaining unassigned peaks at 1959 cm^{-1} and 1915 cm^{-1} were assigned to the $A_1^{(1)}$ mode and to the B_2 mode, respectively, since symmetrical stretching modes of vibration are expected to be at higher frequencies than the corresponding asymmetrical modes of vibration. These assignments are also supported by previous force constant calculations on isostructural molecules,[73,74] e.g., cis-$Fe(CO)_4X_2$.

The CO-intensity data for the group VI metal-olefin carbonyls are presented in Tables 5-8 to 5-10. From a comparison of the specific CO-intensities of the metal-olefin carbonyls with the values for the

TABLE 5-8

Infrared Frequencies, Half-Intensity Band Widths, and Absolute Integrated Absorption Intensities for the CO Stretching Vibrations of the Cycloheptatriene$M(CO)_3$ Complexes in Methylene Chloride Solution

Complex	Normal mode	ν_{max} cm^{-1}	$\Delta\nu_{\frac{1}{2}}^{t*}$ cm^{-1}	E,** 10^4 M^{-1} cm^{-2} Ramsay	Wilson-Wells	Russell-Thompson	Mean
$C_7H_8Cr(CO)_3$	$A^{(1)}$	$1982._1$	13.1	6.10 (± 0.22)	6.98 (± 0.53)	7.14 (± 0.75)	6.74 (± 0.50)
$C_7H_8Mo(CO)_3$	$A^{(1)}$	$1983._6$	11.9	7.23 (± 0.22)	7.62 (± 0.60)	7.63 (± 0.71)	7.49 (± 0.51)
$C_7H_8W(CO)_3$	$A^{(1)}$	$1981._4$	11.0	6.72 (± 0.22)	7.90 (± 0.45)	8.09 (± 0.56)	7.57 (± 0.41)
$C_7H_8Cr(CO)_3$	$A^{(2)}$	$1916._0$	19.1	6.68 (± 0.17)	7.50 (± 0.45)	7.64 (± 0.56)	7.27 (± 0.39)
$C_7H_8Mo(CO)_3$	$A^{(2)}$	$1912._2$	22.0	7.93 (± 0.35)	9.17 (± 1.07)	9.24 (± 1.33)	8.78 (± 0.92)
$C_7H_8W(CO)_3$	$A^{(2)}$	$1908._3$	20.6	7.50 (± 0.13)	8.06 (± 0.53)	8.13 (± 0.60)	7.90 (± 0.42)
$C_7H_8Cr(CO)_3$	$A^{(3)}$	$1886._9$	26.0	6.51 (± 0.35)	8.17 (± 0.61)	8.31 (± 0.73)	7.66 (± 0.56)
$C_7H_8Mo(CO)_3$	$A^{(3)}$	$1880._2$	27.0	7.81 (± 0.13)	8.37 (± 0.14)	8.48 (± 0.13)	8.22 (± 0.13)
$C_7H_8W(CO)_3$	$A^{(3)}$	$1873._1$	25.8	7.37 (± 0.04)	7.33 (± 0.27)	7.32 (± 0.29)	7.34 (± 0.20)

*,**As defined in Table 5-1.

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TABLE 5-9

Infrared Frequencies, Half-Intensity Band Widths, and Absolute Integrated Absorption Intensities for the CO Stretching Vibrations of the (Bicycloheptadiene)M(CO)$_4$ Complexes in n-Hexane Solution

Complex	Normal mode	ν_{max} cm^{-1}	$\Delta\nu^{t*}_{\frac{1}{2}}$ cm^{-1}	E,** 10^4 M^{-1} cm^{-2} Ramsay	Wilson-Wells	Russell-Thompson	Mean
nor-$C_7H_8Cr(CO)_4$	$A_1^{(2)}$	$2033._6$	1.62	3.14 (± 0.11)	3.54 (± 0.42)	3.58 (± 0.54)	3.42 (± 0.36)
nor-$C_7H_8Mo(CO)_4$	$A_1^{(2)}$	$2044._4$	1.50	2.62 (± 0.06)	2.57 (± 0.25)	2.55 (± 0.25)	2.58 (± 0.19)
nor-$C_7H_8W(CO)_4$	$A_1^{(2)}$	$2043._9$	1.95	2.81 (± 0.06)	2.79 (± 0.08)	2.79 (± 0.09)	2.80 (± 0.03)
nor-$C_7H_8Cr(CO)_4$	$A_1^{(1)}$	$1958._7$	2.86	1.92 (± 0.11)	2.26 (± 0.52)	2.26 (± 0.58)	2.15 (± 0.40)
	B_1	$1944._4$	3.38	9.29 (± 0.26)	9.57 (± 1.24)	9.49 (± 1.42)	9.45 (± 0.97)
nor-$C_7H_8Mo(CO)_4$	$[A_1^{(1)}, B_1]$	$1959._2$	3.74	12.2 (± 0.4)	13.8 (± 0.4)	14.0 (± 0.4)	13.3 (± 0.4)
nor-$C_7H_8W(CO)_4$	$[A_1^{(1)}, B_1]$	$1957._3$	3.50	12.2 (± 0.4)	14.4 (± 1.0)	14.8 (± 1.1)	13.8 (± 0.8)
nor-$C_7H_8Cr(CO)_4$	B_2	$1914._8$	3.74	7.76 (± 0.13)	7.99 (± 0.28)	8.02 (± 0.34)	7.92 (± 0.25)
nor-$C_7H_8Mo(CO)_4$	B_2	$1913._6$	3.86	9.19 (± 0.35)	9.90 (± 0.52)	9.97 (± 0.64)	9.69 (± 0.50)
nor-$C_7H_8W(CO)_4$	B_2	$1910._1$	3.40	8.13 (± 0.17)	8.37 (± 0.43)	8.41 (± 0.47)	8.30 (± 0.36)

*,** As defined in Table 5-1.

TABLE 5-10

Specific Intensities for the CO Stretching Vibrations of the Group VI Metal-Olefin Carbonyl Complexes

		Specific Intensity,* 10^4 M^{-1} cm^{-2}			
Complex	Solvent	Ramsay	Wilson-Wells	Russell-Thompson	Mean
$C_7H_8Cr(CO)_3$	Methylene chloride	6.43 (± 0.25)	7.55 (± 0.53)	7.69 (± 0.68)	7.22 (± 0.49)
$C_7H_8Mo(CO)_3$	Methylene chloride	7.66 (± 0.23)	8.39 (± 0.60)	8.45 (± 0.72)	8.17 (± 0.52)
$C_7H_8W(CO)_3$	Methylene chloride	7.20 (± 0.13)	7.76 (± 0.42)	7.85 (± 0.43)	7.60 (± 0.34)
nor-$C_7H_8Cr(CO)_4$	n-Hexane	5.53 (± 0.15)	5.84 (± 0.62)	5.84 (± 0.72)	5.74 (± 0.50)
nor-$C_7H_8Mo(CO)_4$	n-Hexane	6.01 (± 0.20)	6.56 (± 0.31)	6.62 (± 0.32)	6.40 (± 0.28)
nor-$C_7H_8W(CO)_4$	n-Hexane	5.78 (± 0.16)	6.40 (± 0.35)	6.49 (± 0.41)	6.22 (± 0.31)

*As defined in Table 5-2.

parent hexacarbonyl, $M(CO)_6$ (Tables 5-2 and 5-5), it is evident that a marked enhancement of CO-intensity occurs upon replacement of some of the carbonyl groups with either cycloheptatriene or bicyclo[2.2.1]-hepta-2,5-diene. However, the intensity measurements of the cycloheptatriene complexes were taken in a rather polar solvent, methylene chloride, while those for the hexacarbonyl compounds were determined in non-polar n-hexane. Strictly, therefore, one should not compare the two results, as part of the increase in the CO-intensity value for the cycloheptatriene species could be explained on the basis of solvent effects alone [i.e., the marked band broadening in methylene chloride (Tables 5-8 and 5-9) indicates that considerable solvent effects were present]. In the case of the bicyclo[2.2.1]hepta-2,5-diene derivatives, a comparison with the parent hexacarbonyls is valid because both sets of intensity measurements were taken in n-hexane.

The increase in specific CO-intensity for the bicyclo[2.2.1]hepta-2,5-diene derivatives may be interpreted as evidence that there is an increase in M-CO π-electron transfer from metal to CO in the nor-$C_7H_8M(CO)_4$ species over that in the $M(CO)_6$ molecule. The enhanced M-CO π bonding upon substitution may arise from the decrease in M-L π bonding or the increase in M-L σ bonding that occurs when a ligand with lesser π-acceptor or greater π-donor ability replaces CO as donor group. Undoubtedly both these factors are important. A similar enhancement of intensity has been reported for substituted octahedral carbonyls.[60,25,65]

A comparison of CO-frequency, band-width, and intensity data for all of the group VI metal-olefin carbonyls studied shows that there is little change in the corresponding values as the metal is varied both when cycloheptatriene and when bicyclo[2.2.1]hepta-2,5-diene act as ligand. No correlation between CO-frequency or half-intensity band width and size of the metal atom is apparent; however, there seems to be a slight tendency for the CO-intensity to increase in the order Cr < W < Mo. Although the variation is small and considerable overlapping of values is present, the trend was considered to be significant because it is observed in both studies. Thus, it would appear that the extent of metal-CO π bonding is greater in molybdenum than in tungsten in the olefin complexes studied here, and hence the results are not in accord with the general trend (i.e., that for any particular type of complex, as one increases the atomic number of the transition metal atom the CO-intensities increase). So, it appears that these two series of group VI metal-olefin carbonyls are also exceptional in their behaviour in this regard.

Molybdenum- and Manganese-Phosphine Carbonyls

Another observation which has been consistently reported in the metal carbonyl CO-intensity literature is that if there is a halogen atom bonded directly to a transition metal atom, a relatively low specific CO-intensity compared to the parent carbonyl will result (Tables 5-11 to 5-13). The trend which has been generally observed is that the specific CO-intensity of a metal-halogen carbonyl complex decreases in the order I > Br > Cl; although some conflicting results have been reported, they are the exception rather than the rule. The established trend is in good agreement with π-bonding arguments since one would expect that the highly electronegative halogen atoms would withdraw charge from the central metal atom leaving less metal dπ-electron density available for backbonding with the CO groups.

TABLE 5-11

Specific Intensities for the CO Stretching Vibrations of Some Series of Group VI Metal-Halogen Carbonyl Complexes[a]

Complex	Solvent	Specific Intensity[b] 10^4 M^{-1} cm^{-2}	Reference
$Cr(CO)_6$	Tetrahydrofuran	6.10	c
$Cr(CO)_5Cl^-$	Chloroform	4.47	d
$Cr(CO)_5Br^-$	Chloroform	4.52	d
$Cr(CO)_5I^-$	Chloroform	6.28	d
$W(CO)_6$	Tetrahydrofuran	7.75	c
$W(CO)_5Cl^-$	Chloroform	6.24	d
$W(CO)_5Br^-$	Chloroform	6.08	d
$W(CO)_5I^-$	Chloroform	6.20	d

[a] S. F. A. Kettle and I. Paul in "Advances in Organometallic Chemistry," Vol. X, F. G. A. Stone and R. West, Ed., Academic Press, Inc., New York, N. Y., 1972, p 225.

[b] As defined in Table 5-2.

[c] W. Beck and R. E. Nitzmann, Z. Naturforsch., 17b, 577 (1962).

[d] E. W. Abel and I. S. Butler, Trans. Faraday Soc., 63, 45 (1967).

TABLE 5-12

Specific Intensities for the CO Stretching Vibrations of Some Series of Group VII Metal-Halogen Carbonyl Complexes[a]

Complex	Solvent	Specific Intensity[b] 10^4 M^{-1} cm^{-2}	Reference
$Mn(CO)_6^+$	Tetrahydrofuran	2.52	e
$Mn(CO)_5Cl$	Chloroform	3.06	d
$Mn(CO)_5Br$	Chloroform	3.76	d
$Mn(CO)_5I$	Chloroform	4.23	d
cis-$Mn(CO)_4ClBr^-$	Chloroform	2.77	d
cis-$Mn(CO)_4Br_2^-$	Chloroform	3.47	d
cis-$Mn(CO)_4BrI^-$	Chloroform	3.48	d
cis-$Mn(CO)_4I_2^-$	Chloroform	3.99	d
$Mn_2(CO)_{10}$	Chloroform	3.53	e
$Mn_2(CO)_8Cl_2$	Chloroform	2.51	d
$Mn_2(CO)_8Br_2$	Chloroform	2.70	d
$Mn_2(CO)_8I_2$	Chloroform	3.54	d
$Re(CO)_6^+$	Chloroform	2.11	e
$Re(CO)_5Br$	Chloroform	4.25	d
$Re(CO)_5I$	Chloroform	4.19	d

[a] S. F. A. Kettle and I. Paul in "Advances in Organometallic Chemistry," Vol. X, F. G. A. Stone and R. West, Ed., Academic Press, Inc., New York, N. Y., 1972, pp 224, 225, 226, 230.

[b] As defined in Table 5-2.

[c] W. Beck and R. E. Nitzmann, Z. Naturforsch., 17B, 577 (1962).

[d] E. W. Abel and I. S. Butler, Trans. Faraday Soc., 63, 45 (1967).

[e] R. M. Wing and D. C. Crocker, Inorg. Chem., 6, 289 (1967).

TABLE 5-13

Specific Intensities for the CO Stretching Vibrations of Some Series of Iron-Halogen Carbonyl Complexes[a]

Complex	Solvent	Specific Intensity[b] 10^4 M^{-1} cm^{-2}	Reference
$Fe(CO)_5$	n-Hexane	3.46	c
cis-$Fe(CO)_3Cl \cdot H_2C{=}CH{-}CH_2$	n-Hexane	2.83	c
cis-$Fe(CO)_3Br \cdot H_2C{=}CH{-}CH_2$	n-Hexane	2.83	c
cis-$Fe(CO)_3Cl \cdot H_2C{=}CH{-}CHCH_3$	n-Hexane	2.90	c
cis-$Fe(CO)_3Br \cdot H_2C{=}CH{-}CHCH_3$	n-Hexane	2.80	c
cis-$Fe(CO)_4Cl_2$	Tetrachloroethylene	1.66	c
cis-$Fe(CO)_4Br_2$	n-Hexane	1.84	c
cis-$Fe(CO)_4I_2$	n-Hexane	2.30	c
$\pi{-}C_5H_5Fe(CO)_2Cl$	n-Hexane	2.7	d
$\pi{-}C_5H_5Fe(CO)_2Br$	n-Hexane	2.9	d
$\pi{-}C_5H_5Fe(CO)_2I$	n-Hexane	3.1	d
$\pi{-}C_5H_5Fe(CO)_2Cl$	Chloroform	3.69	e
$\pi{-}C_5H_5Fe(CO)_2I$	Chloroform	3.64	e

[a] S. F. A. Kettle and I. Paul in "Advances in Organometallic Chemistry," Vol. X, F. G. A. Stone and R. West, Ed., Academic Press, Inc., New York, N. Y., 1972, pp 226-228.

[b] As defined in Table 5-2.

[c] K. Noack, Helv. Chim. Acta, 45, 1847 (1962)

[d] J. Dalton, I. Paul and F. G. A. Stone, J. Chem. Soc., A, 2744 (1969).

[e] D. J. Darensbourg, Inorg. Chem., 11, 1606 (1972).

TABLE 5-14

Specific Intensities for the CO Stretching Vibrations of Some Series of Metal-Carbonyl Complexes with Phosphorus, Silicon, and Tin Ligands

Complex	Solvent	Specific Intensity[a] 10^4 M^{-1} cm^{-2}	Reference
$Mo(CO)_6$	*n*-Hexane	5.33	b
$Mo(CO)_5PCl_3$	*n*-Hexane	5.22	b
$Mo(CO)_5P(C_6H_5)_3$	*n*-Hexane	6.14	b
$Mo(CO)_6$	Cyclohexane	4.2	c
fac-$Mo(CO)_3(PCl_3)_3$	Cyclohexane	4.2	c
$Co(CO)_4SiCl_3$	*n*-Hexane	3.15	d
$Co(CO)_4Si(C_6H_5)_3$	*n*-Hexane	3.80	d
π-$C_5H_5Fe(CO)_2SnCl_3$	Chloroform	3.1	e
π-$C_5H_5Fe(CO)_2Sn(C_6H_5)_3$	Chloroform	3.1	e

[a] As defined in Table 5-2.

[b] T. L. Brown and D. J. Darensbourg, *Inorg. Chem.*, 6, 971 (1967); D. J. Darensbourg and T. L. Brown, *Inorg. Chem.*, 7, 959 (1968).

[c] D. Benlian and M. Bigorgne, *Bull. Soc. Chim. France*, 4106 (1967).

[d] D. J. Darensbourg, *Inorg. Chim. Acta*, 4, 597 (1970).

[e] J. Dalton, I. Paul, and F. C. A. Stone, *J. Chem. Soc.*, A, 2744 (1969).

Noack has shown that the halogen effect was additive for some of the iron halogen derivatives (Table 5-13) that he studied. It would be interesting to see if his observation could be extended to other halogen-containing metal carbonyl complexes where the halogen is not bonded directly to the central metal atom. In metal-halophosphine carbonyls, for instance, one would expect that the halogen effect, although somewhat diminished in magnitude, would be transmitted through the phosphorus atom to the central metal atom and so on to the CO groups.

With this idea in mind, a preliminary investigation of a series of *fac*-$Mo(CO)_3[P(C_6H_5)_{3-x}Cl_x]_3$ (x = 1-3) was undertaken. The CO frequencies and half-intensity band widths were examined to see if any definitive trends could be observed (Table 5-15). Both band characteristics seemed to be affected in the expected manner with successive substitution of chlorine atoms onto the phosphine ligand. Moreover, a comparison of the $\Delta\nu_{\frac{1}{2}}^{t}$ values for the *fac*-$Mo(CO)_3(PCl_3)_3$ complex measured in a rather polar solvent, methylene chloride, and in non-polar *n*-hexane indicated a rather strong solvent effect on band characteristics as well. The results for the series suggest that solvent and substitution effects act in the same way.

It is difficult to define the properties which mainly affect the $\Delta\nu_{\frac{1}{2}}^{t}$ values. It may be supposed that the extent of polarization of the carbonyl groups and their ability to interact with their environment depend upon a combined action of the σ-donor and π-acceptor properties of the ligands.[67] However, steric effects should not be overlooked; the largest $\Delta\nu_{\frac{1}{2}}^{t}$ values were obtained in the more strongly reacting solvent as well as with the bulkier substituent ligands. Likewise, the CO frequencies reflect the combined action of σ-donor and π-acceptor properties of the substituents; that is, the steady decrease in CO frequencies along the series fac-$Mo(CO)_3(PCl_3)_3$, fac-$Mo(CO)_3[P(C_6H_5)Cl_2]_3$, and fac-$Mo(CO)_3[P(C_6H_5)_2Cl]_3$ implies that there is either a net decrease in M-CO σ-bond strength, or an increase in M-CO π bonding, or both.

In order to gain more insight into the σ and π contributions to the bonding in the various phosphine ligands, we decided to measure the CO intensities of the compounds. Since the preliminary investigation of the fac-$Mo(CO)_3[P(C_6H_5)_{3-x}Cl_x]_3$ (x = 1-3) complexes revealed such definite trends in CO frequencies and half-intensity band widths with successive substitution of chlorine onto the phosphine, and since specific CO intensities for a similar series of complexes demonstrated the expected dependence on chlorine (Table 5-14), a study of the CO-intensities for this series of compounds was undertaken to see if a similar trend would occur.

The fac-$Mo(CO)_3[P(C_6H_5)_{3-x}Cl_x]_3$ (x = 1-3) molecules are octahedral with the three carbonyl groups arranged cis to one another (Figure 5-7); the formal symmetry is C_{3v}. The three carbonyls are expected to give rise to two infrared-active CO stretching modes: a symmetric A_1 stretching mode and a degenerate E mode (Figure 5-8). All three compounds display two strong bands in the CO stretching region as predicted.

The CO-intensity data for the molybdenum-phosphine carbonyls are presented in Tables 5-15 to 5-17. The results are somewhat surprising. Firstly, although there is a marked solvent effect upon the $\Delta\nu_{\frac{1}{2}}^{t}$ values, no solvent effect upon the integrated intensities is apparent in this study. Intensity results for fac-$Mo(CO)_3(PCl_3)_3$ determined in polar methylene chloride and in non-polar n-hexane show no significant change;

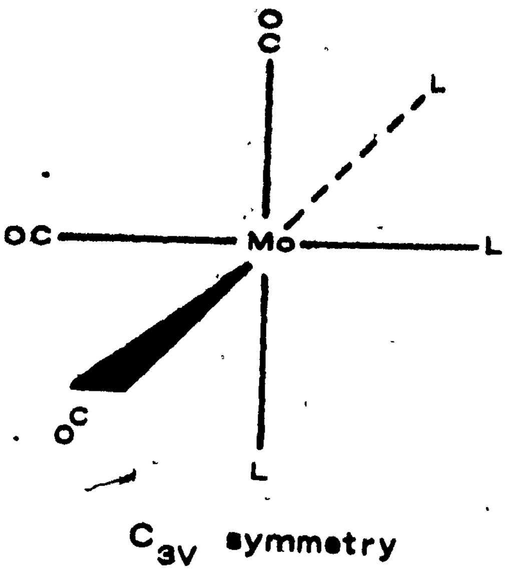

Figure 5-7. Structure of the *fac*-Mo(CO)$_3$L$_3$ Molecule [L = PCl$_3$, P(C$_6$H$_5$)Cl$_2$, P(C$_6$H$_5$)$_2$Cl].

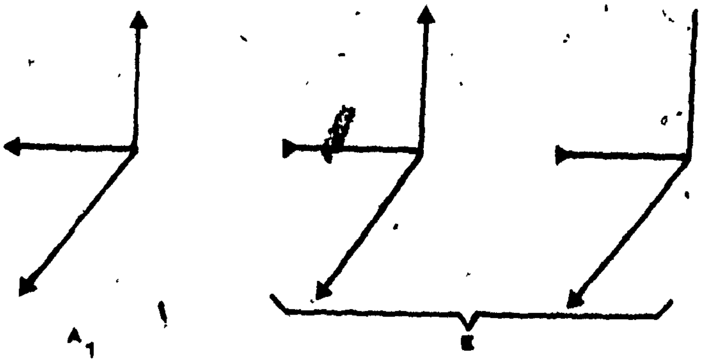

Figure 5-8. Infrared-Active CO Stretching Vibrations of the *fac*-Mo(CO)$_3$L$_3$ Molecule [L = PCl$_3$, P(C$_6$H$_5$)Cl$_2$, P(C$_6$H$_5$)$_2$Cl].

TABLE 5-15

Infrared Frequencies, Half-Intensity Band Widths, and Absolute Integrated Absorption Intensities for the CO Stretching Vibrations of the *fac*-$Mo(CO)_3(Phosphine)_3$ Complexes

			ν_{max}	$\Delta\nu_{\frac{1}{2}}$*	E,** 10^4 M^{-1} cm^{-2}			
Complex	Solvent	Normal mode	cm^{-1}	cm^{-1}	Ramsay	Wilson-Wells	Russell-Thompson	Mean
fac-$Mo(CO)_3(PCl_3)_3$	n-Hexane	A_1	$2040._2$	1.43	6.64 (± 0.22)	7.17 (± 0.34)	7.29 (± 0.35)	7.03 (± 0.30)
fac-$Mo(CO)_3(PCl_3)_3$	Methylene chloride	A_1	$2039._9$	10.5	6.10 (± 0.13)	6.07 (± 0.40)	6.64 (± 0.43)	6.07 (± 0.32)
fac-$Mo(CO)_3[P(C_6H_5)Cl_2]_3$	Methylene chloride	A_1	$2006._0$	12.9	5.77 (± 0.09)	5.90 (± 0.32)	5.90 (± 0.36)	5.86 (± 0.26)
fac-$Mo(CO)_3[P(C_6H_5)_2Cl]_3$	Methylene chloride	A_1	$1970._5$	13.6	6.20 (± 0.17)	6.17 (± 1.00)	5.92 (± 0.79)	6.10 (± 0.65)
fac-$Mo(CO)_3(PCl_3)_3$	n-Hexane	E	$1991._1$	4.46	10.1 (± 0.3)	10.7 (± 0.5)	10.7 (± 0.6)	10.5 (± 0.5)
fac-$Mo(CO)_3(PCl_3)_3$	Methylene chloride	E	$1986._6$	26.8	11.3 (± 0.3)	11.2 (± 1.1)	11.1 (± 1.1)	11.2 (± 0.8)
fac-$Mo(CO)_3[P(C_6H_5)Cl_2]_3$	Methylene chloride	E	$1940._8$	33.2	11.0 (± 0.1)	10.8 (± 0.5)	10.8 (± 0.6)	10.9 (± 0.4)
fac-$Mo(CO)_3[P(C_6H_5)_2Cl]_3$	Methylene chloride	E	$1889._4$	37.0	12.1 (± 0.5)	11.4 (± 3.0)	10.8 (± 2.7)	11.4 (± 2.1)

*,** As defined in Table 5-1.

TABLE 5-16

Intensity Ratio of the Symmetric to the Antisymmetric CO Stretching Vibration for the *fac*-$Mo(CO)_3(Phosphine)_3$ Complexes

Complex	Solvent	E,* 10^4 M^{-1} cm^{-2}		$\frac{E_s}{E_a}$
		A_1	E	
fac-$Mo(CO)_3(PCl_3)_3$	*n*-Hexane	7.03 (± 0.30)	10.5 (± 0.5)	0.670
fac-$Mo(CO)_3(PCl_3)_3$	Methylene chloride	6.07 (± 0.32)	11.2 (± 0.5)	0.542
fac-$Mo(CO)_3[P(C_6H_5)Cl_2]_3$	Methylene chloride	5.86 (± 0.26)	10.9 (± 0.4)	0.538
fac-$Mo(CO)_3[P(C_6H_5)_2Cl]_3$	Methylene chloride	6.10 (± 0.65)	11.4 (± 2.1)	0.535

*As defined in Table 5-1. The numbers reported are the mean values for the three methods of determination; the average standard deviations for the three methods are in parentheses.

TABLE 5-17

Specific Intensities for the CO Stretching Vibrations of the fac-$Mo(CO)_3(Phosphine)_3$ Complexes and of the cis-$Mn(CO)_4LBr$ Complexes

Complex	Solvent	Specific Intensity,* 10^4 M^{-1} cm^{-2} Ramsay	Wilson-Wells	Russell-Thompson	Mean
fac-$Mo(CO)_3(PCl_3)_3$	n-Hexane	5.57 (± 0.17)	5.96 (± 0.29)	6.01 (± 0.32)	5.85 (± 0.26)
fac-$Mo(CO)_3(PCl_3)_3$	Methylene chloride	5.81 (± 0.14)	5.74 (± 0.49)	5.71 (± 0.51)	5.75 (± 0.38)
fac-$Mo(CO)_3[P(C_6H_5)Cl_2]_3$	Methylene chloride	5.58 (± 0.06)	5.56 (± 0.28)	5.56 (± 0.31)	5.57 (± 0.22)
fac-$Mo(CO)_3[P(C_6H_5)_2Cl]_3$	Methylene chloride	6.11 (± 0.22)	5.85 (± 1.34)	5.56 (± 1.18)	5.84 (± 0.91)
cis-$Mn(CO)_4[P(C_6H_5)_3]Br$	n-Hexane	3.50 (± 0.12)	3.70 (± 0.25)	3.73 (± 0.28)	3.64 (± 0.22)
cis-$Mn(CO)_4[As(C_6H_5)_3]Br$	n-Hexane	3.62 (± 0.11)	3.60 (± 0.30)	3.59 (± 0.32)	3.60 (± 0.24)
cis-$Mn(CO)_4[Sb(C_6H_5)_3]Br$	n-Hexane	3.70 (± 0.12)	3.93 (± 0.18)	3.96 (± 0.20)	3.86 (± 0.17)

*As defined in Table 5-2.

apparently, the increase in band width with the polar solvent is roughly compensated by the decrease in peak height. It should be noted, however, that Penlian and Bigorgne's[63] value (determined by the Wilson-Wells method) for fac-$Mo(CO)_3(PCl_3)_3$ in cyclohexane solution, $4.2 \times 10^4\ M^{-1}\ cm^{-2}$, is considerably lower than our results (also obtained by the Wilson-Wells extrapolation method) for both n-hexane and methylene chloride solution, 5.96 and $5.74 \times 10^4\ M^{-1}\ cm^{-2}$, respectively. This may reflect either a difference in measuring technique or a solvent effect or both.

Second, if our result (obtained by Ramsay's method) for fac-$Mo(CO)_3$-$(PCl_3)_3$ in n-hexane solution is compared with the published value (also determined by Ramsay's method) for $Mo(CO)_6$ (Table 5-5) measured in the same solvent, it is evident that there is no significant change in the specific CO-intensity as one goes from the parent hexacarbonyl, $5.39 \times 10^4\ M^{-1}\ cm^{-2}$,[60] to the phosphine complex, $5.57 \times 10^4\ M^{-1}\ cm^{-2}$ [a point observed by Penlian and Bigorgne[63] as well in their measurements on $Mo(CO)_6$ and $Mo(CO)_3(PCl_3)_3$ (Table 5-14)]. This may be interpreted as evidence that there is little change in the M-CO π-electron transfer from metal to CO in the phosphine derivative compared to the $Mo(CO)_6$ molecule. Evidently any increase in the M-L σ bonding due to withdrawal of charge by the highly electronegative chlorine atoms is roughly compensated by a decrease in M-L π bonding so that the expected decrease in the M-CO π bonding upon substitution does not occur.

Moreover, unlike the $\Delta\nu_{\frac{1}{2}}^{t}$ values and the CO frequencies, no effect of ligand upon the integrated intensities is evident, indicating that there is essentially no change in the extent of M-CO π bonding in the three substituents, PCl_3, $P(C_6H_5)Cl_2$ and $P(C_6H_5)_2Cl$. This observation strongly suggests that the decrease in CO frequency as one goes from PCl_3 to

$P(C_6H_5)_2Cl$ stems mainly from a weakening of the CO σ bond, and not from an increase in π bonding. The fact that there is no appreciable change in the intensity ratios either with the three ligands (Table 5-16) further supports this conclusion. Although this is not the expected result, similar conclusions concerning M-P bonding characteristics have been reported.[65,75-78] It should be emphasised, however, that when bulky ligand groups are present, intensity results should not be interpreted simply on the basis of the π-acceptor and σ-donor ligand abilities alone. Geometrical factors, particularly as far as steric distortion by the substituent ligand is concerned, should also be considered.

Another interesting aspect of CO-intensity studies on metal-phosphine carbonyls is with phosphine-like ligands such as arsines and stibines. Several studies have been carried out on series of metal carbonyl complexes with phosphorus, arsenic, and antimony (or with silicon, germanium and tin) donor ligands (Tables 5-19 and 5-20); however, no general trend is apparent.

From a comparison of the CO frequencies and half-intensity band widths for the series of *cis*-$Mn(CO)_4LBr$ complexes containing triphenylphosphine, -arsine, and -stibine ligands (Table 5-18), it is clear that there is no obvious trend. It appears, therefore, that there is either no difference in the σ- and π-bonding abilities in the three ligands or that any differences in σ and π bonding complement one another (i.e., a decrease in σ bonding in any one ligand may be compensated by an increase in π bonding and *vice versa*). In the hope of gaining some more information concerning the bonding characteristics of the three ligands, we decided to measure the CO intensities of the tetracarbonyl complexes.

TABLE 5-18

Infrared Frequencies, Half-Intensity Band Widths, and Absolute Integrated Absorption Intensities for the CO Stretching Vibrations of the *cis*-$Mn(CO)_4LBr$ Complexes in *n*-Hexane Solution

Complex	Normal mode	ν_{max} cm^{-1}	$\Delta\nu_{\frac{1}{2}}^{t*}$ cm^{-1}	E,** 10^4 M^{-1} cm^{-2} Ramsay	Wilson-Wells	Russell-Thompson	Mean
cis-$Mn(CO)_4[P(C_6H_5)_3]Br$	$A'^{(2)}$	$2089._2$	2.66	1.61 (± 0.03)	1.62 (± 0.11)	1.63 (± 0.12)	1.62 (± 0.09)
cis-$Mn(CO)_4[As(C_6H_5)_3]Br$	$A'^{(2)}$	$2091._8$	2.60	1.58 (± 0.02)	1.51 (± 0.06)	1.51 (± 0.06)	1.53 (± 0.05)
cis-$Mn(CO)_4[Sb(C_6H_5)_3]Br$	$A'^{(2)}$	$2087._5$	3.06	1.87 (± 0.06)	2.00 (± 0.11)	2.02 (± 0.12)	1.96 (± 0.10)
cis-$Mn(CO)_4[P(C_6H_5)_3]Br$	$A'^{(1a)}$	$2024._6$	5.83	3.25 (± 0.11)	3.42 (± 0.26)	3.45 (± 0.29)	3.38 (± 0.22)
cis-$Mn(CO)_4[As(C_6H_5)_3]Br$	$A'^{(1a)}$	$2023._7$	6.00	3.91 (± 0.17)	4.20 (± 0.42)	4.19 (± 0.48)	4.10 (± 0.36)
cis-$Mn(CO)_4[Sb(C_6H_5)_3]Br$	$A'^{(1a)}$	$2021._6$	5.48	3.34 (± 0.11)	3.62 (± 0.09)	3.65 (± 0.11)	3.54 (± 0.11)
cis-$Mn(CO)_4[P(C_6H_5)_3]Br$	A''	$2006._4$	6.58	5.33 (± 0.26)	5.75 (± 0.52)	5.82 (± 0.59)	5.63 (± 0.46)
cis-$Mn(CO)_4[As(C_6H_5)_3]Br$	A''	$2011._4$	6.48	5.21 (± 0.13)	5.15 (± 0.35)	5.13 (± 0.37)	5.16 (± 0.28)
cis-$Mn(CO)_4[Sb(C_6H_5)_3]Br$	A''	$2009._2$	6.91	5.57 (± 0.22)	6.01 (± 0.27)	6.09 (± 0.30)	5.89 (± 0.26)
cis-$Mn(CO)_4[P(C_6H_5)_3]Br$	$A'^{(b)}$	$1960._8$	11.0	3.80 (± 0.09)	4.01 (± 0.11)	4.04 (± 0.12)	3.95 (± 0.11)
cis-$Mn(CO)_4[As(C_6H_5)_3]Br$	$A'^{(b)}$	$1962._3$	10.5	3.77 (± 0.12)	3.54 (± 0.36)	3.51 (± 0.36)	3.61 (± 0.28)
cis-$Mn(CO)_4[Sb(C_6H_5)_3]Br$	$A'^{(b)}$	$1960._4$	10.5	4.01 (± 0.09)	4.07 (± 0.26)	4.07 (± 0.28)	4.05 (± 0.21)

*,** As defined in Table 5-1.

TABLE 5-19

Specific Intensities for the CO Stretching Vibrations of Some Series of Metal-Carbonyl Complexes with Phosphorus, Arsenic and Antimony Ligands[a]

Complex	Solvent	Specific Intensity[b] $10^4\ M^{-1}\ cm^{-2}$	Reference
$Mo(CO)_6$	*n*-Hexane	5.33	c
$Mo(CO)_5P(C_6H_5)_3$	*n*-Hexane	6.14	c
$Mo(CO)_5As(C_6H_5)_3$	*n*-Hexane	5.67	c
$Mo(CO)_5Sb(C_6H_5)_3$	*n*-Hexane	5.78	c
$Mo(CO)_6$	Cyclohexane	4.20	d
cis-$Mo(CO)_4[P(C_2H_5)_3]_2$	Cyclohexane	4.50	d
cis-$Mo(CO)_4[Sb(C_2H_5)_3]_2$	Cyclohexane	4.80	d
$Co(CO)_3NO$	Cyclohexane	3.2	e
$Co(CO)_2NOP(C_6H_5)_3$	Cyclohexane	4.0	e
$Co(CO)_2NOAs(C_6H_5)_3$	Cyclohexane	3.9	e
$Co(CO)_2NOSb(C_6H_5)_3$	Cyclohexane	3.3	e
π-$C_5H_5Mn(CO)_3$	Carbon disulphide	4.2	f
π-$C_5H_5Mn(CO)_2P(C_6H_5)_3$	Carbon disulphide	4.7	f
π-$C_5H_5Mn(CO)_2As(C_6H_5)_3$	Carbon disulphide	4.8	f
π-$C_5H_5Mn(CO)_2Sb(C_6H_5)_3$	Carbon disulphide	4.7	f

[a] S. F. A. Kettle and I. Paul in "Advances in Organometallic Chemistry," Vol. X, F. G. A. Stone and R. West, Ed., Academic Press, Inc., New York, N. Y., 1972, pp 225, 229.

[b] As defined in Table 5-2.

[c] T. L. Brown and D. J. Darensbourg, Inorg. Chem., 6, 971 (1967); D. J. Darensbourg and T. L. Brown, Inorg. Chem., 7, 959 (1968).

[d] D. Benlian and M. Bigorgne, Bull. Soc. Chim. France, 4100 (1967).

[e] A. Poletti, A. Foffani, R. Cataliotti, Spectrochim. Acta, 26A, 1063 (1970).

[f] W. P. Anderson, T. B. Brill, A. R. Schoenberg, and C. W. Stanger, Jr., J. Organometal. Chem., 44, 161 (1972).

TABLE 5-20

Specific Intensities for the CO Stretching Vibrations of Some Series of Iron-Carbonyl Complexes with Phosphorus, Silicon, Germanium, and Tin Ligands

Complex	Solvent	Specific Intensity[a] 10^4 M^{-1} cm^{-2}	Reference
$Fe(CO)_5$	n-Hexane	3.46	b
$Fe(CO)_4P(C_6H_5)_3$	n-Hexane	4.00	c
π-$C_5H_5Fe(CO)_2SiCl_3$	Chloroform	3.2	d
π-$C_5H_5Fe(CO)_2GeCl_3$	Chloroform	3.0	d
π-$C_5H_5Fe(CO)_2SnCl_3$	Chloroform	3.1	d

[a] As defined in Table 5-2.

[b] K. Noack, Helv. Chim. Acta, 45, 1847 (1962).

[c] D. J. Darensbourg, Inorg. Chim. Acta, 4, 592 (1970).

[d] J. Dalton, I. Paul, and F. G. A. Stone, J. Chem. Soc., A, 2744 (1969).

The *cis*-Mn(CO)$_4$LBr [L = P(C$_6$H$_5$)$_3$, As(C$_6$H$_5$)$_3$, Sb(C$_6$H$_5$)$_3$] molecules have an octahedral structure with a *cis* arrangement of the L and Br groups (Figure 5-9). This configuration results in formal C_s symmetry for which group theory predicts four infrared-active CO stretching frequencies (3A' + A"). The four modes are very similar to those in the *nor*-C$_7$H$_8$M(CO)$_4$ species. The *trans* pair of carbonyls should give rise to a weak symmetric $A'^{(2)}$ mode (analagous to the $A_1^{(2)}$ mode of the *nor*-C$_7$H$_8$M(CO)$_4$ molecule) and to a strong antisymmetric A" stretching mode (analagous to the *nor*-C$_7$H$_8$M(CO)$_4$ B_1 mode). The carbonyl *trans* to the L group should give a symmetric $A'^{(1a)}$ mode of medium intensity and the carbonyl *trans* to the Br group should produce another symmetric $A'^{(1b)}$ mode of comparable intensity (Figure 5-10). The infrared spectra show four well-resolved bands as expected.

Possible assignments for the infrared spectra of the *cis*-Mn(CO)$_4$LBr species were made on the basis of the similarity of the vibrational modes to those of *nor*-C$_7$H$_8$Cr(CO)$_4$. Thus, the highest frequency absorption was assigned to the $A'^{(2)}$ mode and the most intense peak was assigned to the A" mode. The greater inductive character and lower π-bonding ability of the bromide compared with the phosphine, arsine and stibine led to the assignment of the lowest frequency peak to the $A'^{(1b)}$ stretching mode of the carbonyl *trans* to the bromide, and leaving the $A'^{(1a)}$ mode to the remaining unassigned peak. These assignments have now been verified by an infrared spectrascopic study of the exchange reactions of *cis*-Mn(CO)$_4$LBr with ^{13}CO and subsequent approximate force constant calculations.[79]

The CO intensities for the *cis*-Mn(CO)$_4$LBr complexes are presented in Tables 5-17 and 5-18. A comparison of the results shows that, as for the

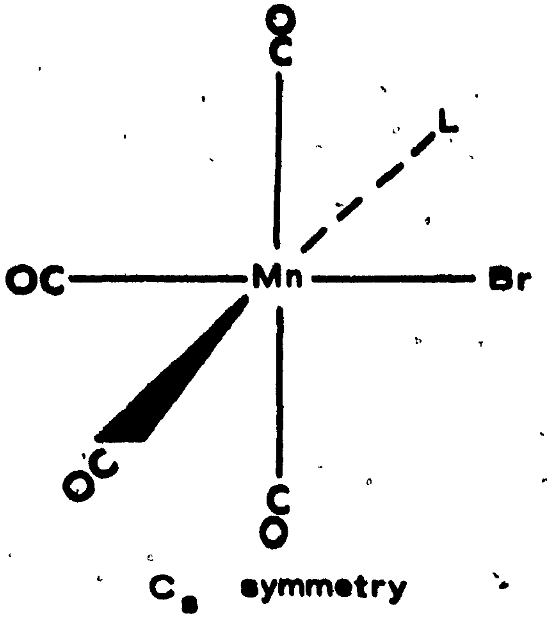

Figure 5-9. Structure of the <u>cis</u>-$Mn(CO)_4LBr$ Molecule [L = $P(C_6H_5)_3$, $As(C_6H_5)_3$, $Sb(C_6H_5)_3$].

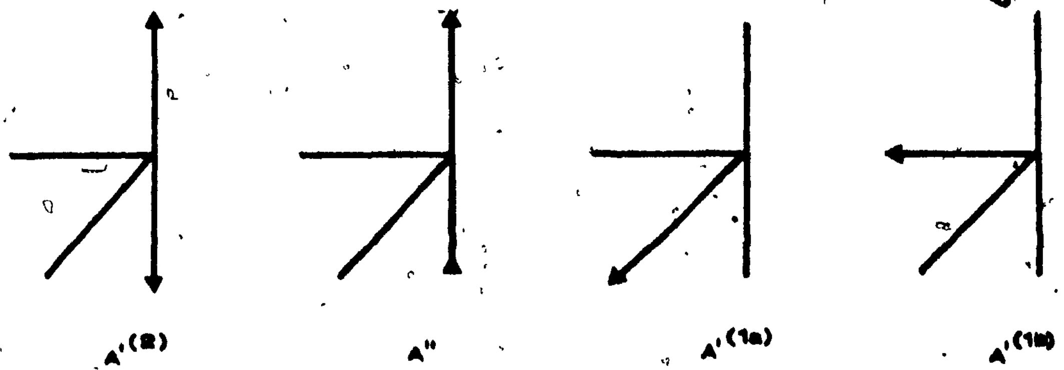

Figure 5-10 Infrared Active CO Stretching Vibrations of the <u>cis</u>-$Mn(CO)_4LBr$ Molecule [L = $P(C_6H_5)_3$, $As(C_6H_5)_3$, $Sb(C_6H_5)_3$].

CO frequencies and half-band widths, the intensity values with L = $P(C_6H_5)_3$, $As(C_6H_5)_3$ and $Sb(C_6H_5)_3$ are very close. So, it may be taken that the extent of metal-ligand π bonding in phosphorus, arsenic and antimony is essentially the same. In conclusion, therefore, it appears that both the σ-donor and the π-acceptor properties of phosphorus, arsenic and antimony towards manganese are equivalent.

Other workers have reached similar conclusions concerning the M-P, M-As and M-Sb bond strengths in molybdenum and nickel complexes. Specifically, (1) CO-frequency studies[44] on tricarbonylmolybdenum compounds containing triphenylphosphine, -arsine and -stibine ligands and (2) dipole-moment measurements[80] on complexes containing Ni-P and Ni-As bonds have indicated that the differences in multiple bonding capacities of phosphorus, arsenic and antimony towards a transition metal atom are virtually negligible. However, as mentioned earlier in the discussion of the molybdenum-phosphine carbonyls (vide supra), steric effects may also be important in the interpretation of infrared results when bulky ligand groups are present. Thus, geometrical factors as well as π-acceptor and σ-donor ligand abilities should be considered when interpreting the results.

π-Cyclopentadienylmanganese(I) Complexes

Clarification of the ability of metal-arene carbonyls to transfer an electronic effect through the transition metal atom is a subject of considerable interest. With this aim in mind, several workers have attempted to correlate the CO intensities of metal-arene carbonyl complexes with the electron acceptor ability of the ring substituents. Nesmeyanov et al.[58] have demonstrated that for a series of

TABLE 5-21

Specific Intensities for the CO Stretching Vibrations of Some Series of Group VII Metal-Cyclopentadienyl Carbonyl Complexes[a]

Complex	Solvent	Specific Intensity[b] $10^4\ M^{-1}\ cm^{-2}$	Reference
$CpMn(CO)_3$	Carbon tetrachloride		c
$Cp = \pi\text{-}C_5H_5$		4.85	
$Cp = \pi\text{-}C_3H_7C_5H_4$		4.86	
$Cp = \pi\text{-}C_6H_5CH_2C_5H_4$		4.83	
$Cp = \pi\text{-}COCH_2C_5H_4$		4.50	
$Cp = \pi\text{-}C_6H_5COC_5H_4$		4.59	
$Cp = \pi\text{-}CF_3COC_5H_4$		4.14	
$Cp = \pi\text{-}(C_2H_5)_2C_5H_3$		5.05	
$Cp = \pi\text{-}C(CH_3)_3(C_6H_5CO)C_5H_3$		4.75	
$Cp = \pi\text{-}(C_2H_5)_2(CH_3CO)C_5H_2$		4.82	
$Cp = \pi\text{-}(C_2H_5)_3(CH_3CO)C_5H$		4.94	
$Cp = \pi\text{-}(C_2H_5)_4(CH_3CO)C_5$		4.97	
$Cp = \pi\text{-}(C_2H_5)_4C_5H$		5.30	
$CpRe(CO)_3$	Carbon tetrachloride		c
$Cp = \pi\text{-}C_5H_5$		5.36	
$Cp = \pi\text{-}CH_3COC_5H_4$		4.92	
$Cp = \pi\text{-}C_6H_5COC_5H_4$		5.14	

[a] S. F. A. Kettle and I. Paul in "Advances in Organometallic Chemistry," Vol. X, F. G. A. Stone and R. West, Ed., Academic Press, Inc., New York, N. Y., 1972, p 227.

[b] As defined in Table 5-2.

[c] A. N. Nesmeyanov, G. G. Dvoryantseva, Kh. P. Pustyl'nik, Yu. N. Sheinker, N. E. Kolobova, and K. N. Anisimov, *Dokl. Akad. Nauk SSSR*, *174*, 368 (1967); *Acad. Sci. USSR Chem.*, *174*, 457 (1967).

TABLE 5-22

Specific Intensities for the CO Stretching Vibrations of Some Series of Arene-Chromium Carbonyl Complexes[a]

Complex	Solvent	Specific Intensity[b] $10^4\ M^{-1}\ cm^{-2}$	Reference
$RC_6H_4COOCH_3Cr(CO)_3$	Carbon tetrachloride		c
R = m-$COOCH_3$		6.07	
R = p-$COOCH_3$		4.73	
R = o-Cl		5.13	
R = m-Cl		4.53	
R = p-Cl		4.23	
R = H		5.03	
R = o-CH_3		5.07	
R = m-CH_3		5.30	
R = p-CH_3		5.73	
R = o-OCH_3		5.60	
R = p-OCH_3		5.20	
$C_6H_6Cr(CO)_3$	Cyclohexane	4.50	d
$(C_2H_5)_6C_6Cr(CO)_3$	Cyclohexane	5.31	d

[a] S. F. A. Kettle and I. Paul in "Advances in Organometallic Chemistry," Vol. X, F. G. A. Stone and R. West, Ed., Academic Press, Inc., New York, N. Y., 1972, p 227.

[b] As defined in Table 5-2.

[c] G. Klopman and K. Noack, Inorg. Chem., 7, 579 (1968).

[d] R. D. Fischer, Spectrochim. Acta, 19, 842 (1963).

π-cyclopentadienyltricarbonylmanganese(I) and -rhenium(I) derivatives the specific CO intensities decrease with the electron acceptor ability of the ring substituents (Table 5-21). That is, the electronic effects on the cyclopentadienyl ring are transmitted to the central metal atom and then to the CO groups. This is in contrast to the observations of Klopman and Noack[64] on a series of substituted benzoic-methyl-ester tricarbonyl chromium derivatives (Table 5-22). These workers observed only small variations in specific intensity which could not be correlated with the properties of the substituents.

In this work, the CO intensities of two ring-substituted derivatives of π-cyclopentadienyltricarbonylmanganese(I) were measured. At the same time, the CO and CS intensities of the thiocarbonyl complex, π-$C_5H_5Mn(CO)_2CS$, were studied to see if we could say something about the relative bonding properties of CO and CS. Thiocarbonyls have been known since 1966, when Baird and Wilkinson[81] synthesized trans-$Rh(CS)[P(C_6H_5)_3]_2X$ (X = Cl, Br). However, as yet, there have been no intensity studies to determine how CS compares to CO as a ligand. Physical and chemical evidence indicate that CS is both a better σ- and π-bonding ligand than CO.[82,83]

The π-$RC_5H_4Mn(CO)_3$ (R = H; CH_3) molecules have a piano-stool-type structure [32] (Figure 5-11). Moreover, since there is free rotation of the cyclopentadienyl ring about the metal-ring axis (irrespective of the presence of substituents on the ring[32]), the molecules possess C_{3v} symmetry. Two infrared-active CO stretching modes (A_1 + E) are expected for structures of this type. The cis carbonyls should give rise to a symmetric A_1 stretching mode and a degenerate E mode (Figure 5-12). The spectra show two well-resolved bands in accordance with the group theoretical predictions.

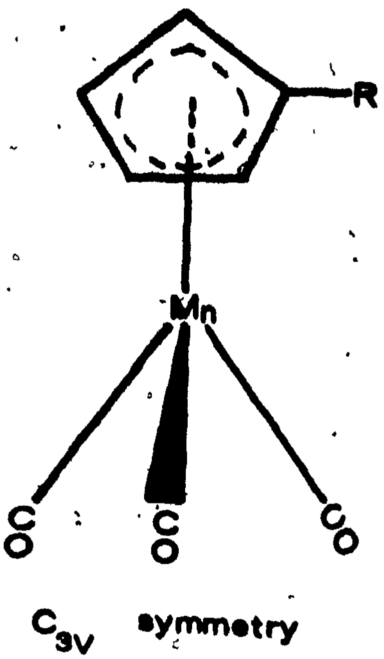

Figure 5-11. Structure of the $(\pi\text{-}RC_5H_4)Mn(CO)_3$ Molecule (R = H, CH_3).

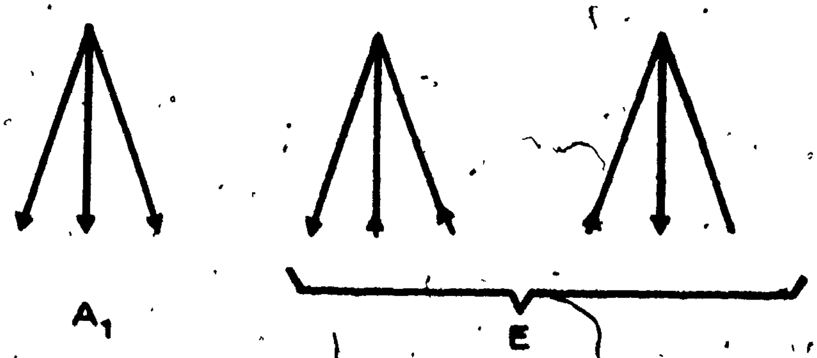

Figure 5-12. Infrared-Active CO Stretching Vibrations of the $(\pi\text{-}RC_5H_4)Mn(CO)_3$ Molecule (R = H, CH_3).

The thiocarbonyl complex, π-$C_5H_5Mn(CO)_2CS$, also has a piano-stool-type structure[84] (Figure 5-13) and the local symmetry of the $Mn(CO)_2(CS)$ moiety is C_s. Two infrared-active CO stretching frequencies (A' + A") and one infrared-active CS stretching frequency (A') should be observed for such an arrangement. The cis carbonyls should give rise to a symmetric A' mode and an antisymmetric A" mode. The thiocarbonyl must of necessity produce a symmetric A' stretching mode (Figure 5-14). The infrared spectrum exhibits the anticipated results: two well-resolved bands in the CO stretching region and one isolated peak in the CS stretching region (1350 - 1200 cm^{-1}).

The CO-intensity data for π-$RC_5H_4Mn(CO)_3$ (R = H, CH_3) and π-$C_5H_5Mn(CO)_2CS$ are given in Tables 5-23 and 5-24. The specific intensity of the tricarbonyl moiety in π-$C_5H_5Mn(CO)_3$ obtained by Ramsay's method in n-hexane ($4.92 \times 10^4\ M^{-1}\ cm^{-2}$) agrees closely with Nesmeyanov et al.'s[58] value ($4.85 \times 10^4\ M^{-1}\ cm^{-2}$) obtained by Ramsay's method for a more polar solvent, carbon tetrachloride; however, it is somewhat higher than the value reported by Anderson et al.[72] in carbon disulphide solution ($4.19 \times 10^4\ M^{-1}\ cm^{-2}$). The low value in the Anderson study is not surprising since they evaluated their absolute integrated intensities by taking the mean of several apparent intensity measurements, while the Ramsay results in this study were obtained by taking the mean of several apparent intensity determinations and then adding 2% (vide supra, page 39). In order to make a meaningful comparison between the two studies, Anderson's value was increased by 2%.

Anderson's adjusted value for π-$C_5H_5Mn(CO)_3$ ($5.01 \times 10^4\ M^{-1}\ cm^{-2}$) compares very well with the corresponding result in this study, even though

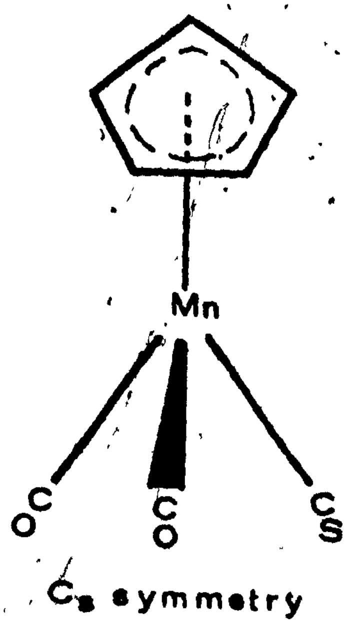

Figure 5-13. Structure of the π-$C_5H_5Mn(CO)_2CS$ Molecule.

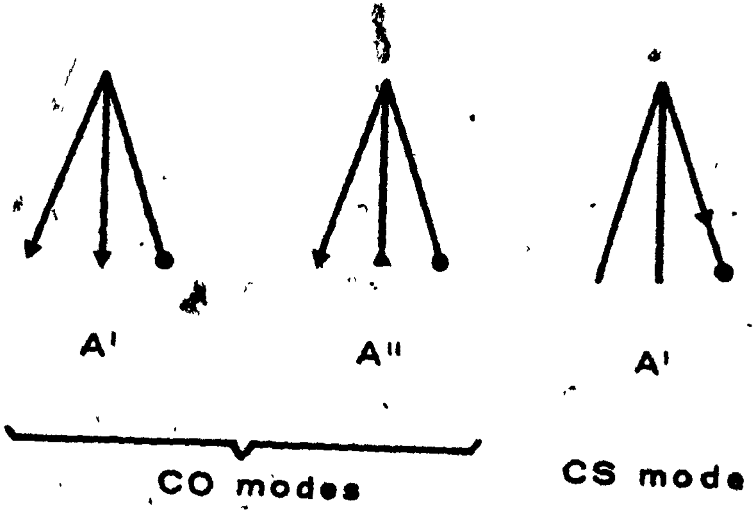

Figure 5-14. Infrared-Active CO and CS Stretching Vibrations of the π-$C_5H_5Mn(CO)_2CS$ Molecule.

TABLE 5-23

Infrared Frequencies, Half-Intensity Band Widths, and Absolute Integrated Absorption Intensities for the CO Stretching Vibrations of the (π-Cyclopentadienyl)Mn(CO)$_3$ Complexes and for the CO and CS Stretching Vibrations of the (π-Cyclopentadienyl)Mn(CO)$_2$CS Complex

CO MODES

			ν_{max}	$\Delta\nu_{\frac{1}{2}}$*	E,** 10^4 M^{-1} cm^{-2}			
Complex	Solvent	Normal mode	cm^{-1}	cm^{-1}	Ramsay	Wilson-Wells	Russell-Thompson	Mean
π-$C_5H_5Mn(CO)_3$	n-Hexane	A_1	$2030._8$	1.86	3.65 (± 0.05)	3.77 (± 0.28)	3.80 (± 0.32)	3.74 (± 0.22)
$(\pi$-$CH_3C_5H_4)Mn(CO)_3$	n-Hexane	A_1	$2026._7$	1.91	3.77 (± 0.05)	3.55 (± 0.36)	3.55 (± 0.37)	3.62 (± 0.26)
π-$C_5H_5Mn(CO)_2CS$	Carbon disulphide	A'	$2009._7$	5.65	4.62 (± 0.09)	4.92 (± 0.17)	5.01 (± 0.20)	4.85 (± 0.15)
π-$C_5H_5Mn(CO)_3$	n-Hexane	E	$1948._6$	4.11	11.1 (± 0.2)	12.0 (± 0.3)	12.1 (± 0.4)	11.6 (± 0.3)
$(\pi$-$CH_3C_5H_4)Mn(CO)_3$	n-Hexane	E	$1944._5$	6.60	11.2 (± 0.4)	12.6 (± 1.3)	12.8 (± 1.5)	12.2 (± 1.1)
π-$C_5H_5Mn(CO)_2CS$	Carbon disulphide	A"	$1956._9$	8.00	6.14 (± 0.13)	6.56 (± 0.23)	6.68 (± 0.29)	6.46 (± 0.22)

CS MODE

			ν_{max}	$\Delta\nu_{\frac{1}{2}}$*	E,** 10^4 M^{-1} cm^{-2}			
Complex	Solvent	Normal mode	cm^{-1}	cm^{-1}	Ramsay	Wilson-Wells	Russell-Thompson	Mean
π-$C_5H_5Mn(CO)_2CS$	Carbon disulphide	A'	$1263._8$	9.15	5.42 (± 0.13)	5.88 (± 0.18)	5.99 (± 0.22)	5.76 (± 0.18)

*,** As defined in Table 5-1.

TABLE 5-24

Specific Intensities for the CO Stretching Vibrations of the (π-Cyclopentadienyl)Mn(CO)$_3$ Complexes and for the CO and CS Stretching Vibrations of the (π-Cyclopentadienyl)Mn(CO)$_2$CS Complex

CO MODES

Complex	Solvent	Specific Intensity,* 10^4 M^{-1} cm^{-2} Ramsay	Wilson-Wells	Russell-Thompson	Mean
π-$C_5H_5Mn(CO)_3$	n-Hexane	4.92 (± 0.08)	5.25 (± 0.21)	5.31 (± 0.23)	5.16 (± 0.17)
(π-$CH_3C_5H_4$)$Mn(CO)_3$	n-Hexane	5.00 (± 0.15)	5.38 (± 0.55)	5.46 (± 0.63)	5.28 (± 0.44)
π-$C_5H_5Mn(CO)_2CS$	Carbon disulphide	5.38 (± 0.07)	5.74 (± 0.20)	5.85 (± 0.25)	5.66 (± 0.17)

CS MODE

Complex	Solvent	Specific Intensity,* 10^4 M^{-1} cm^{-2} Ramsay	Wilson-Wells	Russell-Thompson	Mean
π-$C_5H_5Mn(CO)_2CS$	Carbon disulphide	5.42 (± 0.13)	5.88 (± 0.18)	5.99 (± 0.22)	5.76 (± 0.18)

*As defined in Table 5-2.

the measurement was taken in a more polar solvent (carbon disulphide). The close agreement in intensity values in all three solvents (i.e., n-hexane, carbon tetrachloride and carbon disulphide) suggests that there is little if any difference in solvent effects upon the integrated CO-intensities of π-$C_5H_5Mn(CO)_3$ in these solvents. Apparently, any increase in band width with the more polar solvents is roughly compensated by a decrease in peak height. This appears to be the case for other systems studied here as well (vide supra, page 68). In view of these results, it is evident that our CO-intensity values for π-$C_5H_5Mn(CO)_3$ in n-hexane solution may be reliably compared with those for π-$C_5H_5Mn(CO)_2CS$ in carbon disulphide solution.

However, a word of caution regarding comparison of CO-intensity measurements in different solvents is in order. A notable exception to the foregoing conclusions regarding solvent effects upon CO-intensities is the behaviour of cyclohexane. Fischer's[56] value for π-$C_5H_5Mn(CO)_3$ (4.01×10^4 M^{-1} cm^{-2}) obtained by Ramsay's method in cyclohexane solution is considerably lower than any of the results cited above for more polar solvents. Since similar behaviour in cyclohexane solution was observed in other systems as well (vide supra, page 73), the decrease is considered to be significant and indicates that solvent effects upon CO-intensities should be regarded when comparing measurements in different solvents, especially if one of the solvents is cyclohexane.

The specific CO-intensity seems to increase in going from π-C_5H_5-$Mn(CO)_3$ (5.16×10^4 M^{-1} cm^{-2}) to π-$CH_3C_5H_4Mn(CO)_3$ (5.28×10^4 M^{-1} cm^{-2}) in agreement with the conclusions of Nesmeyanov et al.[58] that electronic effects on the cyclopentadienyl ring are transmitted to the central metal atom and so to the CO groups (i.e., if transmission of electronic effects on the ring to the CO groups occurs, then one would expect from π-bonding arguments that the availability of metal dπ-electron density would increase with the donor ability of the ring substituents). Since a methyl group is a better electron donor than a hydrogen atom, one would anticipate a small increase in CO-intensity with the methyl-substituted derivative. However, it should be kept in mind that the errors in the intensity measurements are such that the two values for $\pi\text{-}C_5H_5Mn(CO)_3$ and $\pi\text{-}CH_3C_5H_4\text{-}Mn(CO)_3$ overlap and so no definitive conclusions may be drawn from these results. Unfortunately, Nesmeyanov et al. did not give any estimate of the errors present in their measurements.

The specific CO-intensity of $\pi\text{-}C_5H_5Mn(CO)_3$ ($5.16 \times 10^4\ M^{-1}\ cm^{-2}$) is significantly lower than that of $\pi\text{-}C_5H_5Mn(CO)_2CS$ ($5.66 \times 10^4\ M^{-1}\ cm^{-2}$). This may reflect a greater σ-donor ability of CS over CO or a lesser π-acceptor ability, or both. However, the specific CS-intensity ($5.76 \times 10^4\ M^{-1}\ cm^{-2}$) of $\pi\text{-}C_5H_5Mn(CO)_2CS$ is comparable to the specific CO-intensity ($5.66 \times 10^4\ M^{-1}\ cm^{-2}$). This may be taken as direct evidence that the π-acceptor ability of CS is at least as good as that of CO. It necessarily follows that the increase in specific CO-intensity in going from $\pi\text{-}C_5H_5\text{-}Mn(CO)_3$ to $\pi\text{-}C_5H_5Mn(CO)_2CS$ is due solely to the greater σ-donor ability of CS over CO and not to a lesser π-acceptor ability.

Dipole moment derivatives were calculated as previously described by Darensbourg[25] using the equation

$$I_T = n\, G_{tt}\, \mu'^{2}_{ML} \qquad (24)$$

where I_T is the total measured intensity for the CO or CS stretching vibrations (obtained by the Wilson-Wells extrapolation) and is defined as

2.303 E x 10^{-4}, and n equals the number of CO or CS groups in the molecules. G_{tt} is the term representing the inverse mass of the CO or CS grouping (based on atomic mass units) and is equal to 0.14585 and 0.11444 for the CO and CS groups, respectively. μ'_{ML} is the respective change in group dipole moment with symmetry coordinates (defined as the effective group dipole moment derivative involving both MC and CO or CS stretching motions) and is expressed in arbitrary units.[25]

The μ'_{MCO}'s, 9.10 and 9.51 for the $Mn(CO)_3$ (where $I_T = 2.303\,[E_{A_1} + E_E] \times 10^{-4} = 2.303\,[3.77 + 12.0] = 36.28$) and the $Mn(CO)_2CS$ (where $I_T = 2.303\,[E_{A'} + E_{A''}] \times 10^{-4} = 2.303\,[4.92 + 6.56] = 26.4$) moieties, respectively, agree closely with Darensbourg's values obtained in molybdenum (9.00), cobalt (7.56), iron (7.74) and iridium (7.78) substituted carbonyls.[65,68,69] However, the μ'_{MCS} for the $Mn(CO)_2CS$ (where $I_T = 2.303\,E_{A'} \times 10^{-4} = 2.303\,[5.88] = 13.5$) species, 10.9, is substantially larger than these. This indicates that the π-acceptor ability of the CS group is considerably greater than that of CO in agreement with molecular orbital calculations on the CS and CO molecules[82] and also with many other experimental data.[83]

PART IV

SUMMARY AND PROSPECTUS

SUMMARY AND PROSPECTUS

Integrated infrared intensity measurements of the CO stretching modes in transition metal-carbonyl complexes have provided useful information concerning the electronic character of the coordinated CO group.[25,54-73] The intensities have been shown to be highly dependent on the π-electron density in the M-CO bond.[25,65] The work in this thesis constitutes an additional study of the infrared intensities of the CO stretching absorptions of some group VI and VII metal-carbonyl complexes. The integrated intensity results were used as a basis for a further investigation of the σ- and π-bonding abilities of the various transition metals and ligands in these complexes.

The results of this study also demonstrate the utility of integrated intensity measurements in assessing π-electronic delocalization in transition metal-thiocarbonyl compounds. The first measurement of the infrared intensity of a CS stretching mode in a metal-thiocarbonyl complex was reported here. The intensity measurements and the calculated dipole moment derivatives reflect the demands made for π-electron density as well as the availability of π-electron density during a ligand stretching vibration. From a comparison of the CO and CS results in the π-C_5H_5-$Mn(CO)_2CS$ molecule, it is clear that CS has a greater π-acceptor ability than CO, in accordance with molecular orbital calculations on the CO and CS molecules[82] and many other experimental findings.[83]

An intriguing aspect of transition metal-thiocarbonyl chemistry, in view of the great similarity in bonding properties of CO and CS, is the surprising difference in infrared frequency shifts (bonded ligand versus free ligand) of M-CO and M-CS bonds. Whereas the CO stretching frequency of free CO decreases from 2143 cm^{-1} to approximately 2000 cm^{-1} (sometimes to as low as 1850 cm^{-1} in the case of terminal CO bonding) upon coordination to a transition metal atom, it appears that the CS stretching frequency can both increase and decrease (i.e., the range of $\nu(CS)$ stretching frequencies in metal-thiocarbonyls is 1381-1193 cm^{-1}) with respect to the frequency of "free" CS (1274 cm^{-1} when trapped in a CS_2 matrix[85]).[83] Since π-backbonding is almost certainly present in metal-CS bonds, it is apparent that frequency values alone cannot lead to meaningful conclusions as to the relative π-acceptor ability of the CS and CO groupings. An interesting project for future consideration would be to attempt to discuss the relative extent of π-electron delocalization in transition metal-thiocarbonyl complexes on the basis of CS intensity measurements. CS-intensity studies would also permit comparisons between analogous series of metal-carbonyl and metal-dinitrogen complexes.

PART V

APPENDICES

Appendix A

PROGRAMS FOR INTEGRATED INTENSITIES

Program I

```
C       PURPOSE
C             (1)  TO COMPUTE THE AREA UNDER THE APPARENT OPTICAL DENSITY CURVE
C                  (FROM BAND WEIGHT DATA)
C             (2)  TO DETERMINE THE APPARENT INTEGRATED ABSORPTION INTENSITY
C
C       DESCRIPTION OF PARAMETERS
C
C       J      = # BANDS
C       K      = # CONCNS
C       R      = CALIBRATION OF RECORDER (CM-1/INCH)
C       PL     = SAMPLE PATHLENGTH (CM)
C       WM     = MOLECULAR WEIGHT SOLUTE (GM)
C       CC     = CONC (GM SOLUTE/LITER SOLUTION)
C       C      = CONC (MILLIMOLES SOLUTE/LITER SOLUTION)
C       CP     = CALIBRATION OF CHART PAPER (GM/INCH)
C       W      = WEIGHT OF BAND (GM)
C       AREA   = AREA UNDER APPARENT OPTICAL DENSITY CURVE (CM-1)
C       AT     = ABSORBANCE AT BAND MAXIMUM (TO BASE 10)
C       T      = LN(T0/T)VMAX (OR 2.303*AT)
C       B      = APPARENT INTEGRATED INTENSITY (M-1 CM-2)*10**4
C
        READ(5,1)J,K,R,PL,WM,CP
      1 FORMAT(2I2,2F7.4,2F10.5)
        WRITE(6,3)
      3 FORMAT(1H0,4X,'R',10X,'PL',9X,'WM',9X,'CP')
        WRITE(6,4)R,PL,WM,CP
      4 FORMAT(1H0,1F10.4,1F11.4,1F14.5,1F9.5)
        WRITE(6,5)
      5 FORMAT(1H0)
        WRITE(6,6)
      6 FORMAT(1H0,4X,'C',10X,'AT',9X,'T',10X,'AREA',7X,'B')
        DO 10 I=1,J
        WRITE(6,7)
      7 FORMAT(1H0)
        DO 20 L=1,K
        READ(5,8)CC,W,AT
      8 FORMAT(2F6.5,1F4.3)
        C=(CC*10**3)/WM
        T=2.303*AT
        AREA=2.303*R*W/CP
        B=AREA/(C*PL)
     20 WRITE(6,9)C,AT,T,AREA,B
      9 FORMAT(1H0,1F10.4,1F10.3,1F12.4,1F11.4,1F12.4)
     10 CONTINUE
        END
```

Program II

```
C       PURPOSE
C               (1)  TO CONVERT FROM TRANSMITTANCE TO OPTICAL DENSITY VALUES
C               (2)  TO COMPUTE THE AREA UNDER THE APPARENT OPTICAL DENSITY CURVE
                     BY SIMPSON'S RULE
C               (3)  TO DETERMINE THE APPARENT INTEGRATED ABSORPTION INTENSITY
C
C       DESCRIPTION OF PARAMETERS
C
C       NDIM   = # POINTS MEASURED
C       R      = CALIBRATION OF RECORDER (CM-1/INCH)
C       PL     = SAMPLE PATHLENGTH (MM)
C       WM     = MOLECULAR WEIGHT SOLUTE (GM)
C       CC     = CONCN (GM SOLUTE/LITER SOLUTION
C       C      = CONCN (MILLIMOLES SOLUTE/LITER SOLUTION)
C       K      = # CONCNS MEASURED
C       N      = # SECTIONS WITH A DIFFERENT INCREMENT OF ARGUMENT
C                VALUES IN A BAND
C       HI     = # INTERVALS/INCH IN A PARTICULAR SECTION
C       H      = INCREMENT OF ARGUMENT VALUES (CM-1)
C       BL     = BASELINE MEASURED FROM SPECTRUM
C       PM     = HEIGHT OF PEAK AT MAXIMUM ABSORPTION
C       P(I)   = POINTS TAKEN FROM CURVE
C       T0     = TRANSMITTANCE OF BASELINE (%)
C       TM     = TRANSMITTANCE OF PEAK AT MAXIMUM ABSORPTION (%)
C       TL     = OPTICAL DENSITY OF CURVE AT MAXIMUM ABSORPTION
C              = LN(T0/TM)VMAX
C       T(I)   = TRANSMITTANCE OF POINTS ON CURVE (%)
C       Y(I)   = OPTICAL DENSITY OF POINTS ON CURVE
C              = INPUT FUNCTION VALUES
C       Z(I)   = RESULTING INTEGRAL VALUES (CM-1)
C       SUM    = SUM OF INTEGRALS (CM-1)
C       AREA   = AREA UNDER APPARENT OPTICAL DENSITY CURVE (CM-1)
C       B      = APPARENT INTEGRATED INTENSITY (M-1 CM-2)*10**4
C
        DIMENSION P(100),T(100),Y(100),Z(100)
        READ(5,1)K,N,R,PL,WM
      1 FORMAT(2I2,2F6.4,1F10.4)
        WRITE(6,3)
      3 FORMAT(1H0,4X,'R',10X,'PL',9X,'WM')
        WRITE(6,4)R,PL,WM
      4 FORMAT(1H0,1F10.4,1F11.4,1F13.4)
        DO 30 J=1,K
        WRITE(6,18)
     18 FORMAT(1H0)
        READ(5,11)CC,BL,PM
     11 FORMAT(1F6.4,2F4.1)
        C=(CC*10**3)/WM
        T0=100.-BL
        TM=100.-PM
        TL=ALOG(T0)-ALOG(TM)
        WRITE(6,8)
      8 FORMAT(1H0,4X,'C',10X,'BL',9X,'PM',9X,'T0',9X,'TM',9X,'TL')
        WRITE(6,9)C,BL,PM,T0,TM,TL
      9 FORMAT(1H0,1F10.4,1F8.1,1F12.1,2F11.1,1F13.4)
        AREA=0.
        DO 20 L=1,N
        READ(5,13)NDIM,HI
     13 FORMAT(1I3,1F4.1)
        H=R/HI
        WRITE(6,14)
     14 FORMAT(1H0,4X,'NDIM',7X,'HI',9X,'H')
        WRITE(6,16)NDIM,HI,H
     16 FORMAT(1H0,1I6,1F12.1,1F14.4)
```

```
      READ(5,2)(P(I),I=1,NDIM)
    2 FORMAT(11F4.1)
      WRITE(6,12)
   12 FORMAT(1H0)
      DO 10 I=1,NDIM
      T(I)=100.-P(I)
      Y(I)=ALOG(T0)-ALOG(T(I))
   10 CONTINUE
      CALL QSF(H,Y,Z,NDIM)
      SUM=Z(NDIM)
      WRITE(6,7)L,SUM
    7 FORMAT(1H0,4X,'AREA UNDER SECTION',112,' =',1F8.4)
   20 AREA=AREA+SUM
      B=AREA/(C*PL)
   30 WRITE(6,15)AREA,B
   15 FORMAT(1H0,4X,'AREA = ',1F8.4,10X,'B =',1F8.4)
      END
```

<u>Program III</u>

```
C        PURPOSE
C              (1)  TO DETERMINE THE ABSOLUTE INTEGRATED ABSORPTION INTENSITY BY RAMSAY'S
C                   METHOD FOR OVERLAPPING BAND SYSTEMS (R. N. JONES, D. A. RAMSAY, D. S.
C                   KEIR, AND K. DOBRINER,  J. AM. CHEM.SOC., 74, 80 (1952))
C
C        DESCRIPTION OF PARAMETERS
C
C        J          = # OF BANDS
C        K          = # OF CONCNS
C        B          = APPARENT INTEGRATED INTENSITY (M-1 CM-2)*10**4
C        SUM        = SUM OF B VALUES FOR EACH BAND
C        AVG        = MEAN B VALUE FOR EACH BAND
C        DIFF       = DEVIATION OF EACH OBSERVATION FROM MEAN B VALUE
C        DIFF**2    = VARIANCE OF EACH OBSERVATION FROM MEAN B VALUE
C        SD         = STANDARD DEVIATION OF B VALUES FROM THE MEAN
C        A          = ABSOLUTE INTEGRATED INTENSITY (M-1 CM-2)*10**4
C                   = MEAN B VALUE + 2% OF MEAN B VALUE
C        E          = A/2.303 (M-1 CM-2)*10**4
C
      DIMENSION B(10)
  100 READ(5,1,END=101)J,K
    1 FORMAT(2I3)
      DO 30 L=1,J
      READ(5,2)(B(I),I=1,K)
    2 FORMAT(6F6.4)
      WRITE(6,3)
    3 FORMAT(1H0,3X,'B',9X,'B - AVG',4X,'(B - AVG)**2')
      WRITE(6,4)
    4 FORMAT(1H0)
      SUM=0.
      DO 10 I=1,K
      SUM=SUM+B(I)
   10 CONTINUE
      AVG=SUM/K
      DSQ=0.
      DO 20 I=1,K
      DIFF=B(I)-AVG
      DIFFSQ=DIFF**2
      WRITE(6,9)B(I),DIFF,DIFFSQ
    9 FORMAT(3F10.4)
   20 DSQ=DSQ+DIFFSQ
      SD=SQRT(DSQ/K)
      A=1.02*AVG
      E=A/2.303
```

```
      WRITE(6,6)
    6 FORMAT(1H0,3X,'SUM',7X,'AVG',7X,'SD',8X,'A',9X,'E')
      WRITE(6,7)SUM,AVG,SD,A,E
    7 FORMAT(1H0,1F8.4,1F11.4,3F10.4)
      WRITE(6,8)
    8 FORMAT(1H0)
   30 CONTINUE
      GO TO 100
  101 STOP
      END
```

Program IV

```
C         PURPOSE
C             (1)   TO DETERMINE THE ABSOLUTE INTEGRATED ABSORPTION INTENSITY BY
C                   (A)  THE WILSON-WELLS EXTRAPOLATION METHOD (E. B. WILSON, JR., AND
C                        A. J. WELLS,  J. CHEM. PHYS., 14, 578 (1946))
C                   (B)  THE RUSSELL-THOMPSON EXTRAPOLATION METHOD (R. A. RUSSELL AND
C                        H. W. THOMPSON, SPECTROCHIM. ACTA, 9, 133 (1957))
C
C         DESCRIPTION OF PARAMETERS
C
C         J         = # BANDS
C         K         = # CONCNS
C         T         = (A) CONCN(MILLIMOLES SOLUTE/LITER SOLUTION) (WILSON-WELLS)
C                   = (B) LN(T0/T)VMAX (RUSSELL-THOMPSON)
C         B         = APPARENT INTEGRATED INTENSITY (M-1 CM-2)*10**4
C         TERCEP    = INTERCEPT = A
C                   = ABSOLUTE INTEGRATED INTENSITY (M-1 CM-2)*10**4
C         E         = A/2.303 (M-1 CM-2)*10**4
C         CALCB     = B CALCULATED FROM T AND SLOPE (M-1 CM-2)*10**4
C         DIFF      = DEVIATION OF EACH OBSERVATION EQUATION
C         DIFF**2   = VARIANCE OF EACH OBSERVATION EQUATION
C         SDPD      = STANDARD DEVIATION OF PARENT DISTRIBUTION
C         SDSL      = STANDARD DEVIATION OF SLOPE
C         SDINT     = STANDARD DEVIATION OF A VALUE
C         SDE       = STANDARD DEVIATION OF E VALUE
C         PSDSL     = % STANDARD DEVIATION OF SLOPE
C         PSDINT    = % STANDARD DEVIATION OF A VALUE
C
      DIMENSION T(10),B(10)
  100 READ(5,1,END=101)J,K
    1 FORMAT(2I3)
      DO 30 L=1,J
      READ(5,2)(T(I),I=1,K)
      READ(5,2)(B(I),I=1,K)
    2 FORMAT(6F6.4)
      WRITE(6,3)
    3 FORMAT('0',3X,'T',9X,'B',9X,'CALCB',5X,'DIFF',6X,'DIFF**2')
      WRITE(6,4)
    4 FORMAT('0')
      SUMT=0.
      SUMB=0.
      SUMTB=0.
      SUMTT=0.
      DO 10 I=1,K
      SUMT=SUMT+T(I)
      SUMB=SUMB+B(I)
      SUMTT=SUMTT+T(I)**2
      SUMTB=SUMTB+T(I)*B(I)
   10 CONTINUE
      DENOM=K*SUMTT-SUMT**2
      SLOPE=(K*SUMTB-SUMT*SUMB)/DENOM
      TERCEP=(SUMTT*SUMB-SUMT*SUMTB)/DENOM
      E=TERCEP/2.303
```

```
      DSQ=0.
      DO 20 I=1,K
      CALCB=SLOPE*T(I)+TERCEP
      DIFF=B(I)-CALCB
      DIFFSQ=DIFF**2
      WRITE(6,5)T(I),B(I),CALCB,DIFF,DIFFSQ
    5 FORMAT(5F10.4)
   20 DSQ=DSQ+DIFFSQ
      SDPD=SQRT(DSQ/K)
      SDSL=SQRT(ABS(DSQ/DENOM))
      PSDSL=SDSL*100./SLOPE
      SDINT=SQRT((SDSL**2)*(SUMT**2)/K)
      SDE=SDINT/2.303
      PSDINT=SDINT*100./TERCEP
      WRITE(6,6)SDPD
    6 FORMAT('0',33X,'SDPD   =',1F9.4)
      WRITE(6,7)SLOPE,TERCEP,E
    7 FORMAT('0',3X,'SLOPE   =',1F8.4,4X,'INTERCEPT   =',1F8.4,4X,'E   =',
     11F8.4)
      WRITE(6,8)SDSL,SDINT,SDE
    8 FORMAT(4X,'SDSL   =',1F8.4,4X,'SDINT        =',1F8.4,4X,'SDE =',1F8.
     14)
      WRITE(6,9)PSDSL,PSDINT
    9 FORMAT(4X,'PSDSL  =',1F8.2,4X,'PSDINT       =',1F8.2)
   30 CONTINUE
      GO TO 100
  101 STOP
      END
```

Subroutine QSF*

```
C       PURPOSE
C                (1)  TO COMPUTE THE VECTOR OF INTEGRAL VALUES FOR A GIVEN EQUIDISTANT
C                       TABLE OF FUNCTION VALUES.
C
C       DESCRIPTION OF PARAMETERS
C
C          H      = THE INCREMENT OF ARGUMENT VALUES.
C          Y      = THE INPUT VECTOR OF FUNCTION VALUES.
C          Z      = THE RESULTING VECTOR OF INTEGRAL VALUES.  Z MAY BE
C                    IDENTICAL WITH Y.
C          NDIM   = THE DIMENSION OF VECTORS Y AND Z.
C
C       REMARKS
C          NO ACTION IN CASE NDIM LESS THAN 3.
C
C       SUBROUTINES AND FUNCTION SUBPROGRAMS REQUIRED
C          NONE
C
C       METHOD
C          BEGINNING WITH Z(1)=0, EVALUATION OF VECTOR Z IS DONE BY
C          MEANS OF SIMPSON'S RULE TOGETHER WITH NEWTON'S 3/8 RULE OR A
C          COMBINATION OF THESE TWO RULES.  TRUNCATION ERROR IS OF
C          ORDER H**5 (I.E., FOURTH ORDER METHOD).  ONLY IN CASE NDIM=3
C          TRUNCATION ERROR OF Z(2) IS OF ORDER H**4.
C          FOR REFERENCE, SEE
C          (1) F.B.HILLEBRAND, INTRODUCTION TO NUMERICAL ANALYSIS,
C              MCGRAW-HILL, NEW YORK/TORONTO/LONDON, 1956, PP. 71-76.
C          (2) R. ZURMUEHL, PRAKTISCHE MATHEMATIK FUER INGENIEURE UND
C              PHYSIKER, SPRINGER, BERLIN/GOETTINGEN/HEIDELBERG, 1963,
C              PP. 214-221.
C
        SUBROUTINE QSF(H,Y,Z,NDIM)
C
        DIMENSION Y(1),Z(1)
C
        HT=.3333333*H
        IF(NDIM-5)7,8,1
C
C       NDIM IS GREATER THAN 5.  PREPARATIONS OF INTEGRATION LOOP
      1 SUM1=Y(2)+Y(2)
        SUM1=SUM1+SUM1
        SUM1=HT*(Y(1)+SUM1+Y(3))
        AUX1=Y(4)+Y(4)
        AUX1=AUX1+AUX1
        AUX1=SUM1+HT*(Y(3)+AUX1+Y(5))
        AUX2=HT*(Y(1)+3.875*(Y(2)+Y(5))+2.625*(Y(3)+Y(4))+Y(6))
        SUM2=Y(5)+Y(5)
        SUM2=SUM2+SUM2
        SUM2=AUX2-HT*(Y(4)+SUM2+Y(6))
        Z(1)=0.
        AUX=Y(3)+Y(3)
        AUX=AUX+AUX
        Z(2)=SUM2-HT*(Y(2)+AUX+Y(4))
        Z(3)=SUM1
        Z(4)=SUM2
        IF(NDIM-6)5,5,2
```

---

*"SCIENTIFIC SUBROUTINE PACKAGE," IBM CO. LTD., pp 291-2.

```
C          INTEGRATION LOOP
    2 DO 4 I=7,NDIM,2
      SUM1=AUX1
      SUM2=AUX2
      AUX1=Y(I-1)+Y(I-1)
      AUX1=AUX1+AUX1
      AUX1=SUM1+HT*(Y(I-2)+AUX1+Y(I))
      Z(I-2)=SUM1
      IF(I-NDIM)3,6,6
    3 AUX2=Y(I)+Y(I)
      AUX2=AUX2+AUX2
      AUX2=SUM2+HT*(Y(I-1)+AUX2+Y(I+1))
    4 Z(I-1)=SUM2
    5 Z(NDIM-1)=AUX1
      Z(NDIM)=AUX2
      RETURN
    6 Z(NDIM-1)=SUM2
      Z(NDIM)=AUX1
      RETURN
C          END OF INTEGRATION LOOP
C
    7 IF(NDIM-3)12,11,8
C
C          NDIM IS EQUAL TO 4 OR 5
    8 SUM2=1.125*HT*(Y(1)+Y(2)+Y(2)+Y(2)+Y(3)+Y(3)+Y(3)+Y(4))
      SUM1=Y(2)+Y(2)
      SUM1=SUM1+SUM1
      SUM1=HT*(Y(1)+SUM1+Y(3))
      Z(1)=0.
      AUX1=Y(3)+Y(3)
      AUX1=AUX1+AUX1
      Z(2)=SUM2-HT*(Y(2)+AUX1+Y(4))
      IF(NDIM-5)10,9,9
    9 AUX1=Y(4)+Y(4)
      AUX1=AUX1+AUX1
      Z(5)=SUM1+HT*(Y(3)+AUX1+Y(5))
   10 Z(3)=SUM1
      Z(4)=SUM2
      RETURN
C
C          NDIM IS EQUAL TO 3
   11 SUM1=HT*(1.25*Y(1)+Y(2)+Y(2)-.25*Y(3))
      SUM2=Y(2)+Y(2)
      SUM2=SUM2+SUM2
      Z(3)=HT*(Y(1)+SUM2+Y(3))
      Z(1)=0.
      Z(2)=SUM1
   12 RETURN
      END
```

Appendix B[*]

INTENSITY MEASUREMENT PARAMETERS

Description of Terms: Tables B-1 to B-6

ν_{max}	denotes the frequency at maximum absorption.
Slope	represents: (1) the slope of the apparent intensity versus concentration plot (Wilson-Wells[a] method for determining the absolute integrated intensity of a band); or (2) the slope of the apparent intensity versus apparent peak optical density plot (Russell-Thompson[b] method for determining the absolute integrated intensity). The errors listed are the standard deviations in the slopes from least-squares analyses of (1) the intensity versus concentration plots (Wilson-Wells); or (2) the intensity versus peak optical density plots (Russell-Thompson).
s	represents the spectral slit width at ν_{max}.
$\Delta\nu^{t}_{\frac{1}{2}}$, $\Delta\nu^{a}_{\frac{1}{2}}$[*]	are the true and apparent half-intensity band widths.
$\Delta\nu^{a}_{\frac{1}{2}} / \Delta\nu^{t}_{\frac{1}{2}}$[*]	is a ratio given in Ramsay's[c] Table II, and is expressed as a function of $\Delta\nu^{a}_{\frac{1}{2}}$ and the ratio $s/\Delta\nu^{a}_{\frac{1}{2}}$.
$\nu-\nu_0$	signifies the frequency interval on either side of the band centre, ν_0 (ν_{max}), over which the integration was performed.
$\Delta\nu$	is the increment of the argument value used in the computation of band area by Simpson's Rule.

---

[*] Infrared spectra were recorded at at least four, usually five different concentrations for each sample. The values reported in the tables are the average values for the five or so different concentrations.

[a] E. B. Wilson, Jr., and A. J. Wells, J. Chem Phys., 14, 578 (1946).

[b] R. A. Russell and H. W. Thompson, Spectrochim. Acta, 9, 133 (1957).

[c] D. A. Ramsay, J. Am. Chem. Soc., 74, 72 (1952).

TABLE B-1

Slope of Intensity versus Concentration Plot, Spectral Slit Width, Half-Intensity Band Width, Integration Interval and Increment of Argument Values (Simpson's Rule) for the CO Stretching Absorption of $Cr(CO)_6$ in n-Hexane Solution

		ν_{max}	Slope, M^{-2} cm^{-2}		s	$\Delta\nu^a_{\frac{1}{2}}$	$\frac{s}{\Delta\nu^a_{\frac{1}{2}}}$	$\frac{\Delta\nu^a_{\frac{1}{2}}}{\Delta\nu^t_{\frac{1}{2}}}$	$\Delta\nu^t_{\frac{1}{2}}$	$\nu-\nu_0$	$\frac{\nu-\nu_0}{\Delta\nu^t_{\frac{1}{2}}}$	$\Delta\nu$	$\frac{\Delta\nu^t_{\frac{1}{2}}}{\Delta\nu}$
Complex	Integration method	cm^{-1}	Wilson-Wells	Russell-Thompson	cm^{-1}	cm^{-1}			cm^{-1}	cm^{-1}		cm^{-1}	
$Cr(CO)_6$	Simpson's	$1986._9$	-4.83 ± 1.72	-3.50 ± 1.35	2.81	3.75	0.75	1.95	1.92	25	13.0	0.42	4.6
$Cr(CO)_6$	Weighing	$1987._2$	-5.14 ± 1.18	-4.19 ± 1.00	2.81	3.80	0.74	1.90	2.00	24	12.0		

TABLE B-2

Slopes of Intensity versus Concentration Plots, Spectral Slit Widths, Half-Intensity Band Widths, Integration Intervals and Increments of Argument Values (Simpson's Rule) for the CO Stretching Absorptions of the (Cycloheptatriene)M(CO)$_3$ Complexes in Methylene Chloride Solution

Complex	ν_{max} cm^{-1}	Slope, M^{-2} cm^{-2}		s cm^{-1}	$\Delta\nu_{\frac{1}{2}}^{a}$ cm^{-1}	$\frac{s}{\Delta\nu_{\frac{1}{2}}^{a}}$	$\frac{\Delta\nu_{\frac{1}{2}}^{a}}{\Delta\nu_{\frac{1}{2}}^{t}}$	$\Delta\nu_{\frac{1}{2}}^{t}$ cm^{-1}	$\nu-\nu_0$ cm^{-1}	$\frac{\nu-\nu_0}{\Delta\nu_{\frac{1}{2}}^{t}}$	$\Delta\nu$ cm^{-1}	$\frac{\Delta\nu_{\frac{1}{2}}^{t}}{\Delta\nu}$
		Wilson-Wells	Russell-Thompson									
$C_7H_8Cr(CO)_3$	$1982._1$	- 1.40 ± 0.30	- 1.79 ± 0.47	2.81	13.5	0.21	1.03	13.1	64	4.9		
	$1916._0$	- 1.33 ± 0.26	- 2.88 ± 0.61	2.70	19.5	0.14	1.02	19.1	72	3.8		
	$1886._9$	- 2.49 ± 0.35	- 5.92 ± 0.92	2.68	26.3	0.10	1.01	26.0	72	3.1		
$C_7H_8Mo(CO)_3$	$1983._6$	- 1.15 ± 0.58	- 0.96 ± 0.56	2.81	12.4	0.23	1.04	11.9	30	2.5	2.5	4.8
	$1912._2$	- 2.60 ± 0.88	- 3.78 ± 1.53	2.70	22.3	0.12	1.01	22.0	50	2.3	2.5	8.8
	$1880._2$	- 1.33 ± 0.12	- 2.37 ± 0.16	2.66	27.3	0.10	1.01	27.0	50	1.9	2.5	10.8
$C_7H_8W(CO)_3$	$1981._4$	- 2.28 ± 0.32	- 2.50 ± 0.38	2.81	11.5	0.24	1.05	11.0	64	5.8		
	$1908._3$	- 1.22 ± 0.38	- 2.17 ± 0.68	2.70	21.0	0.13	1.02	20.6	72	3.5		
	$1873._1$	- 0.17 ± 0.19	- 0.30 ± 0.39	2.63	26.0	0.10	1.01	25.8	72	2.8		

TABLE B-3

Slopes of Intensity versus Concentration Plots, Spectral Slit Widths, Half-Intensity Band Widths, Integration Intervals and Increments of Argument Values (Simpson's Rule) for the CO Stretching Absorptions of the (Bicycloheptadiene)M(CO)$_4$ Complexes in n-Hexane Solution

Complex	ν_{max} cm^{-1}	Slope, M^{-2} cm^{-2} Wilson-Wells	Slope, M^{-2} cm^{-2} Russell-Thompson	s cm^{-1}	$\Delta\nu_{\frac{1}{2}}^{a}$ cm^{-1}	$\frac{s}{\Delta\nu_{\frac{1}{2}}^{a}}$	$\frac{\Delta\nu_{\frac{1}{2}}^{a}}{\Delta\nu_{\frac{1}{2}}^{t}}$	$\Delta\nu_{\frac{1}{2}}^{t}$ cm^{-1}	$\nu-\nu_0$ cm^{-1}	$\frac{\nu-\nu_0}{\Delta\nu_{\frac{1}{2}}^{t}}$	$\Delta\nu$ cm^{-1}	$\frac{\Delta\nu_{\frac{1}{2}}^{t}}{\Delta\nu}$
nor-$C_7H_8Cr(CO)_4$	$2033._6$	- 0.14 ± 0.06	- 1.05 ± 0.51	2.90	3.73	0.78	2.30	1.62	20	12.4	0.42	3.9
	$1958._7$	- 0.12 ± 0.07	- 1.50 ± 1.02	2.77	4.51	0.61	1.58	2.86	15	5.2	0.83	3.4
	$1944._4$	- 0.25 ± 0.33	- 0.58 ± 1.09	2.74	4.66	0.59	1.38	3.38	20	5.9	0.83	4.2
	$1914._8$	- 0.18 ± 0.06	- 0.74 ± 0.28	2.70	4.98	0.54	1.33	3.74	25	6.7	0.83	4.5
nor-$C_7H_8Mo(CO)_4$	$2044._4$	+ 0.00 ± 0.07	+ 0.08 ± 0.52	2.92	3.74	0.78	2.50	1.50	10	6.7	0.42	3.6
	$1959._2$	- 1.28 ± 0.16	- 3.19 ± 0.32	2.77	4.98	0.56	1.33	3.74	20	5.4	0.83	4.5
	$1913._6$	- 0.55 ± 0.14	- 2.01 ± 0.59	2.70	5.14	0.53	1.33	3.86	25	6.5	0.83	4.8
nor-$C_7H_8W(CO)_4$	$2043._9$	- 0.01 ± 0.01	- 0.10 ± 0.11	2.91	4.00	0.73	2.08	1.95	32	16.4		
	$1957._3$	- 1.74 ± 0.35	- 4.32 ± 0.83	2.77	4.75	0.58	1.36	3.50	32	9.2		
	$1910._1$	- 0.24 ± 0.12	- 0.85 ± 0.41	2.70	4.75	0.57	1.40	3.40	24	7.1		

TABLE B-4

Slopes of Intensity versus Concentration Plots, Spectral Slit Widths, Half-Intensity Band Widths, Integration Intervals and Increments of Argument Values (Simpson's Rule) for the CO Stretching Absorptions of the *fac*-$Mo(CO)_3(Phosphine)_3$ Complexes in Methylene Chloride Solution

Complex	ν_{max}	Slope, M^{-2} cm^{-2}		s	$\Delta\nu^{a}_{\frac{1}{2}}$	$\frac{s}{\Delta\nu^{a}_{\frac{1}{2}}}$	$\frac{\Delta\nu^{a}_{\frac{1}{2}}}{\Delta\nu^{t}_{\frac{1}{2}}}$	$\Delta\nu^{t}_{\frac{1}{2}}$	$\nu-\nu_0$	$\frac{\nu-\nu_0}{\Delta\nu^{t}_{\frac{1}{2}}}$	$\Delta\nu$	$\frac{\Delta\nu^{t}_{\frac{1}{2}}}{\Delta\nu}$
	cm^{-1}	Wilson-Wells	Russell-Thompson	cm^{-1}	cm^{-1}			cm^{-1}	cm^{-1}		cm^{-1}	
fac-$Mo(CO)_3(PCl_3)_3$*	$2040._2$	- 6.12 ± 1.56	- 2.10 ± 0.42	2.91	3.58	0.81	2.50	1.43	20	14.0	0.42	3.4
	$1991._1$	- 8.25 ± 2.35	- 2.45 ± 0.78	2.81	5.75	0.49	1.29	4.46	25	5.6	0.83	5.4
fac-$Mo(CO)_3(PCl_3)_3$	$2039._9$	- 0.24 ± 0.49	- 0.14 ± 0.46	2.91	11.2	0.26	1.06	10.5	40	3.8	1.2	8.8
	$1936._6$	- 0.15 ± 1.30	+ 0.08 ± 1.56	2.81	27.0	0.10	1.01	26.8	60	2.2	2.5	10.7
fac-$Mo(CO)_3[P(C_6H_5)Cl_2]_3$	$2006._0$	- 0.36 ± 0.19	- 0.44 ± 0.26	2.84	13.3	0.21	1.03	12.9	48	3.7		
	$1940._8$	- 0.01 ± 0.32	+ 0.01 ± 0.53	2.73	33.5	0.08	1.01	33.2	96	2.9		
fac-$Mo(CO)_3[P(C_6H_5)_2Cl]_3$	$1970._5$	- 0.17 ± 0.84	+ 0.36 ± 0.80	2.79	14.0	0.20	1.03	13.6	48	3.5		
	$1889._4$	+ 0.97 ± 2.56	+ 3.18 ± 3.47	2.68	37.0	0.07	1.00	37.0	96	2.6		

*n-Hexane solution

TABLE B-5

Slopes of Intensity versus Concentration Plots, Spectral Slit Widths, Half-Intensity Band Widths, Integration Intervals and Increments of Argument Values (Simpson's Rule) for the CO Stretching Absorptions of the *cis*-$Mn(CO)_4LBr$ Complexes in *n*-Hexane Solution

Complex	ν_{max} cm^{-1}	Slope, M^{-2} cm^{-2} Wilson-Wells	Slope, M^{-2} cm^{-2} Russell-Thompson	s cm^{-1}	$\Delta\nu^a_{\frac{1}{2}}$ cm^{-1}	$\frac{s}{\Delta\nu^a_{\frac{1}{2}}}$	$\frac{\Delta\nu^a_{\frac{1}{2}}}{\Delta\nu^t_{\frac{1}{2}}}$	$\Delta\nu^t_{\frac{1}{2}}$ cm^{-1}	$\nu-\nu_0$ cm^{-1}	$\frac{\nu-\nu_0}{\Delta\nu^t_{\frac{1}{2}}}$	$\Delta\nu$ cm^{-1}	$\frac{\Delta\nu^t_{\frac{1}{2}}}{\Delta\nu}$
cis-$Mn(CO)_4[P(C_6H_5)_3]Br$	$2089._2$	- 0.09 ± 0.10	- 0.15 ± 0.16	3.00	4.53	0.66	1.70	2.66	20	7.5	0.42	6.3
	$2024._6$	- 0.49 ± 0.24	- 0.57 ± 0.28	2.88	6.88	0.42	1.18	5.83	20	3.4	0.83	7.0
	$2006._4$	- 1.37 ± 0.61	- 1.12 ± 0.49	2.84	7.50	0.38	1.14	6.58	25	3.8	0.83	8.0
	$1960._8$	- 0.59 ± 0.10	- 0.89 ± 0.15	2.78	11.6	0.24	1.05	11.0	25	2.3	0.83	13.3
cis-$Mn(CO)_4[As(C_6H_5)_3]Br$	$2091._8$	+ 0.11 ± 0.07	+ 0.17 ± 0.10	3.00	4.53	0.66	1.74	2.60	20	7.7	0.42	6.2
	$2023._7$	- 0.92 ± 0.47	- 0.82 ± 0.50	2.88	7.03	0.41	1.17	6.00	20	3.3	0.83	7.2
	$2011._4$	- 0.12 ± 0.48	- 0.05 ± 0.36	2.84	7.50	0.38	1.14	6.48	25	3.9	0.83	7.8
	$1962._3$	+ 0.41 ± 0.40	+ 0.59 ± 0.52	2.78	10.9	0.25	1.04	10.5	20	1.9	0.83	12.7
cis-$Mn(CO)_4[Sb(C_6H_5)_3]Br$	$2087._5$	- 0.44 ± 0.12	- 0.63 ± 0.18	3.00	4.84	0.62	1.58	3.06	20	6.5	0.42	7.3
	$2021._6$	- 0.89 ± 0.10	- 0.93 ± 0.12	2.88	6.56	0.44	1.20	5.48	20	3.6	0.83	6.6
	$2009._2$	- 1.72 ± 0.37	- 1.37 ± 0.29	2.84	7.81	0.36	1.13	6.91	25	3.6	0.83	8.3
	$1960._4$	- 0.36 ± 0.30	- 0.45 ± 0.39	2.78	10.9	0.25	1.04	10.5	20	1.9	0.83	12.7

TABLE B-6

Slopes of Intensity versus Concentration Plots, Spectral Slit Widths, Half-Intensity Band Widths, Integration Intervals and Increments of Argument Values (Simpson's Rule) for the CO Stretching Absorptions of the (π-Cyclopentadienyl)Mn(CO)$_3$ Complexes in n-Hexane Solution and for the CO and CS Stretching Absorptions of the (π-Cyclopentadienyl)Mn(CO)$_2$CS Complex in Carbon Disulphide Solution

Complex	ν_{max} cm^{-1}	Slope, M^{-2} cm^{-2} Wilson-Wells	Slope, M^{-2} cm^{-2} Russell-Thompson	s cm^{-1}	$\Delta\nu^a_{\frac{1}{2}}$ cm^{-1}	$\frac{s}{\Delta\nu^a_{\frac{1}{2}}}$	$\frac{\Delta\nu^a_{\frac{1}{2}}}{\Delta\nu^t_{\frac{1}{2}}}$	$\Delta\nu^t_{\frac{1}{2}}$ cm^{-1}	$\nu-\nu_o$ cm^{-1}	$\frac{\nu-\nu_o}{\Delta\nu^t_{\frac{1}{2}}}$	$\Delta\nu$ cm^{-1}	$\frac{\Delta\nu^t_{\frac{1}{2}}}{\Delta\nu}$
π-C$_5$H$_5$Mn(CO)$_3$	2030.$_8$	- 0.10 ± 0.06	- 0.69 ± 0.45	2.90	3.91	0.74	2.10	1.86	20	10.8	0.42	4.4
	1948.$_6$	- 0.73 ± 0.10	- 2.31 ± 0.30	2.76	5.31	0.52	1.29	4.11	30	7.3	0.83	5.0
(π-CH$_3$C$_5$H$_4$)Mn(CO)$_3$	2026.$_7$	+ 0.06 ± 0.07	+ 0.37 ± 0.42	2.89	3.91	0.74	2.05	1.91	20	10.5	0.42	4.5
	1944.$_5$	- 0.95 ± 0.35	- 3.75 ± 1.41	2.74	6.88	0.40	1.15	6.60	30	4.6	0.83	8.0
π-C$_5$H$_5$Mn(CO)$_2$CS	2009.$_7$	- 0.08 ± 0.01	- 0.91 ± 0.15	2.84	6.96	0.41	1.15	5.65	32	5.7		
	1956.$_9$	- 0.11 ± 0.02	- 1.28 ± 0.23	2.77	8.72	0.32	1.09	8.00	72	9.0		
	1263.$_8$	- 0.11 ± 0.01	- 1.62 ± 0.22	2.14	9.52	0.23	1.04	9.15	56	6.1		

Appendix C

INTEGRATED INTENSITY RESULTS

Description of Terms: Tables C-1 to C-19

ν_{max}	signifies the frequency at maximum absorption.
Concn	represents the concentration of solute.
$T_{o\nu_{max}}$, $T_{\nu_{max}}$*	are the apparent intensities of incident and transmitted radiation at maximum absorption.
$\log_{10}(\frac{T_o}{T})_{\nu_{max}}$, $\ln(\frac{T_o}{T})_{\nu_{max}}$*	are the apparent absorbance at maximum absorption and the conversion to the Naperian base, the apparent peak optical density.
Band weight*	denotes the weight of the absorbance curve profile cut-outs.
Band area*	denotes the area under the apparent optical density curve and is expressed by $\int_{band}\ln(T_o/T)_\nu d\nu$.
B*	represents the apparent integrated absorption intensity defined as $(1/cl)\int_{band}\ln(T_o/T)_\nu d\nu$, where c is the concentration of solute in moles per liter, l is the cell path length in cm, and T_{o_ν} and T_ν are the apparent intensities of the incident and transmitted radiation when the spectrophotometer is set at frequency ν.
A	equals the absolute integrated absorption intensity defined as $(1/cl)\int_{band}\ln(I_o/I)_\nu d\nu$, where I_{o_ν} and I_ν are the incident and transmitted intensities of monochromatic radiation of frequency ν.
E	is the absolute integrated absorption intensity expressed in practical units (i.e., A/2.303).

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*Four individual recordings of the infrared spectra were taken at each concentration; the values reported in the tables are the average values for the four recordings.

Ramsay[a]	A is computed by taking the mean of the B values obtained at a number of different concentrations and increasing it by 2%. The errors listed are the standard deviations from the mean.
Wilson-Wells[b]	A is evaluated by extrapolating the B values taken at a number of different concentrations to zero concentration. The errors listed are the standard deviations in the intercepts, A, from least-squares analyses of the B versus c plots.
Russell-Thompson[c]	A is determined by extrapolating the B values taken at several different concentrations to zero apparent peak optical density. The errors listed are the standard deviations in the intercepts, A, from least-squares analyses of the B versus $\ln(T_0/T)_{\nu_{max}}$ plots.

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[a] R. N. Jones, D. A. Ramsay, D. S. Keir, and K. Dobriner, J. Am. Chem. Soc., 74, 80 (1952).

[b] E. B. Wilson, Jr., and A. J. Wells, J. Chem. Phys., 14, 578 (1946).

[c] R. A. Russell and H. W. Thompson, Spectrochim. Acta, 9, 133 (1957).

TABLE C-1

Integrated Intensity of the CO Stretching Absorption of $Cr(CO)_6$ in n-Hexane Solution by Simpson's Rule

ν_{max}	Concn	$To_{\nu_{max}}$	$T_{\nu_{max}}$	$\ln(\frac{To}{T})_{\nu_{max}}$	Band area	$10^{-4}B$	$10^{-4}A$, M^{-1} cm^{-2}			$10^{-4}Z$, M^{-1} cm^{-2}		
cm^{-1}	mM	%	%		cm^{-1}	M^{-1} cm^{-2}	Ramsay	Wilson-Wells	Russell-Thompson	Ramsay	Wilson-Wells	Russell-Thompson
$1986._9$	0.684	94.7	34.7	1.00	4.90	66.8	65.1	68.7	68.7	28.3	29.8	29.8
	0.832	95.5	29.9	1.16	5.65	63.4	± 1.4	± 4.3	± 4.7	± 0.6	± 1.9	± 2.0
	0.929	97.1	27.4	1.27	6.37	64.0						
	1.09	97.2	21.5	1.51	7.27	62.7						
	1.19	96.4	18.4	1.66	8.00	62.8						
	1.35	97.7	15.2	1.86	9.18	63.1						

Molecular weight = 220.1 g mol^{-1} Chart scale = 4.96 cm^{-1} $inch^{-1}$ Cell path length = 0.107 mm

TABLE C-2

Integrated Intensity of the CO Stretching Absorption of $Cr(CO)_6$ in n-Hexane Solution by the Weighing Method

ν_{max}	Concn	$\log_{10}(\frac{I_0}{I})_{\nu_{max}}$	$\ln(\frac{I_0}{I})_{\nu_{max}}$	Band weight	Band area	$10^{-4}B$	$10^{-4}A$, M^{-1} cm^{-2}			$10^{-4}\Gamma$, M^{-1} cm^{-2}		
cm^{-1}	mM			g	cm^{-1}	M^{-1} cm^{-2}	Ramsay	Wilson-Wells	Russell-Thompson	Ramsay	Wilson-Wells	Russell-Thompson
1987.2	0.654	0.398	0.917	0.071	4.57	65.2	64.3	62.8	69.2	28.2	29.9	30.1
	0.827	0.486	1.12	0.089	5.71	64.4	± 1.4	± 2.9	± 3.3	± 0.6	± 1.3	± 1.4
	0.963	0.554	1.28	0.103	6.60	65.3						
	1.09	0.624	1.44	0.113	7.25	62.3						
	1.22	0.695	1.60	0.128	8.17	62.3						
	1.35	0.765	1.76	0.140	8.98	62.1						

Molecular weight = 220.1 g mol^{-1} Chart weight = 0.256 g $inch^{-1}$ Chart scale = 7.95 cm^{-1} $inch^{-1}$ Cell path length = 0.107 mm

TABLE C-3

Integrated Intensities of the CO Stretching Absorptions of (Cycloheptatriene)$Cr(CO)_3$ in Methylene Chloride Solution by the Weighing Method

ν_{max}	Concn	$\log_{10}(\frac{T_o}{T})\nu_{max}$	$\ln(\frac{T_o}{T})\nu_{max}$	Chart weight	Band weight	Band area	$10^{-4}B$	$10^{-4}A$, M^{-1} cm^{-2}			$10^{-4}E$, M^{-1} cm^{-2}		
cm^{-1}	mM			g $inch^{-1}$	g	cm^{-1}	M^{-1} cm^{-2}	Ramsay	Wilson-Wells	Russell-Thompson	Ramsay	Wilson-Wells	Russell-Thompson
$1982._1$	1.05	0.460	1.06	0.285	0.258	16.2	14.7	14.0	16.1	16.4	6.10	6.98	7.14
	1.58	0.628	1.45	0.285	0.361	22.6	13.7	± 0.5	± 1.2	± 1.7	± 0.22	± 0.53	± 0.75
	1.70	0.649	1.50	0.296	0.391	23.6	13.3						
	1.79	0.697	1.61	0.290	0.417	25.6	13.7						
	1.85	0.710	1.64	0.296	0.432	26.0	13.5						
	1.93	0.751	1.73	0.296	0.454	27.4	13.6						
$1916._0$	1.05	0.262	0.603	0.285	0.279	17.5	15.9	15.4	17.3	17.6	6.68	7.50	7.64
	1.58	0.362	0.834	0.285	0.396	24.8	15.1	± 0.4	± 1.0	± 1.3	± 0.17	± 0.45	± 0.56
	1.70	0.383	0.882	0.296	0.433	26.1	14.7						
	1.79	0.406	0.935	0.290	0.462	28.4	15.2						
	1.85	0.418	0.963	0.296	0.476	28.7	14.9						
	1.93	0.437	1.01	0.296	0.490	29.5	14.7						
$1886._9$	1.05	0.219	0.504	0.285	0.287	18.0	16.4	15.0	18.8	19.1	6.51	8.17	8.31
	1.58	0.311	0.716	0.285	0.383	24.0	14.6	± 0.8	± 1.4	± 1.7	± 0.35	± 0.61	± 0.73
	1.70	0.331	0.762	0.296	0.418	25.2	14.2						
	1.79	0.351	0.808	0.290	0.437	26.9	14.4						
	1.85	0.361	0.831	0.296	0.465	28.0	14.5						
	1.93	0.379	0.873	0.296	0.472	28.5	14.2						

Molecular weight = 228.2 g mol^{-1} Chart scale = 7.74 cm^{-1} $inch^{-1}$ Cell path length = 1.04 mm

TABLE C-4

ν_{max}	Concn	$T_{0_{\nu_{max}}}$	$T_{\nu_{max}}$	$\ln(\frac{T_0}{T})_{\nu_{max}}$	Band area	$10^{-4}B$	$10^{-4}A$, M^{-1} cm^{-2}			$10^{-4}\varepsilon$, M^{-1} cm^{-2}		
							Ramsay	Wilson-Wells	Russell-Thompson	Ramsay	Wilson-Wells	Russell-Thompson
cm^{-1}	mM	%	%		cm^{-1}	M^{-1} cm^{-2}						
$1983._6$	0.662	97.3	41.5	0.852	12.6	16.6	16.6	17.5	17.6	7.23	7.62	7.63
	0.882	97.5	32.6	1.13	17.2	17.0	± 0.5	± 1.4	± 1.6	± 0.22	± 0.60	± 0.71
	1.10	97.2	25.5	1.34	20.1	15.8						
	1.29	97.4	19.9	1.59	24.4	15.5						
	1.40	98.8	19.0	1.65	25.3	15.7						
$1912._2$	0.882	96.5	49.9	0.660	18.9	18.6	18.3	21.1	21.3	7.93	9.17	9.24
	1.10	96.2	43.3	0.798	22.9	18.0	± 0.8	± 2.5	± 3.1	± 0.35	± 1.07	± 1.33
	1.29	96.2	37.3	0.947	27.5	18.6						
	1.40	97.3	36.2	0.989	28.3	17.6						
	1.54	97.0	33.1	1.08	29.5	16.6						
$1880._2$	0.882	96.2	53.2	0.592	18.4	18.2	18.0	19.3	19.5	7.81	8.37	8.48
	1.10	96.5	46.8	0.724	22.5	17.8	± 0.3	± 0.3	± 0.3	± 0.13	± 0.14	± 0.13
	1.29	95.3	41.2	0.839	25.9	17.5						
	1.40	96.8	40.1	0.881	28.1	17.5						
	1.54	97.2	37.0	0.996	30.6	17.2						

Molecular weight = 272.1 g mol^{-1} Chart scale = 4.97 cm^{-1} $inch^{-1}$ Cell path length = 1.15 mm

TABLE C-5

Integrated Intensities of the CO Stretching Absorptions of (Cycloheptatriene)W(CO)$_3$ in Methylene Chloride Solution by the Weighing Method

ν_{max}	Concn	$\log_{10}(\frac{T_0}{T})\nu_{max}$	$\ln(\frac{T_0}{T})\nu_{max}$	Band weight	Band area	10^{-4}B	10^{-4}A, M^{-1} cm^{-2}			10^{-4}Z, M^{-1} cm^{-2}		
cm^{-1}	mM			g	cm^{-1}	M^{-1} cm^{-2}	Ramsay	Wilson-Wells	Russell-Thompson	Ramsay	Wilson-Wells	Russell-Thompson
1971.4	1.02	0.479	1.10	0.276	17.0	16.1	15.5	18.2	18.6	6.72	7.90	8.07
	1.16	0.542	1.25	0.304	18.7	15.5	± 0.5	± 1.0	± 1.3	± 0.22	± 0.45	± 0.56
	1.27	0.574	1.32	0.321	19.8	15.0						
	1.37	0.621	1.43	0.351	21.6	15.1						
	1.50	0.679	1.56	0.379	23.3	14.9						
	1.63	0.716	1.65	0.400	24.7	14.5						
1908.3	1.02	0.280	0.645	0.302	18.6	17.6	17.3	18.6	18.7	7.50	8.06	8.13
	1.16	0.317	0.730	0.332	20.5	16.9	± 0.3	± 1.2	± 1.4	± 0.13	± 0.53	± 0.60
	1.27	0.341	0.785	0.359	22.1	16.8						
	1.37	0.367	0.845	0.395	24.3	17.0						
	1.50	0.402	0.926	0.429	26.4	16.9						
	1.63	0.428	0.986	0.456	28.1	16.5						
1873.1	1.02	0.243	0.560	0.289	17.8	16.8	17.0	16.9	16.9	7.37	7.33	7.32
	1.16	0.274	0.631	0.325	20.0	16.5	± 0.1	± 0.6	± 0.7	± 0.04	± 0.27	± 0.29
	1.27	0.296	0.682	0.357	22.0	16.7						
	1.37	0.322	0.742	0.387	23.9	16.7						
	1.50	0.353	0.813	0.425	26.2	16.8						
	1.63	0.372	0.857	0.456	28.0	16.5						

Molecular weight = 360.0 g mol^{-1} Chart weight = 0.297 g inch^{-1} Chart scale = 7.96 cm^{-1} inch^{-1} Cell path length = 1.04 mm

TABLE C-6

Integrated Intensities of the CO Stretching Absorptions of (Bicycloheptadiene)$Cr(CO)_4$ in n-Hexane Solution by Simpson's Rule

ν_{max}	Concn	$T_{0_{\nu_{max}}}$	$T_{\nu_{max}}$	$\ln(\frac{T_0}{T})_{\nu_{max}}$	Band area	$10^{-4}B$	$10^{-4}A$, M^{-1} cm^{-2}			$10^{-4}E$, M^{-1} cm^{-2}		
cm^{-1}	mM	%	%		cm^{-1}	M^{-1} cm^{-2}	Ramsay	Wilson-Wells	Russell-Thompson	Ramsay	Wilson-Wells	Russell-Thompson
2033.$_6$	5.47	97.5	41.3	0.859	4.08	7.55	7.24	8.15	8.25	3.14	3.54	3.58
	6.60	97.8	36.1	0.997	4.63	7.10	± 0.26	± 0.97	± 1.25	± 0.11	± 0.42	± 0.54
	7.08	97.7	34.1	1.05	4.78	6.85						
	8.08	98.0	28.4	1.24	5.72	7.17						
	9.43	97.6	25.8	1.33	6.36	6.83						
1958.$_7$	5.47	97.4	61.9	0.453	2.63	4.86	4.41	5.19	5.20	1.92	2.26	2.26
	6.60	97.0	57.7	0.520	2.72	4.18	± 0.27	± 1.20	± 1.33	± 0.11	± 0.52	± 0.58
	7.08	97.0	55,3	0.562	2.90	4.14						
	8.08	96.8	50.4	0.653	3.33	4.18						
	9.43	96.8	46.3	0.738	3.98	4.27						
1944.$_4$	3.17	98.4	31.1	1.15	6.67	21.3	21.4	22.0	21.8	9.29	9.57	9.49
	3.94	99.8	24.8	1.39	8.35	21.5	± 0.6	± 2.9	± 3.2	± 0.26	± 1.24	± 1.42
	4.76	98.7	20.1	1.59	9.36	19.9						
	5.47	98.2	14.9	1.89	11.4	21.2						
1914.$_8$	3.17	98.4	40.5	0.898	5.61	17.9	17.9	18.4	18.5	7.76	7.99	8.02
	3.94	99.8	33.7	1.09	6.91	17.8	± 0.3	± 0.6	± 0.8	± 0.13	± 0.28	± 0.34
	4.76	98.7	29.1	1.22	8.08	17.2						
	5.47	98.2	22.9	1.46	9.42	17.5						
	6.60	99.0	18.2	1.69	11.3	17.3						

Molecular weight = 256.1 g mol^{-1} Chart scale = 4.98 cm^{-1} $inch^{-1}$ Cell path length = 0.0987 mm

TABLE C-7

Integrated Intensities of the CO Stretching Absorptions of (Bicycloheptadiene)$Mo(CO)_4$ in n-Hexane Solution by Simpson's Rule

ν_{max}	Concn	$T_{o\nu_{max}}$	$T_{\nu_{max}}$	$\ln(\frac{T_o}{T})_{\nu_{max}}$	Band area	$10^{-4}B$	$10^{-4}A$, M^{-1} cm^{-2}			$10^{-4}E$, M^{-1} cm^{-2}		
cm^{-1}	mM	%	%		cm^{-1}	M^{-1} cm^{-2}	Ramsay	Wilson-Wells	Russell-Thompson	Ramsay	Wilson-Wells	Russell-Thompson
$2044._4$	3.07	97.8	63.9	0.426	1.80	5.98	6.04	5.91	5.87	2.62	2.57	2.55
	3.60	97.9	59.7	0.495	2.14	6.04	± 0.15	± 0.57	± 0.59	± 0.06	± 0.25	± 0.25
	4.13	97.9	56.8	0.544	2.30	5.67						
	6.00	97.1	43.4	0.805	3.54	6.00						
$1959._2$	2.00	98.1	38.7	0.930	5.77	29.3	28.1	31.7	32.2	12.2	13.8	14.0
	3.07	98.5	24.3	1.40	8.25	27.4	± 1.0	± 1.0	± 0.9	± 0.4	± 0.4	± 0.4
	3.60	98.2	19.6	1.61	9.58	27.1						
	4.13	99.1	16.6	1.79	10.8	26.6						
$1913._6$	2.00	99.2	53.2	0.623	4.22	21.5	21.2	22.8	23.0	9.19	9.90	9.97
	3.07	99.8	38.8	0.945	6.42	21.3	± 0.8	± 1.2	± 1.5	± 0.35	± 0.52	± 0.64
	3.60	99.8	33.7	1.09	7.60	21.5						
	4.13	100.0	30.9	1.17	8.09	19.9						
	6.00	99.2	18.3	1.69	11.6	19.5						

Molecular weight = 300.0 g mol^{-1} Chart scale = 4.99 cm^{-1} $inch^{-1}$ Cell path length = 0.0983 mm

TABLE C-8

Integrated Intensities of the CO Stretching Absorptions of (Bicycloheptadiene)W(CO)$_4$ ~~in n-~~Hexane Solution by the Weighing Method

ν_{max}	Concn	$\log_{10}(\frac{I_0}{I})_{\nu max}$	$\ln(\frac{I_0}{I})_{\nu max}$	Chart weight	Band weight	Band area	$10^{-4}B$	$10^{-4}A$, M^{-1} cm^{-2}			$10^{-4}E$, M^{-1} cm^{-2}		
cm^{-1}	mM			g $inch^{-1}$	g	cm^{-1}	M^{-1} cm^{-2}	Ramsay	Wilson-Wells	Russell-Thompson	Ramsay	Wilson-Wells	Russell-Thompson
2043.$_9$	3.13	0.189	0.435	0.292	0.034	2.17	6.47	6.48	6.43	6.43	2.81	2.79	2.79
	3.61	0.216	0.497	0.292	0.038	2.38	6.15	± 0.13	± 0.19	± 0.20	± 0.06	± 0.08	± 0.09
	3.90	0.230	0.530	0.292	0.043	2.70	6.45						
	5.63	0.342	0.788	0.283	0.060	3.89	6.44						
	13.3	0.735	1.69	0.283	0.138	9.92	6.25						
1957.$_3$	2.56	0.520	1.20	0.292	0.127	7.96	29.0	28.0	33.2	34.0	12.2	14.4	14.8
	3.13	0.623	1.44	0.292	0.147	9.24	27.5	± 1.0	± 2.3	± 2.5	± 0.4	± 1.0	± 1.1
	3.61	0.708	1.63	0.292	0.163	10.3	26.5						
	3.90	0.756	1.74	0.292	0.179	11.3	26.9						
1910.$_1$	2.56	0.356	0.820	0.292	0.083	5.21	19.0	18.7	19.3	19.4	8.13	8.37	8.41
	3.13	0.427	0.983	0.292	0.099	6.19	18.4	± 0.4	± 1.0	± 1.1	± 0.17	± 0.43	± 0.47
	3.61	0.489	1.13	0.292	0.110	6.94	17.9						
	3.90	0.518	1.19	0.292	0.123	7.69	18.4						
	5.63	0.737	1.70	0.283	0.169	10.9	18.1						

Molecular weight = 388.0 g mol^{-1} Chart scale = 7.95 cm^{-1} $inch^{-1}$ Cell path length = 0.107 mm

TABLE C-9

Integrated Intensities of the CO Stretching Absorptions of *fac*-$Mo(CO)_3(PCl_3)_3$ in *n*-Hexane Solution by Simpson's Rule

ν_{max}	Concn	$T_{0\,\nu_{max}}$	$T_{\nu_{max}}$	$\ln(\frac{T_0}{T})_{\nu_{max}}$	Band area	$10^{-4}B$	$10^{-4}A$, M^{-1} cm^{-2}			$10^{-4}\Sigma$, M^{-1} cm^{-2}		
cm^{-1}	mM	%	%		cm^{-1}	M^{-1} cm^{-2}	Ramsay	Wilson-Wells	Russell-Thompson	Ramsay	Wilson-Wells	Russell-Thompson
$2040._2$	0.135	96.0	56.1	0.537	2.43	15.6	15.3 ± 0.5	16.5 ± 0.8	16.8 ± 0.8	6.64 ± 0.22	7.17 ± 0.34	7.29 ± 0.35
	0.169	95.2	49.1	0.662	3.00	15.4						
	0.220	95.2	41.7	0.826	3.84	15.2						
	0.270	96.0	34.7	1.02	4.42	14.2						
	0.338	95.8	29.0	1.20	5.63	14.5						
$1991._1$	0.135	97.0	59.2	0.494	3.60	23.2	23.2 ± 0.7	24.6 ± 1.2	24.7 ± 1.4	10.1 ± 0.3	10.7 ± 0.5	10.7 ± 0.6
	0.169	96.2	51.8	0.619	4.61	23.7						
	0.220	96.2	44.3	0.775	5.67	22.4						
	0.270	96.9	36.7	0.971	7.09	22.8						
	0.338	96.5	30.7	1.15	8.41	21.7						

Molecular weight = 592.0 g mol^{-1} Chart scale = 4.98 cm^{-1} $inch^{-1}$ Cell path length = 1.1[illegible] mm

TABLE C-10

Integrated Intensities of the CO Stretching Absorptions of *fac*-$Mo(CO)_3(PCl_3)_3$ in Methylene Chloride Solution by Simpson's Rule

ν_{max}	Concn	$T_{o\,\nu_{max}}$	$T_{\nu_{max}}$	$\ln(\frac{T_o}{T})_{\nu_{max}}$	Band area	$10^{-4}B$	$10^{-4}A$, M^{-1} cm^{-2}			$10^{-4}E$, M^{-1} cm^{-2}		
cm^{-1}	mM	%	%		cm^{-1}	M^{-1} cm^{-2}	Ramsay	Wilson-Wells	Russell-Thompson	Ramsay	Wilson-Wells	Russell-Thompson
$2039._9$	0.510	95.8	52.7	0.598	8.16	13.9	14.0	14.0	13.9	6.10	6.07	6.04
	0.679	95.5	43.3	0.791	11.0	14.1	± 0.3	± 0.9	± 1.0	± 0.13	± 0.40	± 0.43
	0.845	95.7	38.5	0.911	12.9	13.3						
	1.02	95.9	31.0	1.13	16.1	13.7						
	1.18	95.9	25.4	1.33	18.9	13.9						
$1986._6$	0.510	96.9	61.2	0.460	15.1	25.8	26.1	25.7	25.5	11.3	11.2	11.1
	0.679	97.0	53.2	0.601	20.4	26.1	± 0.7	± 2.5	± 2.6	± 0.3	± 1.1	± 1.1
	0.845	97.0	47.8	0.708	24.2	24.9						
	1.02	97.0	40.9	0.864	29.1	24.7						
	1.18	98.0	35.0	1.03	35.9	26.4						

Molecular weight = 592.0 g mol^{-1} Chart scale = 4.98 cm^{-1} $inch^{-1}$ Cell path length = 1.15 mm

TABLE C-11

Integrated Intensities of the CO Stretching Absorptions of *fac*-$Mo(CO)_3[P(C_6H_5)Cl_2]_3$ in Methylene Chloride Solution by the Weighing Method

ν_{max}	Concn	$\log_{10}(\frac{T_0}{T})_{\nu max}$	$\ln(\frac{T_0}{T})_{\nu max}$	Band weight	Band area	$10^{-4}B$	$10^{-4}A$, M^{-1} cm^{-2}			$10^{-4}\varepsilon$, M^{-1} cm^{-2}		
cm^{-1}	mM			g	cm^{-1}	M^{-1} cm^{-2}	Ramsay	Wilson-Wells	Russell-Thompson	Ramsay	Wilson-Wells	Russell-Thompson
$2006._0$	1.12	0.432	0.995	0.251	15.5	13.2	13.3	13.6	13.6	5.77	5.90	5.90
	1.30	0.500	1.15	0.298	17.7	13.1	± 0.2	± 0.7	± 0.8	± 0.09	± 0.32	± 0.36
	1.43	0.538	1.24	0.313	19.3	12.9						
	1.62	0.614	1.41	0.364	22.4	13.3						
	1.79	0.655	1.51	0.389	24.0	12.9						
	1.95	0.717	1.65	0.423	26.0	12.8						
$1940._8$	1.12	0.319	0.735	0.474	29.2	24.9	25.3	24.8	24.8	11.0	10.8	10.8
	1.30	0.369	0.850	0.542	33.4	24.6	± 0.2	± 1.2	± 1.3	± 0.1	± 0.5	± 0.6
	1.43	0.402	0.926	0.596	36.7	24.7						
	1.62	0.457	1.05	0.691	42.6	25.2						
	1.79	0.496	1.14	0.746	46.0	24.7						
	1.95	0.539	1.24	0.815	50.2	24.7						

Molecular weight = 716.9 g mol^{-1} Chart weight = 0.298 g $inch^{-1}$ Chart scale = 7.96 cm^{-1} $inch^{-1}$ Cell path length = 1.04 mm

TABLE C-12

Integrated Intensities of the CO Stretching Absorptions of *fac*-$Mo(CO)_3[P(C_6H_5)_2Cl]_3$ in Methylene Chloride Solution by the Weighing Method

ν_{max}	Concn	$\log_{10}(\frac{T_0}{T})\nu_{max}$	$\ln(\frac{T_0}{T})\nu_{max}$	Band weight	Band area	$10^{-4}B$	$10^{-4}A$, M^{-1} cm^{-2}			$10^{-4}\varepsilon$, M^{-1} cm^{-2}		
cm^{-1}	mM			g	cm^{-1}	M^{-1} cm^{-2}	Ramsay	Wilson-Wells	Russell-Thompson	Ramsay	Wilson-Wells	Russell-Thompson
$1970._5$	0.935	0.300	0.691	0.228	14.0	13.7	14.8	14.2	13.6	6.20	6.17	5.92
	1.05	0.413	0.951	0.259	16.0	14.6	± 0.4	± 2.3	± 1.8	± 0.17	± 1.00	± 0.79
	1.21	0.442	1.02	0.281	17.3	13.7						
	1.36	0.497	1.15	0.324	20.0	14.1						
	1.43	0.546	1.26	0.350	21.6	14.0						
$1889._4$	0.935	0.261	0.601	0.426	26.3	25.6	27.9	26.2	24.8	12.1	11.4	10.8
	1.05	0.323	0.744	0.509	31.4	28.7	± 1.1	± 7.0	± 6.2	± 0.5	± 3.0	± 2.7
	1.21	0.348	0.901	0.563	34.7	27.5						
	1.36	0.337	0.891	0.648	40.0	28.1						
	1.48	0.425	0.979	0.673	41.5	26.9						

Molecular weight = 941.0 g mol^{-1} Chart weight = 0.298 g $inch^{-1}$ Chart Scale = 7.96 cm^{-1} $inch^{-1}$ Cell path length = 1.04 mm

TABLE C-13

Integrated Intensities of the CO Stretching Absorptions of *cis*-$Mn(CO)_4[P(C_6H_5)_3]Br$ in *n*-Hexane Solution by Simpson's Rule

ν_{max}	Concn	$T_{o\nu_{max}}$	$T_{\nu_{max}}$	$\ln(\frac{T_o}{T})_{\nu_{max}}$	Band area	$10^{-4}B$	$10^{-4}A$, M^{-1} cm^{-2}			$10^{-4}E$, M^{-1} cm^{-2}		
cm^{-1}	mM	%	%		cm^{-1}	M^{-1} cm^{-2}	Ramsay	Wilson-Wells	Russell-Thompson	Ramsay	Wilson-Wells	Russell-Thompson
$2099._2$	0.663	80.7	49.1	0.497	2.81	3.65	3.70	3.73	3.75	1.61	1.62	1.63
	0.791	84.8	48.0	0.569	3.39	3.73	± 0.08	± 0.25	± 0.23	± 0.03	± 0.11	± 0.12
	1.09	80.0	36.6	0.782	4.45	3.53						
	1.33	80.2	32.1	0.916	5.38	3.53						
	1.58	84.7	29.2	1.07	6.70	3.68						
$2024._6$	0.663	79.6	39.8	0.693	5.76	7.56	7.48	7.87	7.94	3.25	3.42	3.45
	0.791	83.6	37.5	0.802	6.91	7.60	± 0.25	± 0.59	± 0.66	± 0.11	± 0.26	± 0.29
	1.09	78.7	26.7	1.08	9.17	7.28						
	1.33	78.1	22.0	1.27	10.5	6.91						
	1.58	83.0	18.7	1.49	13.3	7.32						
$2006._4$	0.547	79.8	35.3	0.816	7.87	12.5	12.3	13.2	13.4	5.33	5.75	5.82
	0.663	80.7	31.2	0.950	9.00	11.8	± 0.6	± 1.2	± 1.4	± 0.26	± 0.52	± 0.59
	0.791	84.8	28.2	1.10	11.7	12.5						
	1.09	80.0	17.7	1.51	14.8	11.8						
	1.33	80.2	13.9	1.75	17.2	11.3						
$1960._8$	0.663	80.7	48.3	0.513	6.67	8.74	8.76	9.23	9.30	3.80	4.01	4.04
	0.791	84.5	46.5	0.601	8.09	8.89	± 0.21	± 0.24	± 0.27	± 0.09	± 0.11	± 0.12
	1.09	80.0	35.2	0.821	10.8	8.58						
	1.33	80.2	30.7	0.960	12.8	8.40						
	1.58	84.7	27.7	1.12	15.1	8.31						

Molecular weight = 509.2 g mol^{-1} | Chart scale = 4.98 cm^{-1} $inch^{-1}$ | Cell path length = 1.15 mm

TABLE C-14

Integrated Intensities of the CO Stretching Absorptions of *cis*-$Mn(CO)_4[As(C_6H_5)_3]Br$ in *n*-Hexane Solution by Simpson's Rule

ν_{max} cm^{-1}	Concn mM	T_{o_ν} %	T_ν %	$\ln(\frac{T_o}{T})\nu_{max}$	Band area cm^{-1}	$10^{-4}B$ M^{-1} cm^{-2}	$10^{-4}A$, M^{-1} cm^{-2} Ramsay	Wilson-Wells	Russell-Thompson	$10^{-4}E$, M^{-1} cm^{-2} Ramsay	Wilson-Wells	Russell-Thompson
$2091._8$	0.594	93.0	61.2	0.419	2.39	3.50	3.65	3.47	3.47	1.58	1.51	1.51
	0.631	94.5	60.8	0.441	2.58	3.56	± 0.05	± 0.14	± 0.15	± 0.02	± 0.06	± 0.06
	0.884	92.4	48.9	0.636	3.70	3.64						
	1.19	93.4	40.9	0.826	4.86	3.55						
	1.26	94.7	39.6	0.872	5.28	3.63						
$2023._7$	0.594	92.0	47.3	0.665	6.06	8.86	9.00	9.67	9.65	3.91	4.20	4.19
	0.632	93.5	45.8	0.714	6.59	9.07	± 0.39	± 0.96	± 1.11	± 0.17	± 0.42	± 0.48
	0.884	91.4	32.8	1.03	9.54	9.39						
	1.19	92.4	25.9	1.27	11.4	8.32						
	1.26	93.7	24.2	1.35	12.3	8.49						
$2011._4$	0.442	92.2	49.0	0.632	5.88	11.6	12.0	11.9	11.8	5.21	5.15	5.13
	0.594	93.0	40.1	0.841	7.92	11.6	± 0.3	± 0.8	± 0.8	± 0.13	± 0.35	± 0.37
	0.632	94.5	37.9	0.914	8.80	12.1						
	0.882	92.4	25.9	1.27	12.3	12.1						
	1.19	93.4	18.1	1.64	15.7	11.5						
$1962._3$	0.594	93.0	58.2	0.469	5.47	8.00	8.69	8.14	8.09	3.77	3.59	3.51
	0.632	94.5	56.2	0.520	6.33	8.72	± 0.27	± 0.82	± 0.84	± 0.12	± 0.36	± 0.36
	0.884	92.4	45.6	0.706	8.83	8.69						
	1.19	93.4	37.1	0.923	11.6	8.47						
	1.26	94.7	35.1	0.993	12.6	8.71						

Molecular weight = 553.1 g mol^{-1} Chart scale = 4.98 cm^{-1} $inch^{-1}$ Cell path length = 1.15 mm

TABLE C-15

Integrated Intensities of the CO Stretching Absorptions of *cis*-$Mn(CO)_4[Sb(C_6H_5)_3]Br$ in *n*-Hexane Solution by Simpson's Rule

ν_{max}	Concn	$T_{o\,\nu_{max}}$	$T_{\nu_{max}}$	$\ln(\frac{T_o}{T})_{\nu_{max}}$	Band area	$10^{-4}B$	$10^{-4}A$, M^{-1} cm^{-2}			$10^{-4}\varepsilon$, M^{-1} cm^{-2}		
cm^{-1}	mM	%	%		cm^{-1}	M^{-1} cm^{-2}	Ramsay	Wilson-Wells	Russell-Thompson	Ramsay	Wilson-Wells	Russell-Thompson
$2037._5$	0.550	92.5	59.1	0.448	2.70	4.26	4.30	4.61	4.64	1.87	2.00	2.02
	0.633	92.2	56.1	0.497	3.21	4.40	± 0.14	± 0.25	± 0.27	± 0.06	± 0.11	± 0.12
	0.933	94.9	46.2	0.720	4.61	4.29						
	1.10	92.5	40.8	0.819	5.16	4.08						
	1.27	91.5	35.4	0.950	5.86	4.02						
$2021._6$	0.550	91.8	50.1	0.606	4.99	7.89	7.70	8.34	8.41	3.34	3.62	3.65
	0.633	91.2	46.1	0.682	5.66	7.77	± 0.25	± 0.21	± 0.24	± 0.11	± 0.09	± 0.11
	0.933	93.9	35.7	0.967	8.07	7.52						
	1.10	91.5	30.0	1.12	9.19	7.26						
	1.27	90.5	24.9	1.29	10.6	7.30						
2009.2	0.467	94.7	46.9	0.703	7.15	13.3	12.8	13.8	14.0	5.57	6.01	6.09
	0.550	92.5	41.0	0.814	8.14	12.9	± 0.5	± 0.6	± 0.7	± 0.22	± 0.27	± 0.30
	0.633	92.2	36.7	0.921	9.05	12.4						
	0.933	94.9	26.1	1.29	13.1	12.2						
	1.10	92.5	20.6	1.50	15.3	12.1						
$1960._4$	0.550	92.5	57.9	0.469	5.95	9.40	9.23	9.37	9.37	4.01	4.07	4.07
	0.633	92.2	54.8	0.520	6.43	8.83	± 0.20	± 0.59	± 0.64	± 0.09	± 0.26	± 0.28
	0.933	94.9	44.1	0.766	9.80	9.13						
	1.10	92.5	38.6	0.874	11.4	9.02						
	1.27	91.5	33.1	1.02	12.9	8.88						

Molecular weight = 600.0 g mol^{-1} Chart scale = 4.98 cm^{-1} $inch^{-1}$ Cell path length = 1.15 mm

TABLE C-16

Integrated Intensities of the CO Stretching Absorptions of π-$C_5H_5Mn(CO)_3$ in n-Hexane Solution by Simpson's Rule

ν_{max}	Concn	$To_{\nu_{max}}$	$T_{\nu_{max}}$	$\ln(\frac{To}{T})_{\nu_{max}}$	Band area	$10^{-4}B$	$10^{-4}A$, M^{-1} cm^{-2}			$10^{-4}B$, M^{-1} cm^{-2}		
cm^{-1}	mM	%	%		cm^{-1}	M^{-1} cm^{-2}	Ramsay	Wilson-Wells	Russell-Thompson	Ramsay	Wilson-Wells	Russell-Thompson
$2030._8$	3.45	99.0	54.3	0.601	2.85	8.27	8.41	8.68	8.75	3.65	3.77	3.90
	3.92	98.9	50.6	0.670	3.28	8.39	± 0.12	± 0.64	± 0.75	± 0.05	± 0.28	± 0.32
	4.50	98.7	46.8	0.746	3.76	8.34						
	4.92	98.3	43.7	0.811	3.96	8.04						
	5.42	98.7	40.6	0.888	4.44	8.19						
$1943._6$	2.56	98.9	38.9	0.933	6.61	25.8	25.6	27.6	27.9	11.1	12.0	12.1
	2.95	99.1	34.1	1.07	7.52	25.5	± 0.5	± 0.8	± 0.8	± 0.2	± 0.3	± 0.4
	3.45	100.1	29.3	1.23	8.56	24.8						
	3.92	100.0	25.6	1.36	9.27	24.9						
	4.50	99.9	21.0	1.56	10.9	24.3						

Molecular weight = 204.1 g mol^{-1} Chart scale = 4.98 cm^{-1} $inch^{-1}$ Cell path length = 0.100 mm

TABLE C-17

Integrated Intensities of the CO Stretching Absorptions of $(\pi\text{-}CH_3C_5H_4)Mn(CO)_3$ in n-Hexane Solution by Simpson's Rule

ν_{max}	Concn	$T_{0_{\nu max}}$	$T_{\nu max}$	$\ln(\frac{T_0}{T})_{\nu max}$	Band area	$10^{-4}B$	$10^{-4}A$, M^{-1} cm^{-2}			$10^{-4}E$, M^{-1} cm^{-2}		
cm^{-1}	mM	%	%		cm^{-1}	M^{-1} cm^{-2}	Ramsay	Wilson-Wells	Russell-Thompson	Ramsay	Wilson-Wells	Russell-Thompson
$2026._7$	4.32	98.7	47.1	0.740	3.64	8.43	8.67	8.17	8.17	3.77	3.55	3.55
	4.74	98.8	43.7	0.816	4.08	8.60	± 0.12	± 0.82	± 0.84	± 0.05	± 0.36	± 0.37
	5.24	99.4	40.5	0.898	4.36	8.31						
	5.81	99.6	37.1	0.988	4.99	8.59						
	6.21	100.0	34.7	1.06	5.33	8.58						
$1944._5$	2.78	99.9	42.5	0.855	7.50	27.0	25.9	29.0	29.5	11.2	12.6	12.8
	3.33	99.9	37.1	0.991	8.29	24.9	± 0.9	± 2.9	± 3.5	± 0.4	± 1.3	± 1.5
	3.81	100.5	32.3	1.14	9.66	25.4						
	4.32	100.0	29.2	1.23	10.7	24.8						
	4.74	100.3	26.0	1.35	11.8	24.8						

Molecular weight = 218.1 g mol^{-1} Chart scale = 4.98 cm^{-1} $inch^{-1}$ Cell path length = 0.100 mm

TABLE C-18

Integrated Intensities of the CO Stretching Absorptions of π-$C_5H_5Mn(CO)_2CS$ in Carbon Disulphide Solution by the Weighing Method												
ν_{max}	Concn	$\log_{10}(\frac{T_o}{T})_{\nu max}$	$\ln(\frac{T_o}{T})_{\nu max}$	Band weight	Band area	$10^{-4}B$	$10^{-4}A$, M^{-1} cm^{-2}			$10^{-4}\Sigma$, M^{-1} cm^{-2}		
cm^{-1}	mM			g	cm^{-1}	M^{-1} cm^{-2}	Ramsay	Wilson-Wells	Russell-Thompson	Ramsay	Wilson-Wells	Russell-Thompson
2009.7	7.75	0.391	0.901	0.126	8.96	10.8	10.6	11.3	11.5	4.62	4.92	5.01
	9.25	0.447	1.03	0.147	10.5	10.6	± 0.2	± 0.4	± 0.5	± 0.09	± 0.17	± 0.20
	10.2	0.485	1.12	0.163	11.5	10.6						
	12.1	0.563	1.30	0.188	13.3	10.2						
	13.7	0.624	1.44	0.211	14.9	10.2						
	15.5	0.692	1.57	0.240	17.0	10.2						
1956.9	7.75	0.380	0.875	0.169	12.0	14.4	14.1	15.1	15.4	6.14	6.56	6.68
	9.25	0.435	1.00	0.194	13.7	13.9	± 0.3	± 0.5	± 0.7	± 0.13	± 0.23	± 0.29
	10.2	0.473	1.09	0.215	15.2	14.0						
	12.1	0.548	1.26	0.254	18.0	13.8						
	13.7	0.603	1.39	0.284	20.1	13.7						
	15.5	0.664	1.53	0.313	22.2	13.4						

Molecular weight = 220.1 g mol^{-1} Chart weight = 0.260 g $inch^{-1}$ Chart scale = 8.02 cm^{-1} $inch^{-1}$ Cell path length = 0.107 mm

TABLE C-19

Integrated Intensity of the CS Stretching Absorption of π-$C_5H_5Mn(CO)_2CS$ in Carbon Disulphide Solution by the Weighing Method

ν_{max}	Concn	$\log_{10}(\frac{T_o}{T})_{\nu_{max}}$	$\ln(\frac{T_o}{T})_{\nu_{max}}$	Band weight	Band area	$10^{-4}B$	$10^{-4}A$, M^{-1} cm^{-2}			$10^{-4}E$, M^{-1} cm^{-2}		
cm^{-1}	mM			g	cm^{-1}	M^{-1} cm^{-2}	Ramsay	Wilson-Wells	Russell-Thompson	Ramsay	Wilson-Wells	Russell-Thompson
$1263._8$	7.75	0.304	0.700	0.147	10.4	12.5	12.5	13.5	13.8	5.42	5.88	5.99
	9.25	0.354	0.815	0.176	12.5	12.6	± 0.3	± 0.4	± 0.5	± 0.13	± 0.18	± 0.22
	10.2	0.392	0.880	0.190	13.5	12.4						
	12.1	0.444	1.02	0.224	15.9	12.2						
	13.7	0.491	1.13	0.246	17.4	11.9						
	15.5	0.542	1.25	0.275	19.5	11.8						

Molecular weight = 220.1 g mol^{-1} Chart weight = 0.260 g $inch^{-1}$ Chart scale = 8.02 cm^{-1} $inch^{-1}$ Cell path length = 0.107 mm

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