

to the "best"³⁵ molybdenum-alkyl bond length of 2.383 ± 0.010 Å for $[\text{C}_{10}\text{H}_8\text{Mo}(\text{CO})_3\text{CH}_3]_2$.⁷ It should be remembered, however, that there is a difference of approximately 0.03 Å in the covalent radii of sp^2 - and sp^3 -hybridized carbon atoms. The present molybdenum-acetyl bond length is thus reduced by ~ 0.09 Å (*i.e.*, $\sim 6.5\sigma$) from the idealized $\text{Mo}-\text{C}(\text{sp}^2)$ single-bond distance and corresponds to a bond order of ~ 1.12 .² Since changes in σ -bond strength in going from a molybdenum alkyl to a molybdenum acetyl are likely to be small,³⁶ we believe the observed $\text{Mo}-\text{COCH}_3$ distance to provide a direct qualitative and

(35) This particular value is selected since it has the lowest esd of the measurements available. Other measured bond lengths are 2.397 ± 0.019 Å for the $\text{Mo}-\text{C}_2\text{H}_5$ linkage in $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_2\text{C}_2\text{H}_5$ ^{1b} and 2.41 ± 0.02 Å for the $\text{Mo}-\text{CH}_2$ linkage in $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_2\text{CH}_2\text{CO}_2\text{H}$.³ The molybdenum-alkyl bond length predicted from appropriate covalent radii is 2.38 Å (using half the $\text{Mo}-\text{Mo}$ distance of 3.22 Å in $[\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_2]_2$ ⁶ and the $\text{C}(\text{sp}^2)$ radius of 0.77 Å).

quantitative measure of $d_{\pi}-p_{\pi}$ back-donation from a transition metal to an acyl group.

Infrared studies¹ on $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{COCH}_3$ and $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]\text{COCH}_3$ reveal ketonic stretching frequencies at 1640 and 1595 cm^{-1} (respectively), indicating that the triphenylphosphine ligand is not as good a π acceptor as a carbonyl group. This indicates that the bond order of the molybdenum-acetyl linkage in the present complex may be greater than that in the unsubstituted complex $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{COCH}_3$.

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(36) Since carbon-carbon single-bond distances are 1.510 ± 0.005 Å for $\text{C}-\text{C}=\text{C}$ and 1.506 ± 0.005 Å for $\text{C}-\text{C}=\text{O}$ (see ref 34, p S15s).

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Infrared Intensities of the Carbonyl Stretching Modes and Electronic Spectra of Substituted Molybdenum Carbonyls¹

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Intensity and frequency data for the CO stretching motion in substituted metal carbonyls are presented for compounds of the types $\text{Mo}(\text{CO})_5\text{L}$, *trans*- $\text{Mo}(\text{CO})_4\text{L}_2$, and *cis*- $\text{Mo}(\text{CO})_3\text{L}_3$. The coupling between the two A_1 modes in the monosubstituted complexes has been found not to depend significantly on whether the $\text{M}-\text{C}$ stretching force constant and various associated interaction constants are included in the vibrational analysis. The L matrix elements are used to calculate θ , the angle between axial and radial CO groups, assuming equal MCO group dipole moment derivatives for the two A_1 modes. Dipole moment derivatives have been calculated assuming characteristic moments for the A_1 and E modes. The electronic spectra for these complexes in the ultraviolet and visible regions are reported. The infrared and electronic spectral results indicate that substitution of CO by a ligand capable of π bonding does not necessarily result in any increase in π bonding to the remaining CO groups.

Introduction

In interpreting the infrared intensities of the CO stretching modes in substituted metal carbonyls some assumption must usually be made regarding the number of different characteristic localized MCO group moment derivatives for the various CO groups in a given complex.³⁻⁹

It may be assumed that there is but one characteristic moment derivative, that there is a different deriva-

tive for each of the chemically different CO groups, or that there is a different one for each symmetry mode. In this paper we discuss intensity results for several substituted molybdenum carbonyls. The results can be satisfactorily interpreted in terms of the assumption that each carbonyl stretching symmetry mode exhibits a characteristic MCO group moment derivative.

Coupling of the A_1 Symmetry Coordinates in the A_1 Modes

It is important to establish that the calculated coupling between the two CO stretching modes of A_1 symmetry is not sensitive to the assumptions made regarding the nature of the force field. The coupling between the two A_1 modes in a few select $\text{Mo}(\text{CO})_5\text{L}$ molecules was computed using the simplest possible model, the Cotton-Kraihanzel approximations that $2k_c = k_t$ and $k_{c'} = k_c$.¹⁰ The L matrix elements obtained are shown

(1) This research was supported by a grant from the National Science Foundation.

(2) National Institutes of Health Predoctoral Fellow, 1967-1968.

(3) W. Beck and R. E. Nitzschmann, *Z. Naturforsch.*, **17b**, 577 (1962).

(4) K. Noack, *Helv. Chim. Acta*, **45**, 1847 (1962).

(5) W. Beck, A. Melnikoff, and R. Stahl, *Angew. Chem.*, **77**, 719 (1965).

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

(7) T. L. Brown and D. J. Darensbourg, *ibid.*, **6**, 971 (1967). In order to bring our labeling into accord with the more general practice, we have in the present paper reversed the numbering of the A_1 modes. The higher frequency A_1 mode is now labeled 2, and its intensity I_2 . Thus $|L_{11}| > |L_{12}|$, and $|L_{22}| > |L_{21}|$.

(8) A. R. Manning and J. R. Miller, *J. Chem. Soc., Sect. A*, 1521 (1966).

(9) P. S. Braterman, R. Bau, and H. D. Kaesz, *Inorg. Chem.*, **6**, 2097 (1967).

(10) F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, **84**, 4432 (1962).

in Table I. The force constants used in the calculations are listed in Table II. Calculated frequencies were within $\pm 3 \text{ cm}^{-1}$ of those experimentally observed.

TABLE I
CALCULATED VALUES FOR THE L MATRIX ELEMENTS
OF SOME MOLYBDENUM CARBONYL DERIVATIVES

| Compound | L_{12} | L_{22} |
|--|----------|----------|
| $(\text{CH}_3\text{O})_3\text{PMo}(\text{CO})_5$ | 0.1337 | 0.3576 |
| $(\text{CH}_3\text{O})_3\text{PMo}(\text{CO})_5^a$ | 0.1316 | 0.3583 |
| $\text{Cl}_3\text{PMo}(\text{CO})_5$ | 0.1435 | 0.3538 |
| $\text{C}_2\text{H}_5\text{NM}(\text{CO})_5$ | 0.1064 | 0.3667 |

^a Calculations using a more complex force field as described in text.

TABLE II
VALUES FOR THE FREQUENCIES, FORCE CONSTANTS, AND
INTENSITIES IN SEVERAL SUBSTITUTED MOLYBDENUM CARBONYLS

| Compound | Vibra- tion, ^a cm ⁻¹ | Intens ^b | k_1^c | k_2 | k_1 |
|---|--|---------------------|--------------------|-------|-------|
| $\text{Mo}(\text{CO})_6$ | 1989 (T _{1u}) | 73.6 | 16.52 | 16.52 | 0.27 |
| $\text{C}_6\text{H}_{10}\text{NHMo}(\text{CO})_5$ | 2074 (A ₁) | 0.945 | 15.10 | 15.87 | 0.33 |
| | 1922 (A ₁) | 12.5 | | | |
| | 1941 (E) | 57.2 | | | |
| $\text{C}_2\text{H}_5\text{NM}(\text{CO})_5$ | 2074 (A ₁) | 1.19 | 15.14 | 15.88 | 0.32 |
| | 1922 (A ₁) | 12.2 | | | |
| | 1943 (E) | 55.4 | | | |
| $(\text{C}_6\text{H}_5)_2\text{PMo}(\text{CO})_5$ | 2075 (A ₁) | 3.30 | 15.49 | 15.96 | 0.30 |
| | 1989 (B ₁) | <i>d</i> | | | |
| | 1945 (A ₁) | 66.8 | | | |
| | 1950 (E) | | | | |
| $(\text{C}_6\text{H}_5)_2\text{AsMo}(\text{CO})_5$ | 2076 (A ₁) | 3.47 | 15.51 | 15.98 | 0.30 |
| | 1989 (B ₁) | 0.59 | | | |
| | 1945 (A ₁) | 13.4 | | | |
| | 1952 (E) | 47.8 | | | |
| $(\text{C}_6\text{H}_5)_2\text{SbMo}(\text{CO})_5$ | 2075 (A ₁) | 4.13 | 15.69 | 16.00 | 0.29 |
| | 1989 (B ₁) | <i>d</i> | | | |
| | 1955 (A ₁) | 62.4 | | | |
| 1955 (E) | | | | | |
| $(\text{C}_2\text{H}_5\text{O})_3\text{PMo}(\text{CO})_5$ | 2080 (A ₁) | 1.83 | 15.82 | 16.01 | 0.31 |
| | 1995 (B ₁) | 2.47 | | | |
| | 1966 (A ₁) | 14.1 | | | |
| | 1952 (E) | 47.3 | | | |
| $(\text{CH}_3\text{O})_3\text{PMo}(\text{CO})_5$ | 2082 (A ₁) | 2.08 | 15.90 | 16.06 | 0.31 |
| | 1997 (B ₁) | 1.39 | | | |
| | 1970 (A ₁) | 13.9 | | | |
| | 1956 (E) | 47.0 | | | |
| $(\text{C}_6\text{H}_5\text{O})_3\text{PMo}(\text{CO})_5$ | 2085 (A ₁) | 2.57 | 15.93 | 16.19 | 0.29 |
| | 2000 (B ₁) | <i>d</i> | | | |
| | 1972 (A ₁) | 56.6 | | | |
| | 1967 (E) | | | | |
| $\text{Cl}_3\text{PMo}(\text{CO})_5$ | 2095 (A ₁) | 3.30 | 16.43 | 16.46 | 0.25 |
| | 2013 (B ₁) | <i>d</i> | | | |
| | 2001 (A ₁) | 12.1 | | | |
| | 1988 (E) | 44.7 | | | |
| <i>trans</i> -Mo(CO) ₄ [P(OCH ₃) ₃] ₂ | 2045 (A ₁) | <i>d</i> | 15.61 | | 0.34 |
| | 1973 (B ₁) | <i>d</i> | | | |
| | 1923 (E) | 50.6 | | | |
| <i>trans</i> -Mo(CO) ₄ [P(OC ₂ H ₅) ₃] ₂ | 2054 (A ₁) | <i>d</i> | 15.93 | | 0.33 |
| | 1986 (B ₁) | <i>d</i> | | | |
| | 1945 (E) | 44.0 | | | |
| <i>cis</i> -Mo(CO) ₃ [P(OCH ₃) ₃] ₃ | 1978 (A ₁) | 14.0 | 15.01 ^e | | 0.40 |
| | 1902 ^f (E) | 28.8 | | | |
| | 1886 | | | | |

^a All spectra were measured in hexane solution. ^b $\times 10^{-4} \text{ M}^{-1} \text{ cm}^{-2}$. ^c Units of mdyne/Å. ^d Approximated to be less than 1% of the total measured intensity. ^e E mode frequency of 1902 cm^{-1} used in calculating these force constants.

The sensitivity of the coupling to the assumptions regarding Mo-C stretching and interaction force constants was tested using the $(\text{CH}_3\text{O})_3\text{PMo}(\text{CO})_5$ molecule. Force constants used for the Mo-C stretching and interactions were those found by Jones¹¹ for $\text{Mo}(\text{CO})_6$. These values, in mdyne/Å, were $F_{\text{MC}} = 1.806$,

(11) L. H. Jones, *Spectrochim. Acta*, **19**, 329 (1963).

$F_{\text{MC},\text{MC}'(\text{opposite})} = 0.364$, $F_{\text{MC},\text{MC}'(\text{adjacent})} = 0.121$, $F_{\text{CO},\text{MC}(\text{neighbors})} = 0.487$, $F_{\text{CO},\text{MC}'(\text{opposite})} = -0.209$, $F_{\text{CO},\text{MC}'(\text{adjacent})} = -0.070$. The L matrix elements changed by less than 2% as shown in Table I. We, therefore, conclude that the Cotton-Kraihanzel force field is adequate for determination of L matrix elements involving the CO stretches.

Using the calculated L matrix elements the ratios of the two A₁ intensities (Table II) can be computed assuming a mixing of the radial and axial modes as the *only* means by which the radial stretch gains intensity. These values are found in Table III where ρ is the ratio L_{12}/L_{11} as described in ref 8, and ρ^2 equals I_2/I_1 if the above assumptions are met. By a comparison with the observed ratios it is clear that, for many of the compounds studied, some other effect in addition to coupling must be responsible for the intensity of the radial A₁ mode. This is also found to be the case in $\text{Mn}(\text{CO})_5\text{X}$ complexes.^{8,12} This difference in intensity ratio might be attributed to either a deviation from planarity for the four radial CO groups or to a difference in the dipole moment derivatives for the radial and axial CO groups in the A₁ symmetry modes.

TABLE III
INTENSITY RATIO CALCULATED FROM A
MIXING OF THE A₁ MODES ONLY

| Compound | ρ | ρ^2 | I_2/I_1 (obsd) |
|---|--------|----------|------------------|
| $\text{C}_6\text{H}_{10}\text{NHMo}(\text{CO})_5$ | 0.290 | 0.0841 | 0.0760 |
| $\text{C}_2\text{H}_5\text{NM}(\text{CO})_5$ | 0.292 | 0.0852 | 0.0980 |
| $\text{C}_2\text{H}_5\text{NM}(\text{CO})_5^a$ | ... | 0.0842 | 0.0980 |
| $(\text{C}_6\text{H}_5)_2\text{AsMo}(\text{CO})_5$ | 0.321 | 0.103 | 0.259 |
| $(\text{C}_2\text{H}_5\text{O})_3\text{PMo}(\text{CO})_5$ | 0.377 | 0.142 | 0.130 |
| $(\text{CH}_3\text{O})_3\text{PMo}(\text{CO})_5$ | 0.381 | 0.145 | 0.150 |
| $(\text{CH}_3\text{O})_3\text{PMo}(\text{CO})_5^a$ | ... | 0.140 | 0.150 |
| $\text{Cl}_3\text{PMo}(\text{CO})_5$ | 0.420 | 0.176 | 0.273 |
| $\text{Cl}_3\text{PMo}(\text{CO})_5^a$ | ... | 0.165 | 0.273 |

^a These values were calculated from the individually obtained L matrix elements listed in Table I.

Geometrical Considerations

From the equations derived relating the A₁ mode intensities to the normal coordinates it develops that for $I_2(\text{A}_1^{\text{rad}})$ to increase θ must be less than 90° ⁷

$$I_2(\text{A}_1^{\text{rad}}) = (\mu_{\text{MCO}}^{(1)'}L_{12} + 2 \cos \theta \mu_{\text{MCO}}^{(2)'}L_{22})^2 \quad (1)$$

$$I_1(\text{A}_1^{\text{ax}}) = (\mu_{\text{MCO}}^{(1)'}L_{11} + 2 \cos \theta \mu_{\text{MCO}}^{(2)'}L_{21})^2 \quad (2)$$

$$L_{22} = -L_{11}, \quad L_{12} = L_{21}$$

Assuming $\mu_{\text{MCO}}^{(1)'} = \mu_{\text{MCO}}^{(2)'}$, with a knowledge of the L matrix elements, the angle θ between oscillators can be calculated¹³

$$\cos^{-1} \left[\frac{\sqrt{\frac{I_2}{I_1}}L_{11} - L_{12}}{2L_{22} - \sqrt{\frac{I_2}{I_1}}2L_{21}} \right] = \theta \quad (3)$$

(12) H. D. Kaesz, R. Bau, D. Hendrickson, and J. M. Smith, *J. Am. Chem. Soc.*, **89**, 2844 (1967).

(13) This is very similar to the procedure used by Kaesz and coworkers⁸ except they assumed $\mu_{\text{MCO}}^{(2)'} = \mu_{\text{CO}}^{(2)'}$, the dipole moment derivative obtained from the E mode vibration. The angles calculated by the two different methods agree within $\pm 0.1^\circ$. The assumption made in this work is, however, more reasonable, as the following discussion shows.

From Figure 1 it is easily seen that $\sqrt{I_1}$ is a negative quantity whereas $\sqrt{I_2}$ is positive. Calculated values of θ for several molybdenum compounds are listed in Table IV. It is possible for the axial component of the dipole moment change to be dominating in the $A_1^{(2)}$ mode resulting in a negative value of $\sqrt{I_2}$. However, in order for this to occur, θ has to be unreasonably larger than 90° . For example, a calculation in which $\sqrt{I_2/I_1}$ is taken to be positive for $(\text{CH}_3\text{O})_3\text{PMo}(\text{CO})_5$ yields a value for θ of 116° .

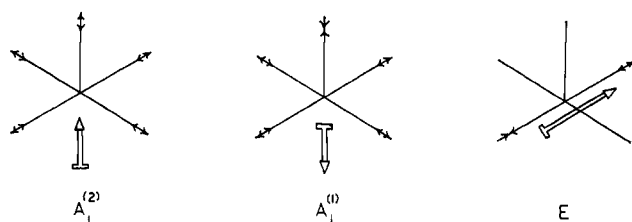


Figure 1.—Symmetry coordinates for the CO modes in $\text{Mo}(\text{CO})_5\text{L}$. Hollow arrows indicate the direction of dipole moment change and are not intended to imply relative magnitudes. Alternatively the $A_1^{(1)}$ motion could be described as in Figure 2, where the dipole moment change is in the opposite direction. The direction chosen here is to ensure consistency with the signs chosen for the L matrix elements.

TABLE IV
VALUES OF θ FOR $\text{Mo}(\text{CO})_5\text{L}$ DERIVATIVES

| Compound | θ^a , deg | θ^b , deg |
|---|------------------|------------------|
| $\text{C}_6\text{H}_{10}\text{NHMo}(\text{CO})_5$ | 90.3 | ... |
| $\text{C}_6\text{H}_5\text{NM}(\text{CO})_5$ | 89.5 | 89.3 |
| $(\text{C}_2\text{H}_5\text{O})_3\text{PMo}(\text{CO})_5$ | 90.4 | ... |
| $(\text{CH}_3\text{O})_3\text{PMo}(\text{CO})_5$ | 89.8 | 89.7 |
| $(\text{C}_6\text{H}_5)_2\text{AsMo}(\text{CO})_5$ | 85.3 | ... |
| $\text{Cl}_3\text{PMo}(\text{CO})_5$ | 87.5 | 87.3 |

^a Calculated from ρ values. ^b Calculated for individual L matrix elements.

Crystal structure data on $\text{Mn}(\text{CO})_5\text{X}$ systems indicate that the radial CO groups deviate from planarity by only a few degrees.¹⁴⁻¹⁶ The values calculated for θ from the intensity data are, therefore, quite reasonable. While the use of infrared intensity data is not advanced here as a method for calculating accurate geometries of molecules, the procedure would appear to have some validity.

The major source of uncertainty in evaluating the angle is the possible nonlinearity of the M-C-O systems. An MCO angle deviating by as much as $5-6^\circ$ from 180° is not uncommon. There are good reasons to expect, however, that the effect of such nonlinearity on the apparent direction of the varying dipole moment vector is not as large as the value of the MCO angle bend might lead one to believe. The π -electronic charge transfer which gives rise to the major part of the MCO group dipole moment change with CO stretch occurs between d_π orbitals centered on the metal and a π^* orbital on CO. Thus the moment vector is from the metal atom to the charge center of the π^* orbital on

CO. The coefficients of the $2p\pi$ orbitals of C and O in the π^* orbital are 0.967 and 0.621, respectively. It is clear that the charge center (which relates to the squares of these coefficients) lies close to C. The direction of the π component of the MCO group dipole moment vector is thus determined essentially by the direction of the M-C bond.

Some consideration must be given to the effect of neglecting the slight allowedness of the B_1 mode, forbidden in strict C_{4v} symmetry. The intensity estimates for this mode are upper limits; it is difficult to evaluate the intensity of a low-intensity band situated as a shoulder on a high-intensity absorption. The B_1 intensity is borrowed from the A_1 or E species mode, depending on the form of the perturbation which removes C_{4v} symmetry. The perturbation is sufficiently small so that the E species mode is not sensibly split, even in $\text{Mo}(\text{CO})_5\text{P}(\text{OC}_2\text{H}_5)_3$, in which the B_1 intensity is highest. The B_1 intensity is not included in the considerations involving angle because it is not clear how much of it derives from the A_1 modes and how much from the E. Any contribution from the A_1 modes must arise largely from the axial A_1 symmetry mode, since it is closer in energy to the B_1 mode and since the radial A_1 mode has little or no intensity of itself. Therefore, any correction to the I_2/I_1 ratio would lower the ratio slightly and thus increase the calculated angle by perhaps 1 or 2° , in the case of the two phosphite derivatives. None of the comparisons based on the total A_1/E intensity ratio or on total intensities is affected significantly by neglect of the B_1 intensity. In light of these considerations, errors in the calculated values of the angles are probably on the order of only $1-2^\circ$. (Anharmonicity corrections may also impose a systematic error on the calculated angles,⁹ but it is unlikely that the relative angles in a related series would be changed significantly.) The calculations do show that deviations from planarity, in addition to coupling, are largely responsible for the observed A_1 intensity ratio.

Calculation of Group Dipole Moment Derivatives

Solving eq 1 and 2 for $\mu_{\text{MCO}}^{(1)'}$ we obtain

$$\mu_{\text{MCO}}^{(1)'} = \frac{L_{21}\sqrt{I_2} - L_{22}\sqrt{I_1}}{L_{21}L_{12} - L_{11}L_{22}} \quad (4)$$

The dipole moment derivative for the axial CO stretch can thus be calculated from only a knowledge of the L matrix elements and the measured intensities. No assumptions need be made about θ or $\mu_{\text{MCO}}^{(2)'}$.

Alternatively $\mu_{\text{MCO}}^{(1)'}$ could be calculated from the equation for the total intensity of the A_1 modes

$$I_1 + I_2 = G_{tt}\mu_{\text{MCO}}^{(1)'}{}^2(1 + 4 \cos^2 \theta) \quad (5)$$

Equivalent dipole moment derivatives for the two A_1 modes and a value for θ ¹⁷ must be assumed. A listing of the calculated derivatives is contained in Table V. Deviations between moment derivatives calculated by

(14) S. J. LaPlaca, W. C. Hamilton, and J. A. Ibers, *Inorg. Chem.*, **3**, 1491 (1964).

(15) H. P. Weber and R. F. Bryan, *Chem. Commun.*, 443 (1966).

(16) R. F. Bryan, *ibid.*, 355 (1967).

(17) Here we may use the values that were calculated earlier for θ in which the assumption that the dipole moment derivatives are equal was also made. However the dipole moment derivative calculated is not very sensitive to the value used for the angle. A change in θ of as much as 3° results in only a 3% change in the calculated derivative.

TABLE V
VALUES OF μ'_{MCO} , THE MCO GROUP
DIPOLE MOMENT DERIVATIVES^e

| Compound | $\mu_{\text{MCO}}^{(1)'}^a$ | $\mu_{\text{MCO}}^{(2)'}^b$ | $\mu_{\text{MCO}}^{(3)'}^c$ | $\mu_{\text{MCO}}^{(1)'} / \mu_{\text{MCO}}^{(3)'}^e$ | μ'_{vib} |
|---|-----------------------------|-----------------------------|-----------------------------|---|---------------------|
| $\text{C}_5\text{H}_{10}\text{NHMo}(\text{CO})_5$ | ... | 9.64 | 9.94 | 0.970 | ... |
| $\text{C}_5\text{H}_9\text{NM}(\text{CO})_5$ | 9.58 | 9.62 | 9.80 | 0.981 | 0.1 |
| $(\text{C}_2\text{H}_5)_3\text{AsMo}(\text{CO})_5$ | ... | 10.64 | 8.99 | 1.18 | 1.9 |
| $(\text{C}_2\text{H}_5\text{O})_3\text{PMo}(\text{CO})_5$ | ... | 10.50 | 9.04 | 1.16 | 1.8 |
| $(\text{CH}_3\text{O})_3\text{PMo}(\text{CO})_5$ | 10.48 | 10.51 | 9.01 | 1.17 | 1.8 |
| $\text{Cl}_3\text{PMo}(\text{CO})_5$ | 10.14 | 10.12 | 8.81 | 1.16 | 1.6 |
| $\text{COMo}(\text{CO})_5$ | ... | ... | 9.23 | ... | ... |
| <i>trans</i> - $[(\text{CH}_3\text{O})_3\text{P}]_2\text{Mo}(\text{CO})_4$ | ... | ... | 9.18 | ... | ... |
| <i>trans</i> - $[(\text{C}_2\text{H}_5\text{O})_2\text{P}]_2\text{Mo}(\text{CO})_4$ | ... | ... | 8.72 | ... | ... |
| <i>cis</i> - $[(\text{CH}_3\text{O})_2\text{P}]_2\text{Mo}(\text{CO})_4^d$ | ... | 9.19 | 10.32 | 0.890 | ... |

^a Calculated from the individual L matrix elements. ^b Calculated assuming $\mu_{\text{MCO}}^{(1)'} = \mu_{\text{MCO}}^{(2)'}$. ^c Calculated from the intensity of the E mode. ^d Calculated assuming a value of θ' , the angle between the threefold axis and dipole, of 52° . ^e Dipole moment derivative values are accurate to ± 0.1 unit. The μ'_{MCO} 's are effective group dipole moment derivatives which involve elements of both MC and CO stretching motions.⁷ The units employed here are arbitrary; the intensities are expressed in units of $10^4 M^{-1} \text{cm}^{-2}$, and L and G terms are based on atomic mass units. For example, using eq 6 $\mu_{\text{MCO}}^{(3)'}$ for the piperidine derivative is $57.2 = 4(0.1458)\mu_{\text{MCO}}^{(3)'}(0.999)$.²

the two methods is less than 0.5%. This is a useful result since by using the latter method the individual L matrix elements need not be known.

The dipole moment derivative for the E mode is calculated from the equation

$$I_E = 4G_{tt}\mu_{\text{MCO}}^{(3)'} \sin^2 \theta \quad (6)$$

For values of θ near 90° this derivative is fairly insensitive to changes in θ .

One would like to determine a different dipole moment derivative for each of the three symmetry modes. This is not possible since it requires solving three equations with four unknowns, namely, $\mu_{\text{MCO}}^{(1)'}$, $\mu_{\text{MCO}}^{(2)'}$, $\mu_{\text{MCO}}^{(3)'}$, and θ .¹⁸ We have chosen to assume that $\mu_{\text{MCO}}^{(1)'} = \mu_{\text{MCO}}^{(2)'}$. This procedure can be justified by considering the effects which determine the magnitude of these derivatives.

Electronic Effects

The μ'_{MCO} 's may be expected to change mainly as a function of the charge on the metal and on the flow of π electrons in the M-L bond. Consider what happens when the M-L bond is a pure σ bond as in the case of the amine compound. Amines are stronger Lewis bases than CO or phosphorus ligands; therefore, the net negative charge on the metal is greater when an amine replaces a CO or phosphite. This has the effect of raising the energies of the d orbitals and increasing the extent of π bonding with the π^* orbitals on CO. We have already shown that the intensities of the infrared carbonyl stretching modes in transition metal carbonyls are due almost entirely to π -electronic charge migration during the CO stretch.⁷ The effect of a strong σ donor such as an amine should thus be to increase the intensities, by raising the energies of the 4d orbitals on the metal. In all of the CO stretching

(18) The angle θ would have to be known very accurately in order to calculate a meaningful value of $\mu_{\text{MCO}}^{(3)'}$. This rules out making reasonable guesses at this quantity.

modes the charge is transferred from the metal to the carbonyl groups; to a first approximation, all of the CO stretching modes should exhibit the same value for the MCO group dipole moment derivative, μ'_{MCO} . There are, however, interaction effects in the intensities analogous to those giving rise to interaction force constants. In the A_1 modes there is a net demand by the CO groups for the π electrons on the metal, whereas in the E mode the net effect experienced at the metal is zero. This idea is expressed diagrammatically in Figure 2, for the three CO stretching modes in an $\text{M}(\text{CO})_5\text{L}$ species.

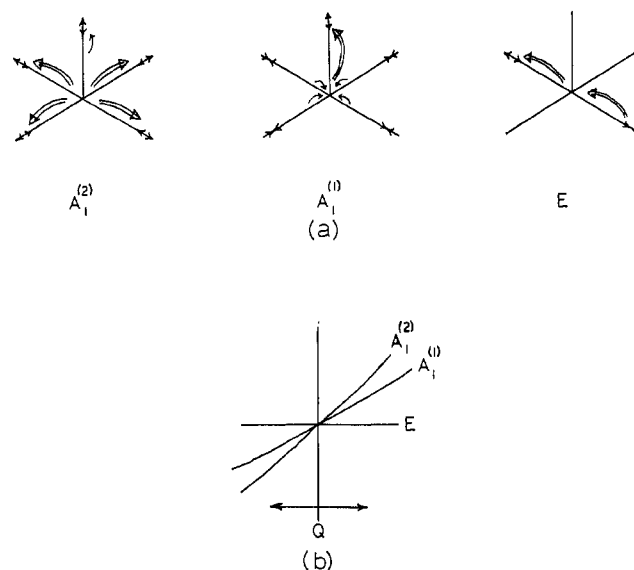


Figure 2.—(a) Schematic illustration of the flow of π -electronic charge between metal d_π and carbonyl π^* orbitals in the CO stretching modes. (b) Variation in π -electron demand at the metal in the CO vibrations depicted in (a).

The CO groups exert a certain demand on the central metal for the π electrons. This demand increases as the CO bond stretches, since the π^* -orbital energy level decreases. In the highest frequency A_1 mode, all five CO groups move in phase, and the gradient of electron demand *vs.* normal coordinate displacement is greatest. In the lower frequency A_1 mode, which is predominantly axial CO stretch, the gradient is smaller because the small contribution from the radial CO is out of phase with, and partially counterbalances, the effect of axial CO motion. In the E species mode the variation in electron demand exerted on the metal by one vibrating CO is precisely counterbalanced by the other. The MCO group dipole moment derivative should thus be greatest for the E species mode and least for the higher frequency A_1 mode, *i.e.*, $\mu_{\text{MCO}}^{(3)'} > \mu_{\text{MCO}}^{(1)'} > \mu_{\text{MCO}}^{(2)'}$. On the basis of these considerations it appears that there should be little error in assuming $\mu_{\text{MCO}}^{(1)'} = \mu_{\text{MCO}}^{(2)'}$, as we have in the above analysis. The assumption $\mu_{\text{MCO}}^{(1)'} = \mu_{\text{MCO}}^{(3)'}$ should in general not be as satisfactory, especially when substituents capable of π bonding are involved.

Those ligands which are presumed to possess some degree of π -acceptor ability, such as phosphines, phos-

phites, etc., are weaker σ donors than amines. Whatever enhanced σ -donor properties these ligands exhibit in metal carbonyls, as compared with their relative basicities toward a hard acid such as the proton, results from their π -acceptor abilities. It follows that substitution of carbonyl by such a ligand can never result in as large an increase in negative charge on the metal as substitution by an amine. The molecular dipole moment derivative in the E species mode is polarized normal to the M-L bond in $M(\text{CO})_5\text{L}$. There can, therefore, be no transfer of charge along the M-L axis in the E species mode. The ligand thus affects $\mu_{\text{MCO}}^{(3)'}$ only through its effect on the equilibrium charge distribution, particularly in the π electron system. One, therefore, expects that $\mu_{\text{MCO}}^{(3)'}$ should be smaller for the π bonding ligands than for amine, as is observed to be the case (Table V).

The A_1 modes, on the other hand, are polarized along the M-L bond axis. If there is π bonding between M and L, transfer of charge from L to M may occur during the A_1 stretches. This constitutes a "vibronic" contribution¹⁹ to $\mu_{\text{MCO}}^{(1)'}$ and $\mu_{\text{MCO}}^{(2)'}$ and results in enhanced intensities in the A_1 modes.

The vibronic contribution to the A_1 modes can be roughly estimated by comparing $\mu_{\text{MCO}}^{(1)'}$ values for compounds substituted by a π -bonded ligand with those of the amine complexes.

To properly evaluate the "vibronic" contribution to the dipole moment derivative of the A_1 modes, the effects of differing σ donation and π withdrawal in changing from piperidine (denoted by N) to a π -bonding ligand, L, must be taken into account

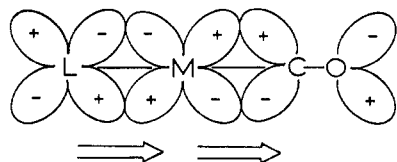
$$\mu_{\text{MCO}}^{\text{vib}'} = (\mu_{\text{MCO}}^{(1)'} - \mu_{\text{MCO}}^{(3)'})_{\text{L}} - \frac{(\mu_{\text{MCO}}^{(3)'})_{\text{L}}}{(\mu_{\text{MCO}}^{(3)'})_{\text{N}}} (\mu_{\text{MCO}}^{(1)'} - \mu_{\text{MCO}}^{(3)'})_{\text{N}} \quad (7)$$

The first term in eq 7 takes into account the fact that the E mode has no vibronic component from the ligand; the second term accounts for differences in σ -donation and π -withdrawal effects. The expression may be rearranged to yield

$$\mu_{\text{MCO}}^{\text{vib}'} = (\mu_{\text{MCO}}^{(1)'})_{\text{L}} - \frac{(\mu_{\text{MCO}}^{(3)'})_{\text{L}}}{(\mu_{\text{MCO}}^{(3)'})_{\text{N}}} (\mu_{\text{MCO}}^{(1)'})_{\text{N}} \quad (8)$$

The calculated vibronic contributions are given in Table V.

The vibronic contribution to the A_1 intensity is unambiguously identified with π bonding. It arises from the transfer of π electronic charge from ligand to metal to CO as the CO groups stretch. Schematically this may be represented as



As expected, the vibronic contribution from pyridine

(19) T. L. Brown, *J. Chem. Phys.*, **43**, 2780 (1965).

is very small. For the other ligands, however, it is a substantial fraction of the total intensity. Unfortunately, there is no simple way to obtain a measure of the vibronic effect for CO as ligand. The sole infrared-allowed CO stretch mode in $M(\text{CO})_6$ of T_{1u} symmetry correlates with the E species mode in the $M(\text{CO})_5\text{L}$ compounds. The intensity results do demonstrate, however, the existence of appreciable π bonding in the P and As ligands.

For all π -bonding ligands studied in the $\text{Mo}(\text{CO})_5\text{L}$ series, $\mu_{\text{MCO}}^{(3)'}$ is lower than the value of μ'_{MCO} calculated from the infrared T_{1u} mode of $\text{Mo}(\text{CO})_6$. The type of CO motion is the same in each case, an antisymmetric motion of *trans*-CO groups. There is an element of uncertainty involved in making quantitative comparisons of the number obtained for $\text{Mo}(\text{CO})_6$ with $\mu_{\text{MCO}}^{(3)'}$ in $\text{Mo}(\text{CO})_5\text{L}$ compounds, since the latter are C_{4v} molecules with appreciable dipole moments, whereas $\text{Mo}(\text{CO})_6$ is of O_h symmetry and nonpolar. However, working with a nonpolar solvent as we have should reduce differences due to factors of this kind to a minimum. Furthermore, solvent effects might be expected to result in higher intensity for the polar molecule. It should also be remarked that ascribing all of the B_1 intensity to the E species mode would not result in a change in $\mu_{\text{MCO}}^{(3)'}$ of even 0.1. It is, therefore, certain that this quantity is indeed lower for the monosubstituted compounds, or at least no larger, than for CO as ligand.

This result can be interpreted directly as evidence that there is about the same or less π -electron transfer from metal to CO in the $\text{Mo}(\text{CO})_5\text{L}$ compounds where L is a π -bonding ligand, as in the parent carbonyl. This in turn means that *there is no increase in π bonding from metal to the remaining CO's when $\text{Mo}(\text{CO})_5\text{L}$ is formed from the parent carbonyl.* If there were increased M-CO π bonding on substitution, it would lead to an increase in $\mu_{\text{MCO}}^{(3)'}$. This is precisely what is seen in the amine and pyridine cases, Table V. It is also evidenced in the dramatic change in intensity in the series⁸ $\text{Mn}(\text{CO})_6^+$, $\text{Cr}(\text{CO})_6$, and $\text{V}(\text{CO})_6^-$. This result is clearly at variance with the notion that all decreases in CO frequencies (or force constants) upon substitution can be ascribed to changes in π bonding.²⁰

Population analysis of a molecular orbital description of $\text{Cr}(\text{CO})_6$ based upon a fairly thorough semiempirical model²¹ indicates that the σ and π systems in the octahedral carbonyls are separable to a good approximation. This means that there are no valence shell orbitals on the metal or CO groups which participate extensively in both σ - and π -symmetry molecular orbitals. The electrons of the π system may then be considered to move under the influence of an effective "core" Hamiltonian which results from the nuclear charges and the σ -electron distribution.²² A change in charge at the metal is transmitted, through the inductive effect, to the carbonyl groups. Since the inductive effect at-

(20) F. A. Cotton, *Inorg. Chem.*, **3**, 702 (1964).

(21) A. F. Schreiner and T. L. Brown, *J. Am. Chem. Soc.*, in press.

(22) R. G. Parr, "Quantum Theory of Molecular Electronic Structure," W. A. Benjamin, Inc., New York, N. Y., 1963, Chapter 3.

tenuates rather rapidly, a change in electron density at the metal, such as might be occasioned by substitution of an amine for CO, causes a larger increase in the energy of the metal π orbitals than in the energies of the π orbitals of the CO groups. There is consequently an increase in M-CO π bonding upon such substitution. It is important to note, however, that the metal-carbon σ bond is almost certainly weakened by the addition of charge to the metal, since it lowers the acidity of the metal toward the CO electrons. This weakening of the σ bond should, of itself, lower the CO frequency, since the CO frequency increases upon σ -bond formation, and in proportion to the strength of the σ bond.^{7,23} Thus, even in this case, the change in CO force constant cannot be taken as a measure of the extent of π bonding, since it is not clear how much of the change is due to variation in σ -bond strength. Indeed, the only firm evidence that there is an increase in the degree of π bonding is the higher value for $\mu_{\text{MCO}}^{(3)'}$ in the amine-substituted compound.

The phosphorus ligands listed in Table II vary considerably in their basicity toward a hard acid such as the proton, but they are all reasonably strong σ donors toward a transition metal carbonyl moiety.²⁴ From the decrease in CO force constant upon substitution it can be inferred that there is a net decrease in M-CO σ -bond strength or an increase in M-CO π bonding or both. It is clear from the intensity data, however, that there is no increase in the extent of metal-CO π bonding. We conclude, therefore, that the decrease in CO force constant upon substitution for CO by such π -bonding ligands as listed in Table V is due primarily to weakening of the metal-CO σ bond and not to an increase in π bonding. This conclusion is fortified by the observation that there is a considerable vibronic effect on the A_1 species modes for these ligands, indicating considerable metal-ligand π bonding. Thus the picture is that these ligands have the effect of increasing the electron density on the metal, weakening the metal-carbonyl σ bond. At the same time, the ligand acts as a π acceptor and lowers the energy of the π orbitals on the metal sufficiently so that there is no net increase in metal-CO π bonding.

Unfortunately, the precision with which the intensities can be determined precludes more than a rough comparison of the effects of various π -bonding ligands. The CO frequencies and/or stretching force constants might better serve as quantitative indicators of the nature of the substituents if some appropriate means were available for separating the σ and π contributions.²⁵

In the *trans*-disubstituted compounds there is only one infrared-active CO mode, corresponding to the E mode in the monosubstituted compound. It is easily seen from Table V that μ'_{MCO} 's are very similar to the values obtained for $\mu_{\text{MCO}}^{(3)'}$ in the analogous $\text{Mo}(\text{CO})_5\text{L}$ compounds.

In the *cis*-trisubstituted compound, $[(\text{CH}_3\text{O})_3\text{P}]_3\text{Mo}(\text{CO})_3$, there is a reversal in the relative ordering of the μ'_{MCO} 's. The E mode is now enhanced over the A_1 mode. The values of μ'_{MCO} derived from these data are sensitive to the angle between the M-C bond and the threefold axis (eq 9 and 10). Crystal structure

$$\mu'_{\text{MCO}}^{(\text{E})} = \frac{\sqrt{I_{\text{E}}}}{\sqrt{3G_{\text{tt}} \sin \theta}} \quad (9)$$

$$\mu'_{\text{MCO}}^{(\text{A}_1)} = \frac{\sqrt{I_{\text{A}_1}}}{\sqrt{3G_{\text{tt}} \cos \theta}} \quad (10)$$

data on the metal tricarbonyl-arene systems show that θ is about 53.8° for several complexes.²⁶⁻²⁸

We would expect the angle to be smaller for bulkier group(s) attached to the $\text{M}(\text{CO})_3$ moiety. For the rather bulky phosphite this angle is probably less than the value of 52° , corresponding to 90° bond angles about the metal, used in the calculations; in the diethylenetriaminechromium tricarbonyl complex an angle of 50.9° is reported.²⁹ Therefore the μ'_{MCO} 's calculated are very probably in the correct relative order (Table V).

In the *cis*- $\text{M}(\text{CO})_3\text{L}_3$ species there is no symmetry restriction on the participation of the phosphite-metal π electrons in either vibrational mode. The totally symmetric stretch should exhibit a lower value for μ'_{MCO} than the E species mode, because of interaction effects between the CO motions, as discussed earlier. This is the effect observed.

Electronic Spectra

The transition metal carbonyl systems are too complex to permit a quantitative treatment of the CO intensities in terms of vibronic theory.¹⁹ Nevertheless, it is evident that the high infrared CO stretching intensities are due to contributions of charge transfer excited states to the ground-state wave function upon molecular distortion. There should therefore be some correlation of the CO intensity results with energies and oscillator strengths in the electronic spectra.

We are interested here in the vibronic contribution M_{vi} to the CO intensity, which relates to the transfer of π -electronic charge from metal to CO. The expression for M_{vi} in terms of first-order perturbation theory is

$$M_{\text{vi}} = \sum_j \frac{2m_{\text{g}i}}{\Delta E_{\text{g}i}} \partial/\partial Q \{ \langle \chi_{\text{g}} | \partial/\partial Q | \chi_{\text{j}} \rangle - E_{\text{g}} \langle \chi_{\text{g}} | \chi_{\text{j}} \rangle \} \quad (11)$$

Where the χ 's are $\chi(g, Q)$, subscripts g and j refer to ground and electronically excited states, respectively, $m_{\text{g}i}$ is the transition moment for the pure electronic transition, and $\Delta E_{\text{g}i}$ is the transition energy. The sum is over all allowed one-electron excitations of appropriate symmetry, as determined by the symmetry of Q. The intense charge-transfer transitions of lower energy should make the major contribution

(23) G. R. Dobson, *Inorg. Chem.*, **4**, 1673 (1965).

(24) R. J. Angelici and M. D. Malone, *ibid.*, **6**, 1731 (1967).

(25) W. A. G. Graham, *ibid.*, **7**, 315 (1968).

(26) M. F. Bailey and L. F. Dahl, *ibid.*, **4**, 1298 (1965).

(27) M. F. Bailey and L. F. Dahl, *ibid.*, **4**, 1314 (1965).

(28) O. Carter, Ph.D. Thesis, University of Illinois, 1967, pp 43, 50.

(29) F. A. Cotton and D. C. Richardson, *Inorg. Chem.*, **5**, 1851 (1966).

to M_{vi} in the metal carbonyls. It is therefore of interest to examine the electronic spectra in the $\text{Mo}(\text{CO})_5\text{L}$ compounds for evidence of changes in the intensities and energies of the charge-transfer absorptions.

We have begun by examining the electronic spectra of substituted molybdenum carbonyl complexes at room temperature. The work will soon be extended to temperatures in the range of liquid helium. Some of the spectra are depicted in Figure 3. The observed energies, in cm^{-1} , and extinction coefficients given in parentheses, in units of $1. \text{cm}^{-1}/\text{mole}^{-1} \times 10^{-3}$, are as follows: $\text{Mo}(\text{CO})_6$, 30,960 (sh), 34,540 (16.1), 37,040 (sh), 42,970 (111.0); $\text{Mo}(\text{CO})_5\text{PCl}_3$, 28,170 (sh), 34,480 (12.1), 40,670 (sh), 43,200 (58.0); $\text{Mo}(\text{CO})_5\text{P}(\text{OC}_2\text{H}_5)_3$, 29,890 (sh), 34,470 (5.0), 39,710 (sh), 43,090 (45.0); $\text{Mo}(\text{CO})_5\text{P}(\text{OCH}_3)_3$, 30,080 (sh), 34,600 (6.9), 39,940 (sh), 43,310 (66.0); $\text{Mo}(\text{CO})_5\text{P}(\text{OC}_6\text{H}_5)_3$, 30,580 (sh), 34,550 (9.2), 38,840 (sh), 42,840 (59.0); $\text{Mo}(\text{CO})_5\text{P}(\text{C}_6\text{H}_5)_3$, 29,200 (sh), 32,260 (sh), 32,740 (3.1), 43,310 (50.0); $\text{Mo}(\text{CO})_5\text{As}(\text{C}_6\text{H}_5)_3$, 29,410 (sh), 31,850 (sh), 33,550 (3.0), 43,730 (52.0); $\text{Mo}(\text{CO})_5\text{NC}_6\text{H}_5$, 25,970 (6.6), 29,760 (sh), 35,710 (sh), 41,150 (47.0); $\text{Mo}(\text{CO})_5\text{HNC}_6\text{H}_{10}$, 25,160 (5.0), 32,390 (sh), 34,890 (sh), 39,750 (58.0). Owing to severe overlap problems no meaningful extinction coefficients were obtained for the shoulders (sh).

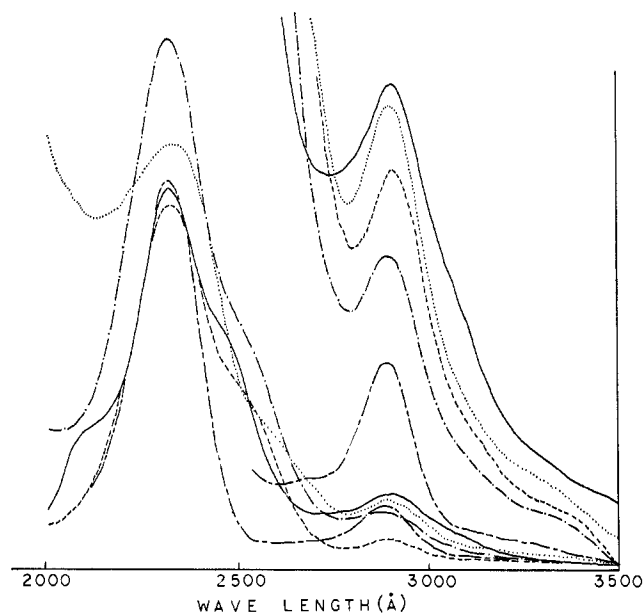


Figure 3.—Electronic spectra in hexane solution: — — —, $\text{Mo}(\text{CO})_6$; — — —, $\text{Mo}(\text{CO})_5\text{PCl}_3$; — · —, $\text{Mo}(\text{CO})_5\text{P}(\text{OCH}_3)_3$; - - - -, $\text{Mo}(\text{CO})_5\text{P}(\text{OC}_2\text{H}_5)_3$; · · · · ·, $\text{Mo}(\text{CO})_5\text{P}(\text{OC}_6\text{H}_5)_3$.

Although firm assignment of these bands must await further theoretical work and low-temperature spectral measurements, it is quite probable that they are all largely charge transfer in nature. However, Gray and Beach³⁰ tentatively assigned the two low-

intensity bands in molybdenum hexacarbonyl to d-d type transitions.

In general the spectra of the $\text{Mo}(\text{CO})_5\text{L}$ complexes, where L is a π -bonding ligand, are very similar to that of $\text{Mo}(\text{CO})_6$ with respect to both energies and intensities (see Figure 3). In the amine complexes, however, there is a band in the visible region far removed from any seen in the phosphorus-substituted complexes. This band probably corresponds to the band at $34,000 \text{ cm}^{-1}$ in the other substituted complexes. The major conclusion to be drawn from these results at present is that the energies of the charge-transfer bands in $\text{Mo}(\text{CO})_5\text{L}$ compounds, where L is a π -bonded ligand, are not significantly lower than in the parent $\text{Mo}(\text{CO})_6$. The amine-substituted compound, on the other hand, exhibits a transition at significantly lower energy. The electronic spectra thus support the conclusion based on the infrared intensity results, *i.e.*, that no significant increase in metal carbonyl π bonding accompanies substitution of CO by π -bonding ligands such as phosphines, phosphites, or PCl_3 .

Experimental Section

Molybdenum hexacarbonyl was generously supplied by Climax Molybdenum Co. and was sublimed before use.

Preparation of (Trichlorophosphine)molybdenum Pentacarbonyl.—This complex was prepared by heating 5 g of $\text{Mo}(\text{CO})_6$ with a large excess of PCl_3 in 30 ml of methylcyclohexane at 90° under a nitrogen atmosphere for 12 hr. Solvent was removed at room temperature under reduced pressure. Unreacted $\text{Mo}(\text{CO})_6$ was filtered off using a medium porosity sintered-glass filter connected to a vacuum pump. The red filtrate was shown to be the desired product plus a trace of the *cis*-disubstituted compound by comparison of its infrared spectrum with those in the literature.³¹ The pure monosubstituted complex was obtained by vacuum distillation (bp $57\text{--}59^\circ$ (0.2 mm)) as a light yellow liquid which crystallized upon cooling (mp about 30°). *Anal.* Calcd for $\text{Cl}_3\text{PMo}(\text{CO})_5$: C, 16.09; Cl, 28.49. Found: C, 16.49; Cl, 28.40.

Preparation of (Trialkyl phosphite)molybdenum Pentacarbonyl.—The trialkyl phosphite and a slight excess of $\text{Mo}(\text{CO})_6$ were refluxed in methylcyclohexane for 5 hr under nitrogen. Solvent was removed under reduced pressure at room temperature leaving a red-brown liquid. The complexes were purified by vacuum distillation. *Anal.* Calcd for $(\text{CH}_3\text{O})_3\text{PMo}(\text{CO})_5$: C, 26.70; H, 2.50. Found: C, 26.92; H, 2.59; bp $64\text{--}65^\circ$ (2 mm). Calcd for $(\text{C}_2\text{H}_5\text{O})_3\text{PMo}(\text{CO})_5$: C, 32.90; H, 3.73. Found: C, 33.12; H, 3.93; bp $76\text{--}78^\circ$ (0.2 mm).

Preparation of (Piperidine)molybdenum Pentacarbonyl.—Piperidine and an excess of $\text{Mo}(\text{CO})_6$ were refluxed in methylcyclohexane for 1 hr under nitrogen. Solvent was removed under reduced pressure. Unreacted $\text{Mo}(\text{CO})_6$ was removed by vacuum sublimation at 50° . The bright yellow product was purified by recrystallization from hexane at -80° . The pyridine analog was prepared and purified similarly. *Anal.* Calcd for $(\text{C}_6\text{H}_{10}\text{NH})\text{Mo}(\text{CO})_5$: C, 37.39; H, 3.43; N, 4.36. Found: C, 37.69; H, 3.50; N, 4.43; mp $79\text{--}80^\circ$ dec. Calcd for $(\text{C}_6\text{H}_5\text{N})\text{Mo}(\text{CO})_5$: C, 38.10; H, 1.59; N, 4.45. Found: C, 38.40; H, 1.68; N, 4.43; mp $87\text{--}89^\circ$ dec. Both complexes were found to decompose in hexane solutions to give $\text{Mo}(\text{CO})_6$ at a measurable rate.³² The rate was found to be approximately first order in the amine complex. (Piperidine)molybdenum pentacarbonyl decomposed at a slightly slower rate than (pyridine)molybdenum pentacarbonyl.

(31) R. Poiblanc and M. Bigorgne, *Bull. Soc. Chim. France*, 1301 (1962).

(32) This was also found to be the case for (amine) $\text{W}(\text{CO})_6$ complexes by Angelici.³⁴

(30) H. B. Gray and N. A. Beach, *J. Am. Chem. Soc.*, **85**, 2922 (1963).

cis-Mo(CO)₂[P(OCH₃)₃]₂ was prepared by the method previously described by Dobson.³³

All other compounds were prepared by the method previously reported.³⁴

Infrared Spectra.—All infrared spectral measurements were made on a Beckman IR-7 spectrophotometer, calibrated using water vapor. The spectrophotometer was equipped with a linear absorbance potentiometer. Spectroscopic grade hexane was used without further treatment. Calibrated 1-mm sodium chloride cells were employed in the measurements. Instrumental conditions were as previously described.^{7,35}

The area under the bands was determined by the weighing technique and was comparable to that obtained with a planimeter. Overlapping bands were separated by graphical procedures, assuming symmetric band shapes. The spectra were integrated over an interval of 30–40 cm⁻¹ on either side of the band maximum or about 8 times the half-intensity width. Intensities were determined at a number of concentrations and extrapolated to zero concentration.³⁶ An example of such a plot is shown in Figure 4 for (C₂H₅O)₃PMo(CO)₅. Slopes were always negative, in general increasing in magnitude with decreasing half-intensity band widths. All data were analyzed by least-squares methods.

Electronic Spectra.—Electronic spectra were recorded on a Cary 14RI spectrophotometer using matched 1.0-cm or 1.0-mm cells. Spectroscopic grade hexane was employed in the measurements without further treatment. In the cases in which the ligand possesses a phenyl ring which absorbs strongly in the ultraviolet region attempts were made to compensate for its absorption using the free ligand as reference. This technique

(33) G. R. Dobson and L. W. Houk, in press.

(34) T. D. Magee, C. N. Matthews, T. S. Wang, and J. H. Wotiz, *J. Am. Chem. Soc.*, **83**, 3200 (1961).

(35) Slightly different instrumental conditions were needed for the amine complexes. It was found that with a scan rate of 20 cm⁻¹/min and a shorter pen response time, good spectra were obtained with decomposition less than 2%.

(36) D. A. Ramsay, *J. Am. Chem. Soc.*, **74**, 72 (1952). Method II, but not including wing corrections.

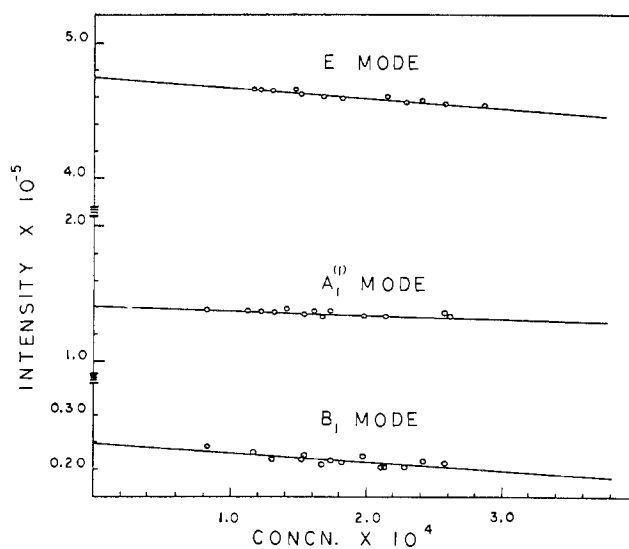


Figure 4.—Intensity vs. concentration for the CO modes in Mo(CO)₅P(OC₂H₅)₃.

rests on the assumption that the absorptions in the free ligand are not perturbed greatly upon complexation. Spectra were recorded from 4500 to 2000 Å.

Calculations.—Frequencies for the normal modes and the *L* matrix elements were calculated in the cases cited using a computer program written by Schachtschneider³⁷ for the IBM-7090 computer and modified for use on the IBM-7094 computer at the University of Illinois.

(37) J. H. Schachtschneider, "Vibrational Analysis of Polyatomic Molecules. III," Technical Report No. 263-62, Shell Development Co., Emeryville, Calif.

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The Solution of Lithium in Hexagonal Potassium Tungsten Bronze¹

BY E. BANKS AND A. GOLDSTEIN

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It has been found that lithium may be dissolved readily in the hexagonal phase of potassium tungsten bronze K_xWO₃ (0.13 ≤ *x* ≤ 0.33). This introduction of Li initially causes a very small expansion in the "a" direction and a large expansion in the "c" direction, followed by a very slight expansion in both directions. A number of compositions of K_xLi_yWO₃ in the hexagonal region have been prepared. Hexagonal bronzes with *x* as low as 0.13 and *x* + *y* as high as 0.51 have been obtained.

Introduction

The tungsten bronzes M₂WO₃,² which have metallic properties over a wide range of compositions, have received considerable attention as metallic conductors with a wide range of electron concentrations. Most studies of electrical properties have concentrated on the

cubic sodium and lithium bronzes, with some attention to specific compositions in other structural modifications. This work was done in order to attempt to extend the electron concentration range in the hexagonal potassium bronze structure by incorporating lithium into sites too small to accommodate sodium or potassium.

Potassium tungsten bronzes were prepared by Laurent³ by reduction of K₂WO₄-WO₃ mixtures with hydrogen. Later preparation methods included reduction of

(1) Abstracted in part from a dissertation to be submitted in partial fulfillment of the requirements for the Ph. D. degree in chemistry at the Polytechnic Institute of Brooklyn.

(2) See, for example, R. Ward, Ed., "Nonstoichiometric Compounds," *Advances in Chemistry Series*, No. 39, American Chemical Society, Washington, D. C., 1963, pp 224–253.

(3) A. Laurent, *Ann. Chem. Phys.*, **67**, 215 (1838).