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Vibrational Spectra and Bonding in Metal Carbonyls. I. Infrared Spectra of Phosphine-substituted Group VI Carbonyls in the CO Stretching Region[1a]

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A simple model is proposed for analyzing and assigning the infrared-active carbonyl stretching frequencies of simple and substituted metal carbonyls of the type $ML_x(CO)_{6-x}$, that is, those with an essentially octahedral distribution of the ligands, L, and carbonyl groups about the metal atom. The model involves qualitative and semiquantitative inferences from valence theory as to the signs and relative magnitudes of CO stretching force constants and the coefficients of quadratic interaction terms coupling the stretching motions of different CO groups. In this paper the theory is applied to the group VI carbonyls, $Cr(CO)_6$, $Mo(CO)_6$ and $W(CO)_6$ and phosphine of substituted derivatives thereof using data in the literature and some previously unpublished data obtained in this laboratory. It is shown that for these compounds the method of analysis gives results which are (a) internally consistent, (b) in agreement with valence theory, (c) consistent with reasoning based on intensities and (d) supported by Raman spectra.

Introduction

The qualitative theory that the metal to carbon monoxide bonding in metal carbonyls involves a combination of C→M dative sigma bonding with M→C dative pi bonding appears now to be universally accepted. It can be formulated in both the valence bond[2] and molecular orbital theories[3] in a qualitative manner quite easily.

It will now be shown that it is possible to interpret this theory in a semiquantitative way in regard to the CO stretching force constants, stretch–stretch interaction constants and thus, ultimately, in terms of the relative frequencies of those normal vibrations of the molecules which may be regarded to a good approximation as pure CO stretching modes. The procedure as it will be outlined presently involves two approximations which should be noted at the outset. First, no account at all is taken of the interaction of CO stretching with other deformations of the molecules. This is probably not a serious defect because the CO stretching frequencies are from three to thirty times higher than any of the skeletal fundamentals of these molecules with which symmetry would permit them to couple and besides, comparisons are being made amongst a homologous series of molecules in which there should be no large variations in the extent of such couplings as do occur. Second, we shall use the observed frequencies of the fundamentals without attempting to make any anharmonicity corrections. This seems to be a sensible procedure for purely practical reasons because sufficient experimental data do not exist for making such corrections except in a very few isolated cases and because the convenience of the procedure for routinely assigning observed bands would be largely lost if anharmonicity corrections were to be required in all cases.

Of course an attempt to correlate the observed frequencies of the normal modes of vibration with the electronic structure of a molecule can be successful only if the observed bands are correctly assigned. There would appear to be three more or less independent and convenient criteria which may be used in making such assignments. First, to some extent, the relative intensities of the infrared bands afford clues to their assignments to the normal modes. In all cases we have examined, such clues have been reliable. The same concepts as we have used in interpreting the relative intensities have been developed independently and recently published by Orgel.[4] Secondly, measurement of the polarization of Raman lines can give very positive evidence for the assignments of some bands. However, there is practically no information of this kind in the literature—except that for unsubstituted metal carbonyls; a program of study in this laboratory to obtain such information is at present too incomplete to warrant discussion. Thirdly, deductions from valence theory as to the relative magnitudes of force constants can be used to select correct assignments or, at least, to limit drastically the acceptable possibilities.

In this paper we present the basic arguments used in the latter treatment and report the results obtained for representative compounds of the type $ML_x(CO)_{6-x}$, where $0 \leq x \leq 4$, M = Cr, Mo and W, and L represents a phosphine or one *n*th of an *n*-polyphosphine.

Relations between Pi Bonding and Force Constants.—As long ago as 1937 Thompson and Linnett[5] observed that guidance as to the relative magnitudes and the signs of stretch–stretch interaction constants could sometimes be obtained from simple valence theory. In a metal carbonyl having six octahedrally disposed ligands, the valence shell orbitals of the metal fall into three groups as shown in the tabulation

Symmetry type		Orbitals	Bonding type
I	A_{1g}	s	σ
	E_g	d_{z^2}, $d_{x^2-y^2}$	σ
II	T_{2g}	d_{xz}, d_{yz}, d_{xy}	π
III	T_{1u}	p_x, p_p, p_z	σ or π

If it is assumed, as is always done implicitly, that the p orbitals are used entirely in the σ bonding, in order that a full set of six octahedral hybrid orbitals, which span the representations $A_{1g} + E_g + T_{1u}$, may be formed, then only the T_{2g} orbitals remain for π bonding. For reasons of

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[1] (a) This work is being supported by the U. S. Atomic Energy Commission. (b) Fellow of the Alfred P. Sloan Foundation.

[2] For a recent and authoritative review see L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960, pp. 331–339.

[3] L. E. Orgel, "An Introduction to Transition-Metal Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1960, pp. 34–38, 132–143.

[4] L. E. Orgel, *Inorg. Chem.*, **1**, 75 (1962).

[5] H. W. Thompson and J. W. Linnett, *J. Chem. Soc.*, 1384 (1937).

symmetry the orbitals of this set cannot mix with any others of the valence shell orbitals so that to a first order approximation the metal-ligand π bonding can be treated quite separately from the σ bonding. This fortunate situation does not occur for tetrahedral or trigonal bipyramidal molecules, where many of the valence shell orbitals belong to representations spanned by both the σ and π bonding systems[6] and there is consequently no qualitative way to make a clean separation, even as a crude approximation, of the σ and π bonding in these other cases.

On the basis of this symmetry-produced "factoring out" of the pi bonding and further, by more detailed consideration of the directional properties of the metal dπ orbitals the following deductions are made.

1. *All (CO stretching)-(CO stretching) interactions should give rise to terms in the potential energy expression with positive coefficients (interaction force constants).* As a CO bond is stretched the π bonding within it is weakened and the π antibonding orbital drops in energy so that it more nearly matches the energy of the metal dπ orbitals. This causes increased metal–CO π interaction resulting in a drift of dπ electrons to this MCO grouping and decreasing the availability of these electrons for M–C π bonding in the other MCO groups of the molecule. This in turn permits the carbon pπ orbitals in these other CO groups to participate more fully in CO π bonding which strengthens the other CO bonds and increases their resistance to stretching. This is not a new result. It has been deduced from a strict valence-bond approach by Jones.[7]

2. *If k_c and k_t are the interaction constants between pairs of cis and trans CO groups, respectively, we should expect that $k_t \approx 2k_c$.* This follows quite simply when it is noted that a pair of *cis* CO groups directly share only one *d*π orbital whereas a pair of *trans* CO groups directly share two *d*π orbitals. This is admittedly an oversimplification but it will be shown that the rule appears to be approximately correct when the group VI metal carbonyls are treated below. By a much more elaborate argument, Jones[7] has reached the same conclusion; however, we do not believe that his reasoning is in essence any more sophisticated than that given above.

Finally, by obvious extensions of the reasoning given above, it is possible to make some further predictions as to the relative magnitudes of force constants in simple and substituted octahedral metal carbonyls.

3. *The CO stretching force constants should decrease steadily as CO groups are successively replaced by other ligands which make less demand for metal dπ electrons.* It would appear that all of the simple ligands, *i.e.*, phosphines, arsines, amines, sulfides, and isonitriles, which are known to occur in substituted group VI carbonyls are of this type and there are already data in the literature to support this generalization in the case of the ligands mentioned.[8-10]

4. *CO groups cis to substituents of the type considered above should have higher stretching force constants than those trans to such substituents.* This follows as a direct corollary to 1 and 3.

5. *Stretch–stretch interaction constants should probably increase with increasing replacement of CO by ligands of lower pi bonding ability.* This might be expected because the total number of dπ electrons per CO increases and this should magnify the effect responsible for the interaction constants as described under *1*, above. We believe that this rule has less *a priori* likelihood than the preceding four, but the experimental data show it to be valid (see below).

The Vibrational Analysis.[11] Kinetic Energy Matrices.—It is assumed that the coupling between the CO groups is entirely non-mechanical. This is a very reasonable approximation in view of the fact that any pair of CO's is separated by two intervening weak bonds and a heavy metal atom. Mathematically it amounts to writing a G^{-1} matrix which is just the unit matrix of appropriate dimension multiplied by the inverse of the reduced mass of the CO oscillator.

Potential Energy Matrices.—The F matrices were set up by standard procedures,[11] expressing the matrix elements as algebraic sums of a CO stretching constant, k, or constants, k_1, k_2 where two are required, and one or more stretch–stretch interaction constants, k_c, k_c', representing interaction of *cis* pairs of CO groups and k_t, representing interaction of a trans pair of CO groups.

There are several known kinds of octahedral carbonyls and substituted carbonyls: $M(CO)_6$, $ML(CO)_5$, *cis*-$ML_2(CO)_4$, *trans*-$ML_2(CO)_4$, *cis*-$ML_3(CO)_3$, *cis*-$ML_4(CO)_2$ and *trans*-$ML_4(CO)_2$, the last known only in solution. In Table I are given the factored secular equations and other relevant information for these cases. In this Table we give both the "exact" secular equations, in which all physically different force constants are distinguished and the "approximate" equations in which we have made the substitutions

$$k_i = k_c = k_c' = k_t/2$$

These substitutions are dictated by rule 2 above and by the assumption that in practice it will be impossible to detect any meaningful difference between k_c and k_c'.

Discussion of Results

The Hexacarbonyls.—Table II summarizes the experimental data for the hexacarbonyls, $Cr(CO)_6$, $Mo(CO)_6$ and $W(CO)_6$, taken from the literature and from some heretofore unpublished measurements. The last column of Table II lists the frequencies we have taken as the best average values

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(6) See for example, H. Eyring, J. Walter and G. E. Kimball, "Quantum Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1944, pp. 227-231.

(7) L. H. Jones in "Advances in the Chemistry of the Coordination Compounds," S. Kirschner, Ed., The Macmillan Co., New York, N. Y., 1961, pp. 398-411.

(8) E. W. Abel, M. A. Bennett and G. Wilkinson, *J. Chem. Soc.*, 2323 (1959).

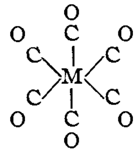
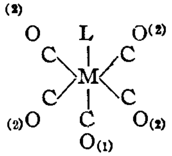
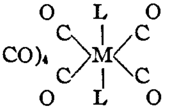
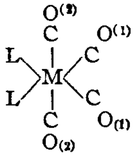
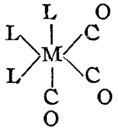
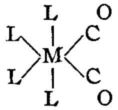
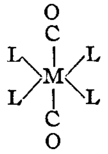
(9) F. A. Cotton and F. Zingales, *Inorg. Chem.*, **1**, 145 (1962).

(10) F. A. Cotton and F. Zingales, *J. Am. Chem. Soc.*, **83**, 351 (1961).

(11) For the general theory of vibrational analyses, see "Molecular Vibrations" by E. B. Wilson, Jr., J. C. Decius and P. C. Cross, McGraw-Hill Book Co., New York, N. Y., 1955.

TABLE I

SECULAR EQUATIONS AND RELATED INFORMATION ON CO STRETCHING MODES[a]

Type of molecule		Molecular symmetry	Symmetry species of CO stretching modes	Activities	Secular equations "Exact"	Secular equations "Approximate"
$M(CO)_6$		O_h	A_{1g}	Raman	$\lambda = \mu(k + k_t + 4k_c)$	$\lambda = \mu(k + 6k_i)$
			E_g	Raman	$\lambda = \mu(k + k_t - 2k_c)$	$\lambda = \mu k$
			T_{1u}	Infrared	$\lambda = \mu(k - k_t)$	$\lambda = \mu(k - 2k_i)$
$ML(CO)_5$		C_{4v}	$A_1^{(1)}$	Infrared and Raman	$\begin{vmatrix} \mu k_1 - \lambda & 2\mu k_c \\ 2\mu k_c & \mu(k_2 + k_t + 2k_c') - \lambda \end{vmatrix} = 0$	$\begin{vmatrix} \mu k_1 - \lambda & 2\mu k_i \\ 2\mu k_i & \mu(k_2 + 4k_i) - \lambda \end{vmatrix} = 0$
			$A_1^{(2)}$			
			B_1	Raman	$\lambda = \mu(k_2 + k_t - 2k_c')$	$\lambda = \mu k_2$
			E	Infrared and Raman	$\lambda = \mu(k_2 - k_t)$	$\lambda = \mu(k_2 - 2k_i)$
trans-$ML_2(CO)_4$		D_{4h}	A_{1g}	Raman	$\lambda = \mu(k + k_t + 2k_c)$	$\lambda = \mu(k + 4k_i)$
			B_{1g}	Raman	$\lambda = \mu(k + k_t - 2k_c)$	$\lambda = \mu k$
			E_u	Infrared	$\lambda = \mu(k - k_t)$	$\lambda = \mu(k - 2k_i)$
cis-$ML_2(CO)_4$		C_{2v}	$A_1^{(1)}$	All are both Infrared and Raman Active	$\begin{vmatrix} \mu(k_2 + k_t) - \lambda & 2\mu k_c \\ 2\mu k_c & \mu(k_1 + k_c') - \lambda \end{vmatrix} = 0$	$\begin{vmatrix} \mu(k_2 + 2k_i) - \lambda & 2\mu k_i \\ 2\mu k_i & \mu(k_1 + k_i) - \lambda \end{vmatrix} = 0$
			$A_1^{(2)}$			
			B_1		$\lambda = \mu(k_2 - k_t)$	$\lambda = \mu(k_2 - 2k_i)$
			B_2		$\lambda = \mu(k_1 - k_c')$	$\lambda = \mu(k_1 - k_i)$
cis-$ML_3(CO)_3$		C_{3v}	A_1	Infrared and Raman	$\lambda = \mu(k + 2k_c)$	$\lambda = \mu(k + 2k_i)$
			E		$\lambda = \mu(k - k_c)$	$\lambda = \mu(k - k_i)$
cis-$ML_4(CO)_2$		C_{2v}	A_1	Infrared and Raman	$\lambda = \mu(k + k_c)$	$\lambda = \mu(k + k_i)$
			B_1		$\lambda = \mu(k - k_c)$	$\lambda = \mu(k - k_i)$
trans-$ML_4(CO)_2$		D_{4h}	A_{1g}	Raman	$\lambda = \mu(k + k_t)$	$\lambda = \mu(k + 2k_i)$
			A_{2u}	Infrared	$\lambda = \mu(k - k_t)$	$\lambda = \mu(k - 2k_i)$

[a] Force constants in dynes cm.$^{-1}$; μ represents the reciprocal of the reduced mass of the CO group, *viz.*, (16.00 + 12.01)/(16.00 × 12.01) = 0.14583; $\lambda = (5.8890 \times 10^{-2})\nu^2$, where ν is the frequency in cm.$^{-1}$.

TABLE II

EXPERIMENTAL CO STRETCHING FREQUENCIES FOR $M(CO)_6$ MOLECULES, CM.$^{-1}$

Symmetry species	Hawkins, *et al.*,[a] infrared, gas	Cotton,[b] infrared, soln.	Danti and Cotton,[c] Raman, soln.	Tobin,[d] Raman, cryst.	This work
			$Cr(CO)_6$		
A_{1g}	2108	....	2063(?)	2102	2100
E_g	2022	....	2021	2013	2020
T_{1u}	2000	1983 ± 10	..	1956(?)	1985
			$Mo(CO)_6$		
A_{1g}	2131	....	2119	2112	2120
E_g	2022	....	2022	2003	2022
T_{1u}	2000	1985 ± 10	..	1967(?)	1990
			$W(CO)_6$		
A_{1g}	..	....	2121	2115	2120
E_g	..	....	2015	1999	2015
T_{1u}	..	1980 ± 10	..	1957(?)	1980

[a] N. J. Hawkins, H. C. Mattraw, W. W. Sabol and D. R. Carpenter, *J. Chem. Phys.*, 23, 2422 (1955). [b] Unpublished experiments. [c] A. Danti and F. A. Cotton, *J. Chem. Phys.*, 28, 736 (1958). [d] Unpublished work of M. C. Tobin, Research Laboratories, American Cyanamid Co. Since the site symmetry of the molecules in the crystals is extremely low, these data must be interpreted with caution.

TABLE III

FORCE CONSTANTS (IN MILLIDYNES/ÅNGSTRÖM) FOR PHOSPHINE SUBSTITUTED CARBONYLS[a]

	Cr			Mo			W		
Type of molecule	k_1	k_2	k_i	k_1	k_2	k_i	k_1	k_2	k_i
$M(CO)_6$	...	16.49	0.22	...	16.52	0.27	...	16.41	0.29
$M(Ph_3P)(CO)_5$	15.50	15.88	.33	15.57	15.99	0.31	15.58	15.85	.30
trans-$M(Ph_3P)_2(CO)_4$	...	15.28	.34	...	15.45	.34	...	...	..
cis-$M[Ph_2P(CH_2)_2PPh_2](CO)_4$	14.49	15.32	.36	14.64	15.41	.36	14.58	15.32	.32
cis-$M[H_3CC(CH_2PPh_2)_3](CO)_3$	13.91	...	.38	14.08	...	.49	14.08	...	.49
trans-$M[o\text{-}C_6H_4(PEt_2)_2](CO)_2$	...	(14.94)[b]	(.40)[b]	...	...	..	...	...	..8
cis-$M[C_2H_4(PPh_2)_2]_2(CO)_2$	13.33[c]	...	.47[c]	13.37	...	.48	13.31	...	.4

[a] k_1 always refers to CO which is *trans* to phosphorus. [b] Estimated value of k_i; see text. [c] Using 1848 and 1708 cm.$^{-1}$ as given in ref. 13 one obtains $k_1 = 12.77$ and $k_i = 1.03$. Since 1708 cm.$^{-1}$ is out of line with the corresponding frequencies for the Mo and W compounds and leads to such unlikely values of the force constants, we have assumed that there is a typographical error and that the correct frequency is 1780 cm.$^{-1}$.

selected from the various experimental values. Numbers followed by question-marks appear suspect, for reasons which are not clear, and have been neglected. It may be seen that the frequencies shift to lower values from the gas phase to solution to solid, which is not unexpected.[12] Our selected average numbers are intended to be those representative of the molecules in solution in typical non-polar solvents. This choice of state was made in preference to the gaseous state since all data on substituted carbonyls are for solutions.

Comparison of the data in Table II with the equations in Table I shows two things. First, the relative energies of the bands are consistent with the conclusion from valence theory that the stretch–stretch interaction constant must be positive. Secondly, the approximation that $k_t = 2k_c$ requires that the ratio $(\lambda_{A_{1g}} - \lambda_{E_g})/(\lambda_{E_g} - \lambda_{T_{1u}}) = 3$. From the numbers in the last column of Table II we obtain the following experimental values of this ratio: $Cr(CO)_6$, 2.4; $Mo(CO)_6$, 3.2; $W(CO)_6$, 3.1. Evidently rule 2 is not a bad approximation. Using the "approximate" equations for the hexacarbonyls we obtain the force constants in Table III.

Phosphine-substituted Group VI Carbonyls.—The literature contains data for various such compounds and calculations have been made using most of the available data. However, Chatt and Watson[13] recently have published a rather extensive table of data for many of the known types of $ML_x(CO)_{6-x}$ compounds including in nearly every case data for the analogous Cr, Mo and W compounds. It seemed worthwhile to recalculate force constants using these data which appear to be of higher precision and are definitely of more uniform quality than the diverse collection of data we had assembled previously. However, we stress that, in general, substantially identical results had been obtained using data from other sources.

For complexes of the types $ML(CO)_5$ and *trans*-$ML_2(CO)_4$, spectral data have been reported recently.[14] However, it was desirable to have data for the $ML(CO)_5$ compounds under higher resolution in order more accurately to assess the position and relative intensity of the band at ~ 1980 cm.$^{-1}$ which appears only as an unresolved shoulder in the spectrum previously published.[14] It was also desired to check the report[14] that two weaker bands appear at a higher frequency than the main band in the $ML_2(CO)_4$ compounds. Therefore the $ML(CO)_5$ and *trans*-$ML_2(CO)_4$ were prepared[14] and their spectra remeasured using a fluorite prism. The results are given in Table IV and typical spectra are shown in Fig. 1 and 2.

TABLE IV

CARBONYL STRETCHING FREQUENCIES OF SOME SUBSTITUTED GROUP VI CARBONYLS ($L = (C_6H_5)_3P$)

Compound	Frequencies, cm.$^{-1}$ and intensities[a]		
$CrL(CO)_5$	2070 w	1989 w	1944 vs
$MoL(CO)_5$	2078 w	1990 w	1951 vs
$WL(CO)_5$	2074 w	1981 w	1943 vs
trans-$CrL_2(CO)_4$	~2010 vvw	1945 w	1889 vs
trans-$MoL_2(CO)_4$	~2005 vvw	1957 w	1900 vs

[a] w = weak; s = strong; v = very.

In the phosphine substituted complexes it would seem reasonable to begin with the approximation that the M–P bonds are axially symmetric. The symmetries and selection rules given in Table I

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[12] G. Herzberg, "Molecular Spectra and Molecular Structure," Vol. II, D. Van Nostrand Co., New York, N. Y., 1945, p. 534.

[13] J. Chatt and H. R. Watson, *J. Chem. Soc.*, 4980 (1961).

[14] T. A. Magee, C. N. Matthews, T. S. Wang and J. H. Wotiz, *J. Am. Chem. Soc.*, 83, 3200 (1961).

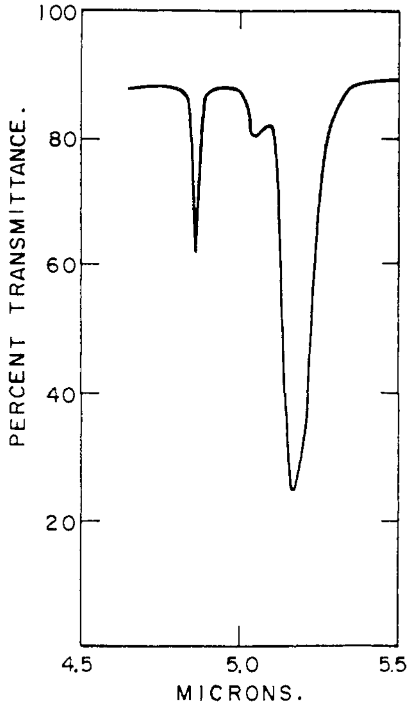

Fig. 1.—The CO stretching region of the infrared spectrum of $Cr[(C_6H_5)_3P](CO)_5$ in $CHCl_3$ (3 mg./ml.): cell thickness: 0.86 mm.; fluorite prism. The spectra of the analogous Mo and W complexes are virtually identical.

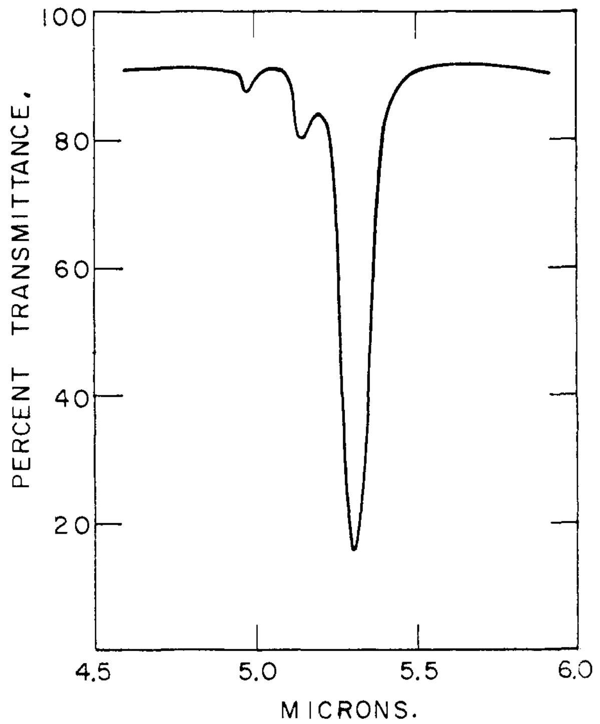

Fig. 2.—The CO stretching region of the infrared spectrum of *trans*-$Cr[(C_6H_5)_3P]_2(CO)_4$ in $CHCl_3$ (12.8 mg./ml.): cell thickness, 0.10 mm.; fluorite prism. The spectra of the analogous Mo and W complexes are virtually identical.

are applicable only when such an assumption is made.

For each of the types of substituted compounds discussions of the assignments used in calculating the force constants listed in Table III are necessary and these will now be given.

$ML(CO)_5$ Compounds.—According to Table I these compounds should have three infrared active CO stretching fundamentals, the two A_1 modes and the E mode. Further, if $k_2 > k_1$, as expected from rule 4, the secular equations show that the E fundamental must be lower in frequency than one of the A_1 fundamentals but its relation to the other A_1 fundamental will depend upon the relative magnitudes of k_i and $k_2 - k_1$. Intensity arguments, as already explained by Orgel,[4] lead us to expect that both A_1 fundamentals will be much weaker than the E fundamental. Inspection of Fig. 1 would lead, in the light of these considerations, to the following seemingly obvious assignment for the chromium compound

$A_1^{(1)}$	2070 cm.$^{-1}$
$A_1^{(2)}$	1989 cm.$^{-1}$
E	1944 cm.$^{-1}$

However, this assignment turns out to be unacceptable because the force constants obtained are $k_1 = 16.24$, $k_2 = 15.79$, $k_i = 0.28$. That is, they contradict the requirement (which was actually used in making the assignment) that k_1 must be less than k_2.

We believe that the way to obtain a reasonable assignment is to assume that the 1985 cm.$^{-1}$ band is the B_1 fundamental. Although this is not infrared active for rigorous C_{4v} symmetry, the true molecular symmetry cannot actually be higher than C_1 because the local symmetry of the $P(C_6H_5)_3$ group cannot be higher than C_3 and when this is combined with the C_{4v} symmetry of the $Cr(CO)_5$ moiety all symmetry elements are annihilated. Thus in principal all fundamentals become infrared active and the degeneracy of the E mode is split. It seems quite reasonable to assume that a slight mechanical coupling of the CO stretching motions to modes in the $P(C_6H_5)_3$ group could enable the B_1 fundamental to gain a little intensity without at the same time producing any detectable splitting of the E mode.

On this basis, we make the assignment (which is consistent with Orgel's)

$A_1^{(1)}$	2070 cm.$^{-1}$
B_1	1989 cm.$^{-1}$
$A_1^{(2)}$	1944 cm.$^{-1}$
E	1944 cm.$^{-1}$

This assignment implies an accidental degeneracy or near degeneracy of the $A_1^{(2)}$ and E modes. Using this assignment we obtain the reasonable force constants in Table III. The above assignment is strongly supported by the Raman spectrum[15] of $Mo(Ph_3P)(CO)_5$, which has a very strong line, obviously a Raman-active fundamental, at 1990 cm.$^{-1}$. So far, decomposition of solutions has prevented reliable measurements of polarizations.

trans-$ML_2(CO)_4$.—Here the assignment of the observed very strong band in each spectrum is unambiguous from the selection rules. These must be the E_u fundamentals. In addition we have also observed two much weaker bands at higher

(15) We are indebted to Dr. Foil A. Miller for this measurement.

frequencies in the Cr and Mo compounds (see Fig. 2 and Table IV). For the Cr compound Magee, *et al.*,[14] also report these two weak bands. The intensities of these bands appear to be reproducible from sample to sample regardless of the procedure of purification and we think it most probable that they do arise from the *trans*-$ML_2(CO)_4$ molecules, although for the highest frequency ones it is difficult to be sure of this since they are extremely weak. For those at 1945 and 1956 cm.$^{-1}$ an assignment as combinations of a fundamental of $\sim$60 cm.$^{-1}$ frequency with the E_u fundamentals appears unlikely since there is no trace of the corresponding difference bands which might be expected to appear with $\sim^1/_4$ the intensity. The most reasonable interpretation is that these weak bands are the A_{1g} and B_{1g} fundamentals which gain some slight intensity because the 3-fold symmetry of the Ph_3P groups reduces the true molecular symmetry to only C_1. In C_1 symmetry the A_{1g} and B_{1g} modes become A′ modes and are infrared active. The general argument here is the same as that given above for the $ML(CO)_5$ compounds.

The secular equations, Table I, require the frequencies of the modes to be in the order $A_{1g} > B_{1g} > E_u$. Moreover, simple intensity considerations suggest that the A_{1g} fundamental might acquire less intensity than the B_{1g} fundamental under the type of perturbation of the D_{4h} symmetry being considered. Therefore the following assignment (for example for the Cr compound) appears reasonable

A_{1g}	$\sim$2010 cm.$^{-1}$
B_{1g}	1945 cm.$^{-1}$
E_u	1886 cm.$^{-1}$

When this assignment is used to evaluate the force constants k_2 and k_i, the results shown in Table III are obtained. There is only one disturbing feature of the results, namely, that if any two of the observed frequencies are used alone to evaluate the force constants and these are then used to calculate the remaining frequency, discrepancies ($\sim$30 cm.$^{-1}$) are obtained. It could be argued that the entire dynamical model being used is sufficiently crude that such a discrepancy is not alarming but in all other cases the agreement has been much better ($\pm$5 cm.$^{-1}$). It is thus possible that the highest and extremely weak bands are not in fact the A_{1g} fundamentals in which case one obtains by using only the other two frequencies about the same values of k_2 but k_i's of $\sim$0.45, which are perhaps a trifle higher than expected but not too unreasonable.

Obviously, a definitive assignment here must await the completion of Raman studies.

cis-$ML_2(CO)_4$.—Table I shows that four CO stretching fundamentals should be infrared active. From rule 4 we expect that $k_1 < k_2$ and this relationship in conjunction with the secular equations shows that one of the A_1 fundamentals must have the highest frequency. The relative frequencies of the remaining three fundamentals cannot be predicted *a priori* since this depends on the value of k_i relative to the difference between k_1 and k_2. Thus there are six assignments possible on the basis of these considerations alone. However, it is possible, by the procedure now to be described to eliminate all but one. This procedure will be illustrated for the particular case of the tungsten compound but the results for the chromium and molybdenum compounds are entirely similar.

On the right side of Table V are listed the six possible assignments for the tungsten compound. Since there are only three force constants to be evaluated and since the band at 1912 cm.$^{-1}$ is reported as a shoulder and therefore has the greatest uncertainty in its frequency, the other three frequencies have in each case been used to evaluate the force constants and the force constants then used to calculate the remaining frequency. Moreover, because the 1912 cm.$^{-1}$ band is a shoulder on the high frequency side of a strong band, the true frequency of this fundamental is very likely somewhat lower (perhaps 10 cm.$^{-1}$) than 1912 cm.$^{-1}$. Table V shows the force constants and the calculated frequency of the "1912 cm.$^{-1}$" band for the six assignments.

TABLE V

FORCE CONSTANTS OBTAINED WITH THE SIX POSSIBLE ASSIGNMENTS IN $W[C_2H_4(PPh_2)_2](CO)_4$

	Assignment				Calcd. force constants			Calcd. freq. of "1912 cm.$^{-1}$ band"
No.	A_1	A_1	B_1	B_2	k_1	k_2	k_i	
1	2016	1876	1901	1912	14.85	14.59	0.38	1893
2	2016	1876	1912	1901	15.14	15.16	0.32	1866
3	2016	1901	1876	1912	14.72	15.01	0.41	1882
4	2016	1901	1912	1876	Imaginary roots obtained			
5	2016	1912	1876	1901	15.01	15.01	0.40	1913
6	2016	1912	1901	1876	14.58	15.32	0.36	1900

The validity of the six assignments can be assessed as follows: (1) is unacceptable because it gives $k_1 > k_2$ and grossly underestimates the frequency of the B_2 fundamental. (2) is unacceptable because it gives $k_1 \approx k_2$ and grossly misplaces the B_1 frequency. (3) gives $k_1 < k_2$ which is correct but gives an unacceptable frequency for the B_2 fundamental. (4) does not permit one to obtain real values of the force constants. (5) gives $k_1 \approx k_2$ which is incorrect and gives too high a frequency for the second A_1 fundamental. Assignment (6) alone is acceptable in all respects giving $k_1 < k_2$ and placing the second A_1 fundamental quite satisfactorily. Assignment (6) is analogous to that proposed by Orgel[4] for an analogous $ML_2(CO)_4$ compound using intensity criteria and a rough estimate of the frequency separations of several of the bands.

***cis*-$ML_3(CO)_3$ Compounds.**—For these the assignments follow unambiguously from the secular equations of Table I. Since k_i must be positive the A_1 fundamental must have the higher frequency.

***cis*-$ML_4(CO)_2$ Compounds.**—Here again the assignments follow unambiguously from the secular equations on requiring that $k_i > 0$.

***trans*-$ML_4(CO)_2$ Compound.**—The one reported band may be assigned unequivocally from the selection rules. In order to estimate the value of

k_2 an estimate of k_i was made by comparison with k_i values in the other compounds. The force constants in Table III for this compound are therefore put in parentheses.

Summary.—The results in Table III clearly show that the five rules proposed are entirely consistent with all the experimental data. Using rules 1 and 2 the force constants in Table III were obtained and they in turn are in complete accord with the expectations from rules 3–5. Thus there are steady decreases in k_1 and k_2 as the number of substituents increases (rule 3); CO's *cis* to substituents have higher *k*'s than those *trans* (rule 4); and there is an upward trend in the k_i's with increasing substitution (rule 5).

It is also interesting to note that the compounds of the same type with Cr, Mo and W as the metal atom have force constants which do not differ significantly. This implies that the extent of pi bonding does not vary much with atomic number for metal atoms in the same group in analogous compounds.

[CONTRIBUTION FROM THE LABORATORY OF MOLECULAR STRUCTURE AND SPECTRA, DEPARTMENT OF PHYSICS AND DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CHICAGO, CHICAGO 37, ILL.]

Molecular Complexes and their Spectra. XV. Iodine Complexes with Thiophene, 2-Methylfuran and N-Methylpyrrole

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The thermodynamic and electronic spectral characteristics of the 1:1 molecular complexes of iodine with thiophene, 2-methylfuran and N-methylpyrrole have been determined from absorption spectrophotometric studies of *n*-heptane solutions. Partial studies were made with furan and pyrrole. In the case of pyrrole a reaction with iodine, producing a precipitate, was found to take place. For the furans and the pyrroles two distinct charge transfer bands were detected. These results show a considerable reduction in electron donor strength for these donors compared to the corresponding sulfides, ethers and amines and are in agreement with the well-known aromatic character of these compounds.

Introduction

Both the chemistry and the physical properties of thiophenes, furans and pyrroles indicate that these compounds have considerable aromatic character; in addition, quantum mechanical calculations support this view.[1] In fact, these compounds behave more like aromatic hydrocarbons than like unsaturated sulfides, ethers and amines.

The thermodynamic and electronic spectral characteristics of iodine complexes with a variety of both n-donors[2] and π-donors[3] have been studied. In general, the K, ΔH° and the "blue shift" of the visible iodine band for the 1:1 iodine complexes are substantially larger for n-donors compared to aromatic π-donors like benzene. Consequently, it should be of considerable interest to compare these characteristics for the iodine complexes of thiophenes, furans and pyrroles with those of the corresponding sulfides, ethers and amines, all n-donors.

Experimental

Materials.—Fisher Certified iodine was resublimed under reduced pressure. Phillips 66 "pure" grade *n*-heptane was washed twice with concentrated sulfuric acid, then three times with water, dried with Drierite and distilled with a Podbielniak column. Matheson Coleman and Bell thiophene was treated with activated silica gel, alumina, Drierite and finally distilled with a Podbielniak column. The distillate was stored over alumina for several days with occasional shaking. Gas chromatography showed no detectable impurities. The final purified thiophene had an odor similar to that of benzene; and *n*-heptane solutions of thiophene, with constant initial iodine concentration, showed an isosbestic point at about 525 mμ for the free and shifted visible iodine bands, indicating that the iodine was not reacting with thiophene or with any impurities in the solutions. (Impure thiophene gave spectra that came below the isosbestic point by 10–20% of the absorbance of the visible iodine band indicating that some reaction was taking place between iodine and an impurity.)

Eastman Kodak Co. practical grade 2-methylfuran and furan were dried over Drierite and then purified by fractional distillation from potassium hydroxide immediately before use. Eastman Kodak Co. practical grade N-methylpyrrole was also dried over Drierite and purified by fractional distillation from potassium hydroxide immediately before use. Eastman Kodak Co. practical grade pyrrole was dried over Drierite and then purified by fractional distillation at reduced pressure immediately before use. Solutions with iodine at constant initial concentration and either 2-methylfuran, furan or N-methylpyrrole, in *n*-heptane, showed isosbestic points in the region around 520 mμ indicating that iodine did not react with these donors. On the other hand, solutions of pyrrole and iodine did not show an isosbestic point and a turbid solution was produced indicating that pyrrole reacted with iodine.

Method.—The experimental method of measuring the spectra and preparing the solutions is described in a previous paper.[4] K and ϵ were calculated by using eq. 3 of this same previous paper, with suitable corrections being made for any overlapping absorption by iodine or the donor.

Results

Thiophene.—The thermodynamic and spectral characteristics of the thiophene-iodine complex are given in Tables I and II. Iodine was at a concentration of about 8×10^{-4} M and thiophene varied from about 0.1 to 0.5 M for the solutions from which the K's were calculated. At the peak of the charge-transfer band there was a very small absorption due to free thiophene and a larger, but still relatively small, absorption due to free iodine which were corrected for. In addition, it was found that when the solvent was changed from *n*-heptane to dichloromethane there

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