Force Constants and the Electronic Structure of Carbonyl Groups. d⁶ Carbonyl Halides and Dihalides

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Using an approximate molecular orbital calculation to describe the electronic structure of the transition metal carbonyl complexes $M(CO)_{6-x}L_x$ (M = Cr, Mn, Fe; L = Cl, Br, I; x = 1, 2), we have been able to correlate the carbonyl force constants with the calculated occupancies of the 5σ and 2π orbitals on the carbonyl. These results indicate that, in addition to the degree of back-bonding to the 2π orbital, the degree of σ donation from the 5σ orbital has an important effect on the carbonyl's force constant. The calculations also indicate that the direct donation of electron density from the halogen's σ orbital to the cis carbonyl's 2π orbital is the most important mechanism by which a change in the halogen effects a change in the carbonyl force constant.

Introduction

In the interpretation of a carbonyl's bond strength in transition metal complexes, approximate force constants calculated by the method of Cotton and Kraihanzel[1] (CK) have proven very useful. Although the CK approach has been criticized,[2,3] Jones[4] has pointed out that this method should yield meaningful trends in the force constants of a closely related series of molecules. Miller[5] has outlined the relationship between nonrigorous force constants and those of a general quadratic valence force field and has concluded that nonrigorous force constants are valid upon proper definition of the form of localized normal coordinates. Cotton[6] has interpreted the trends in the force constants for a large number of six-coordinate complexes in terms of changes in the carbonyl's 2π occupation. On the other hand, Dobson[7] has pointed out that σ donation from the carbonyl group should also affect its force constant, and more recently Darensbourg and Brown[8] have concluded that in some cases the trends in carbonyl force constants are due predominantly to changes in the carbonyl σ bonding rather than in its π bonding.

In previous work on the pentacyanonitrosyl complexes,[9] we were able to correlate the stretching frequencies of the nitrosyl group by considering changes in its π system alone since the degree of σ donation remained constant. However, the trend in the cyanide's stretching frequency could be correlated only by considering changes in both its σ-donating and π-accepting ability. From simple energetic considerations, one might expect the behavior of carbonyls to be intermediate between the behavior of cyanides and nitrosyls. In the case of several manganese carbonyl complexes,[10,11] we were able to interpret the force constants in terms of the 2π occupations even though we observed some changes in the 5σ occupation, which we anticipated might be important.

These previous studies were somewhat limited in that they both were confined to a small amount of data. In addition the cyanide and nitrosyl work was limited to correlation with stretching frequencies rather than force constants, the latter being a more accurate measure of bond strength. In the present work we have undertaken the study of 12 complexes, which include the pentacarbonyl halides of chromium, manganese, and iron and the tetracarbonyl dihalides of manganese and iron. These 12 complexes provide a total of 24 carbonyl force constants[12,13] with which we may compare the results of our approximate molecular orbital (MO) calculation. Through this study we hope to understand what features of the electronic structure are important in determining the carbonyl force constant and how these are influenced by changes in the central metal and in the number and kind of halogens.

Method

The computational method has been described in detail previously.[10,14,15] In general terms, it is an approximate molecular orbital approach, in which the effect of all overlap terms and the effect of the charge distribution on all neighboring atoms are included in the secular equation. The procedure is a self-consistent one and the calculations described have been iterated until the absolute value of the difference in each Mulliken population is less than 0.001. The computer program[15] used for these calculations is a completely general single package which is not limited to any particular symmetry.

Basis Functions.—The basis functions used are atomic Hartree–Fock–Roothaan functions for the free atoms. They are chosen to be consistent with the Mulliken charge and configuration of each atom in the molecular calculation. The carbon and oxygen functions are those of Clementi,[16] where the 1s and 2s were curve fit to reduce the number of exponents. The "best atom" functions of Clementi and Raimondi[17] were used for the halogens. The 1s through 3d functions for the chromium, manganese, and iron were taken from the work of Richardson, *et al.*;[18] the 3d

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

(2) L. M. Bower and M. H. B. Stiddard, *Inorg. Chim. Acta*, **1**, 231 (1967).

(3) L. H. Jones, *Inorg. Chem.*, **7**, 1681 (1968).

(4) L. H. Jones, *ibid.*, **6**, 1269 (1967).

(5) J. R. Miller, *J. Chem. Soc. A*, 1885 (1971).

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

(7) G. R. Dobson, *ibid.*, **4**, 1673 (1965).

(8) D. J. Darensbourg and T. L. Brown, *ibid.*, **7**, 959 (1968).

(9) R. F. Fenske and R. L. DeKock, *ibid.*, submitted for publication.

(10) R. F. Fenske and R. L. DeKock, *ibid.*, **9**, 1053 (1970).

(11) R. L. DeKock, A. C. Sarapu, and R. F. Fenske, *ibid.*, **10**, 38 (1971).

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

(13) Z. Iqbal and T. C. Waddington, *J. Chem. Soc. A*, 2958 (1968).

(14) R. F. Fenske and D. D. Radtke, *Inorg. Chem.*, **7**, 479 (1968).

(15) M. B. Hall and R. F. Fenske, *ibid.*, submitted for publication.

(16) E. Clementi, *J. Chem. Phys.*, **40**, 1944 (1964).

(17) E. Clementi and D. L. Raimondi, *ibid.*, **38**, 2686 (1963).

(18) J. W. Richardson, W. C. Nieuwpoort, R. R. Powell, and W. F. Edgell, *ibid.*, **36**, 1057 (1962).

function corresponds to a metal atom of 1+ charge. The 4s and 4p functions were obtained from the weighted average of the functions that had maximum overlap with the 2p functions of the atoms directly bonded to the metal atom. This procedure is a natural extension of that[10,19] used previously. In all cases the functions were Schmidt orthogonalized beginning with the 1s function.

Bond Distances.—The bond distances employed in these calculations are listed in Table I. The carbonyl

TABLE I
BOND DISTANCES (Å)

	Cr	Mn	Fe
C–O	1.128[a]	1.128[a]	1.128[a]
M–C cis	1.92	1.89[b]	1.82
M–C trans	1.82	1.79[b]	1.72
M–Cl	2.45	2.37[b]	2.27
M–Br	2.60	2.50[c]	2.42
M–I	2.79	2.71	2.61

[a] Reference 20. [b] Reference 22. [c] R. F. Bryan, personal communication.

bond distance was fixed at the value[20] for free CO. This procedure yields common carbonyl ligands for each complex and is compatible with the small changes observed[21] in carbon–oxygen distances for bond orders of 2 to 3. All manganese–carbon distances were taken to be the same as the known values[22] for $Mn(CO)_5$-Cl. Because the structural data are not available, it was necessary to estimate the remaining metal–carbon distances. The chromium–carbon distance for the cis carbonyl was taken to be the same as that for chromium hexacarbonyl,[23] while for the trans carbonyl the distance was shortened 0.10 Å, the same shortening observed[22] in $Mn(CO)_5Cl$. For the iron complexes the metal–carbon distance was estimated from the Fe–C distances[24] in $Mn_2Fe(CO)_{14}$. The cis Fe–C distances for the halides were taken to be 0.03 Å longer than the observed distance in $Mn_2Fe(CO)_{14}$ (1.29 Å). This increase in bond distance was made because there is a corresponding increase in going from the equatorial Mn–C distance in $Mn_2Fe(CO)_{14}$ (1.86 Å) to the cis Mn–C distance in $Mn(CO)_5Cl$. Again the Fe–C distance trans to the halogen was taken to be 0.10 Å shorter than the cis distance.

The unknown metal–halogen distances were estimated from the covalent radii, a procedure that is applicable[10] to the known manganese–halogen distances. The covalent radii of the chlorine, bromine, and iodine are 0.99, 1.14, and 1.33 Å, respectively.[25] The covalent radius of manganese(1+) has been estimated[26] to be 1.38 Å from the metal to ring bond distances in (C_5H_5)-$Mn(CO)_3$. In a similar fashion we have estimated the iron(2+) covalent radius to be 1.28 Å from the bond

distances[27] in ferrocene. For chromium(0) we have used a radius of 1.46 Å. This estimate was chosen by consideration of the work by Andrianov, *et al.*,[28] on chromium π complexes, the chromium to ring-carbon distance[29] in $C_6H_6Cr(CO)_3$, and the chromium-iodine distance[30] in $(Cr(CO)_5)_2I$.

TABLE II
EIGENVECTORS, EIGENVALUES, AND OVERLAP
POPULATIONS FOR FREE CO

	C 2s	C 2p	O 2s	O 2p	Energy, eV	OP[a]
3σ	0.2870	−0.2329	0.6923	0.1056	−42.16	0.373
4σ	0.4291	0.0870	−0.4349	0.7238	−22.60	0.147
5σ	0.6501	0.6812	0.1459	−0.4687	−13.79	−0.128
1π	...	0.4662	...	0.7433	−21.04	0.230
2π	...	0.9522	...	−0.7559	+0.28	−0.478

[a] This is the overlap population between carbon and oxygen for a single electron occupying the molecular orbital.

Results and Discussion

Orbital Occupations and Carbonyl Force Constants.—There are several assumptions involved in attempting to correlate orbital occupations with CK force constants. First, we are assuming that CK force constants reflect the same trends as the true force constants. Second, we are assuming that the trend in the orbital occupancies reflects the trend in the energy changes that occur in stretching the bond, for it is these energy changes which determine the true force constant. We would expect these assumptions to hold only for a series of very similar complexes. For this reason we have confined this study to six-coordinate carbonyl halide complexes, where the central metal is formally d^6.

In Table III the calculated occupancies of the 5σ, $2\pi_x$, and $2\pi_y$ orbitals are listed along with the corresponding CK force constants. The designations $2\pi_x$ and $2\pi_y$ for the antibonding π orbitals of the carbonyl groups are based upon the coordinate system given in Figure 1 and the comments in footnote a of Table III. Although there is some tendency toward weaker force constants with larger 2π occupancies, there are numerous exceptions from which the importance of the 5σ occupations can be inferred. For example, the trans CO in $Fe(CO)_4I_2$ and the cis CO in $Cr(CO)_5Cl^-$ have identical 2π occupations, 0.537, but substantially different force constants, 17.43 and 15.58 mdyn/Å, respectively. Examining the 5σ occupations, we find that the iron complex's occupation is 1.293 while the chromium complex's occupation is 1.457. The fact that the CO with the larger force constant has the lower 5σ occupancy is in agreement with our previous contention that this orbital is antibonding.

Free Carbon Monoxide.—After the calculation is completed in the atomic basis, it is convenient to transform the results to the basis of the free molecular ligand. This procedure isolates in a few of the ligand orbitals those changes which are most important in the bonding of the ligand to the metal.

The eigenvectors, eigenvalues, and overlap populations of free carbon monoxide are given in Table II.

(19) D. D. Radtke, Ph.D. Thesis, The University of Wisconsin, 1966.

(20) G. Herzberg, "Spectra of Diatomic Molecules," Van Nostrand, Princeton, N. J., 1950, p 522.

(21) F. A. Cotton and R. M. Wing, *Inorg. Chem.*, **4**, 314 (1965).

(22) R. F. Bryan, P. T. Greene, and A. R. Manning, Abstracts of American Crystallographic Association, Seattle, Wash., March 1969, No. M6.

(23) (a) L. O. Brockway, R. V. G. Ewens, and M. W. Lister, *Trans. Faraday Soc.*, **34**, 1350 (1938); (b) A. Whitaker and J. W. Jeffery, *Acta Crystallogr.*, **23**, 977 (1967).

(24) P. A. Agron, R. D. Ellison, and H. A. Levy, *ibid.*, 1079 (1967).

(25) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 225.

(26) M. J. Bennett and R. Mason, *Nature (London)*, 760 (1965).

(27) J. D. Dunitz, L. E. Orgel, and A. Rich, *Acta Crystallogr.*, **9**, 373 (1956).

(28) V. G. Andrianov, B. P. Biryukov, and Yu. T. Struchkov, *Zh. Strukt. Khim.*, **10**, 1129 (1969).

(29) M. F. Bailey and L. F. Dahl, *Inorg. Chem.*, **4**, 1314 (1965).

(30) L. B. Handy, J. K. Ruff, and L. F. Dahl, *J. Amer. Chem. Soc.*, **92**, 7327 (1970).

TABLE III
CARBONYL ORBITAL OCCUPANCIES[a] AND FORCE CONSTANTS

Compound		5σ	$2\pi_x$	$2\pi_y$	k, mdyn/Å
Cr(CO)₅Cl⁻	trans	1.407	0.355	0.355	14.07[b]
Cr(CO)₅Br⁻	trans	1.405	0.353	0.353	14.10[b]
Mn(CO)₄I₂⁻	trans	1.354	0.302	0.330	15.48[b]
Mn(CO)₄IBr⁻	trans	1.355	0.302	0.327	15.48[b]
Mn(CO)₄Br₂⁻	trans	1.357	0.302	0.325	15.50[b]
Cr(CO)₅Br⁻	cis	1.456	0.261	0.282	15.56[b]
Cr(CO)₅Cl⁻	cis	1.457	0.261	0.276	15.58[b]
Mn(CO)₅Cl	trans	1.352	0.286	0.286	16.28[b]
Mn(CO)₅Br	trans	1.350	0.286	0.286	16.32[b]
Mn(CO)₅I	trans	1.349	0.286	0.286	16.37[b]
Mn(CO)₄I₂⁻	cis	1.402	0.251	0.251	16.75[b]
Mn(CO)₄IBr⁻	cis	1.404	0.241	0.252	16.77[b]
Mn(CO)₄Br₂⁻	cis	1.406	0.242	0.242	16.91[b]
Mn(CO)₅I	cis	1.394	0.213	0.240	17.29[b]
Mn(CO)₅Br	cis	1.394	0.212	0.228	17.39[b]
Fe(CO)₄I₂	trans	1.293	0.252	0.285	17.43[b]
Mn(CO)₅Cl	cis	1.395	0.211	0.218	17.46[b]
Fe(CO)₄Br₂	trans	1.295	0.250	0.272	17.53[b]
Fe(CO)₅Br⁺	trans	1.287	0.233	0.233	17.93[c]
Fe(CO)₅Cl⁺	trans	1.289	0.233	0.233	17.95[c]
Fe(CO)₄I₂	cis	1.337	0.221	0.221	17.95[b]
Fe(CO)₄Br₂	cis	1.338	0.205	0.205	18.26[b]
Fe(CO)₅Cl⁺	cis	1.325	0.171	0.177	18.99[c]
Fe(CO)₅Br⁺	cis	1.325	0.171	0.193	19.00[c]

[a] The cis and trans designations of the carbonyl groups are in reference to their locations with respect to the halogen or halogens. For the monohalides, this assignment is obvious. For the dihalides, substituted at positions 1 and 5 in Figure 1, ligand positions 2 and 4 are designated cis, since they are cis to both halogens; positions 3 and 6 are designated trans since they are trans to one halogen although cis to the other. [b] Reference 12. [c] Reference 13.
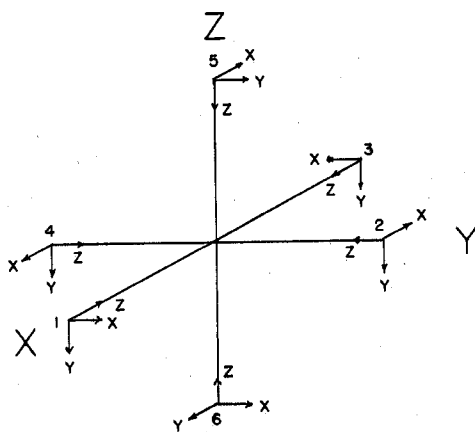

Figure 1.—Coordinate system for the complexes. Each carbonyl has its carbon and oxygen coordinates as indicated by the single ligand atom coordinate system. The monohalides have the halogen placed in ligand position 5. The dihalides have the halogens in positions 5 and 1.

From our previous work we know that carbon monoxide bonds to a transition metal by two mechanisms. (1) A σ bond is created by electron donation from the carbonyl 5σ orbital to the unfilled metal orbitals. (2) A π bond is created by electron donation from the filled metal d orbitals to the unfilled 2π carbonyl orbitals. The other orbitals listed in Table II remain essentially isolated and filled so that the electronic distribution of the bonded carbonyl can be described as $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^4 5\sigma^x 2\pi^y$, where 1σ and 2σ are essentially the 1s orbitals of oxygen and carbon and x and y are variable occupations which will depend on the specific system. Upon examining the overlap population, we see that both the 5σ and 2π are antibonding in character. This means that the electron donation

from the 5σ orbital will strengthen the carbon–oxygen bond, while electron donation to the 2π will weaken the bond. Thus, we expect the competition between the two bonding processes to determine the C–O bond strength in the complex.

For a second example, we will compare two compounds which have the same CO force constant: the trans CO in Fe(CO)₄I₂ and the cis CO in Mn(CO)₅Cl. If the π bonding were the only factor determining the force constants, one would expect similar 2π occupancies for these two complexes, but, in fact, the occupancies are substantially different, 0.54 and 0.43, respectively. Again we can account for this apparent difficulty by considering the effect of the 5σ occupations. The 5σ occupation of the manganese compound is 0.10 larger than that of the iron compound. Since the 5σ and 2π are both antibonding, the difference in the 5σ occupations, which is in the opposite direction, will counteract the difference in the 2π occupations. Thus, it is a balance between these two opposing effects which leads to the observed similarity in the force constants of these two compounds. Numerous other examples can be drawn from the data in Table III, but these two are sufficient to illustrate that changes in both π and σ bonding must be considered to correctly account for the observed differences in the force constants.

Up to this point we have discussed the results in a qualitative fashion. In order to ascertain if a more quantitative relationship might exist, we have calculated the multiple correlation coefficient for the data in Table III. The resulting high value of 0.997 suggests that the 5σ and 2π occupancies can completely account for the variation of the force constants in a quantitative fashion and that we may assume a linear relationship exists between the force constants and the occupancies. Thus

$$k = a(5\sigma) + b(2\pi_x + 2\pi_y) + c \qquad (1)$$

where k is the CK force constant and where (5σ) and $(2\pi_x + 2\pi_y)$ are the total 5σ and 2π occupancies. The results of a standard regression (least-squares) analysis of the 24 force constants are displayed in Table IV.

TABLE IV
SUMMARY OF REGRESSION STATISTICS

	Regression coeff	Std error of regression coeff	Partial correln coeff	F value with 1 and 21 deg of freedom	Significance level, %
5σ	−9.504	0.480	−0.974	392.1	>99.99
2π	−11.729	0.242	−0.996	2347.3	>99.99
Constant	35.813	0.633	0.997	3197.7	>99.99

Note that the coefficients for eq 1 have the expected sign; *i.e.*, an increase in the occupancy of either the 5σ or 2π results in a lower force constant in agreement with our qualitative interpretation that both of these orbitals are antibonding. The importance of all three regression coefficients is reflected in their partial correlation coefficients. The standard F tests indicate that the significance of each coefficient is greater than 99.99%.

Equation 1 predicts the force constants with a standard error of 0.11 mdyn/Å. Since the experimental accuracy of the force constants is 0.1 mdyn/Å,[6] much of the unexplained variation in the force constants, which
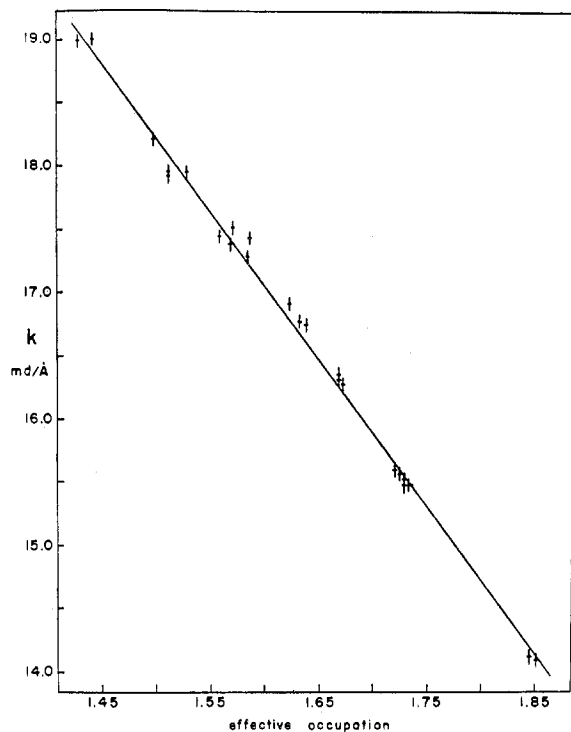
Figure 2.—Force constants *vs.* effective occupations. The vertical bars are approximately ±0.05 mdyn/Å.

Figure 3.—MO diagram for $Cr(CO)_5Br^-$, $Mn(CO)_5Br$, and $Fe(CO)_5Br^+$. The energies of $Cr(CO)_5Br^-$ and $Fe(CO)_5Br^+$ are shifted by −5.50 and +5.50 eV, respectively, to place them on the same energy scale as $Mn(CO)_5Br$.

gives rise to the standard error, can be attributed to experimental error. There is no reason to suppose that this is the only source of error, especially when one considers all the assumptions made in this analysis. However, the relatively small standard error and the extremely high significance level do suggest that the approach used is essentially sound.

It is convenient to rearrange eq 1 in the following form

$$k = b[2\pi_x + 2\pi_y + (a/b)5\sigma] + c \qquad (2)$$

Using the coefficients from Table IV, this equation becomes

$$k = -11.73[2\pi_x + 2\pi_y + (0.810)5\sigma] + 35.81 \qquad (3)$$

In Figure 2 we have plotted k, the force constant, against the expression in brackets, which may be thought of as effective occupation. The excellent agreement between eq 3 and the experimental force constants over the whole range from 19.0 to 14.1 mdyn/Å gives us confidence that our calculations are exhibiting the correct trends in the electronic structure and that our conclusions concerning the importance of both σ and π bonding effects in determining the force constant are correct. Having established a relationship between the force constants and the electronic structure of the carbonyl, we would like to discuss how changes in the carbonyl occupancies are related to changes in the central metal and in the type and number of substituted halogens.

Central Metal.—From the results in Table III we can see that changing the central metal has a substantial effect on the force constants. To gain some insight into what is causing the changes in force constants, we will consider in detail the electronic structures of the monobromides. The conclusions drawn from this
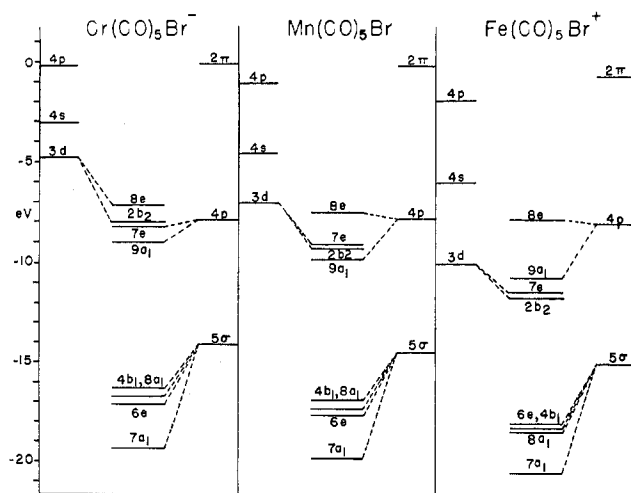
example will be generally valid for the other halide complexes.

In going from chromium to manganese to iron, we see from Table III that the carbonyl becomes a better σ donor and a poorer π acceptor. Both of these changes have the effect of strengthening the C–O bond, and their combined effect is what produces the large increase in the force constant. The reason for the change in occupancy can be seen from an examination of the MO diagram in Figure 3, where a large drop in the energy of the metal levels is the most obvious difference in the three complexes. This energy drop then causes the metal to accept more σ electron density from the carbonyls and to donate less π electron density to them. The occupied molecular orbitals most strongly affected by changing the metal atom are the 8e, 7e, $2b_2$, and $9a_1$ orbitals. These alterations are reflected in the per cent character of the metal and ligands in these MO's as illustrated in Table V. For example, the per cent of 2π in the $2b_2$ molecular orbital drops from 46 to 36 to 25% in going across the series,

TABLE V

PER CENT CHARACTER OF 8e, 7e, $2b_2$, AND $9a_1$
LEVELS IN $M(CO)_5Br$ (M = Cr, Mn, Fe)

Level		$Cr(CO)_4Br^-$	$Mn(CO)_4Br$	$Fe(CO)_4Br^-$
8e	M $3d_{yz}$	41.6	12.1	3.9
	Br p_y	30.7	84.3	95.0
	2CO $2\pi_y$	7.6	0.6	0.1
	4CO $2\pi_y$	7.6	0.6	0.1
	5CO $2\pi_x$	11.7	2.3	0.4
7e	M $3d_{yz}$	17.1	56.6	72.1
	Br p_y	68.7	15.6	3.4
	2CO $2\pi_y$	4.5	8.3	6.3
	4CO $2\pi_y$	4.5	8.3	6.3
	5CO $2\pi_x$	4.1	9.8	8.3
$2b_2$	M $3d_{xy}$	52.7	62.7	71.0
	1CO $2\pi_x$	11.6	8.9	6.3
	2CO $2\pi_x$	11.6	8.9	6.3
	3CO $2\pi_x$	11.6	8.9	6.3
	4CO $2\pi_x$	11.6	8.9	6.3
$9a_1$	M $3d_{z^2}$	8.30	12.30	14.00
	M 4s	1.40	2.10	2.40
	Br p_z	77.30	67.57	58.40
	1–4CO 5σ	0.01	0.02	0.14
	5CO 5σ	0.03	0.18	0.14
	1–4CO $2\pi_y$	1.18	1.57	2.09

and this decrease in the degree of back-bonding is reflected in a decrease in the 2π occupancy.

The reason for the large drop in the energy levels across this series is an increase in the electron–nuclear attraction energy, due to the successive addition of a proton to the central nucleus in this series of iso-electronic complexes. The shifts in the energy are so large, in fact, that there are changes in the order of the final MO levels. Thus, in $Cr(CO)_5Br^-$ the order shown in Figure 3 is 8e, 2b₂, 7e, but in $Mn(CO)_5Br$ the order is 8e, 7e, 2b₂. In the latter compound the order agrees[10] with the photoelectron spectra.[31] In $Fe(CO)_5Br^+$ the 3d level is so low in energy that all the halogen levels are above the predominantly metal 7e and 2b₂. In addition to the shift in the order of the levels, the per cent character of the 8e, 7e, 2b₂, and 9a₁ MO's, displayed in Table V, also varies drastically with a change in metal. For example, the character of the 8e changes from 31% Br in the chromium compound to 84% Br in the manganese compound to 96% Br in the iron compound, while in the 7e the change is in the opposite direction from mostly Br in the chromium complex to mostly 3d metal in the iron complex. These differences suggest that one cannot generalize the results of any one particular compound in this series to encompass the other complexes. The importance of the results discussed lies not in their exact value, which cannot be precisely determined by an approximate calculation, but in their relative magnitude and in the correctness of the trends across the series of complexes.

Halogens.—In our previous work on the manganese compounds,[10] we discussed the changes in bonding that occur in going from the manganese pentacarbonyl chloride to the bromide and iodide. Because there were insufficient data on the manganese complexes alone, we were not able to interpret all the trends in the carbonyl force constants. The more complete data provided by the present series of complexes allow us to extend our previous discussion.

One of the most obvious effects of the halogen is to make the carbon to oxygen bond of the carbonyl trans to it weaker than the carbonyl cis to it. Thus in Table III we see that in $Cr(CO)_5Br^-$ the cis CO has a force constant of 15.56 mdyn/Å, while the trans CO has a force constant of 14.10 mdyn/Å. The large decrease is due to a correspondingly large increase in the 2π occupancy of the trans CO. Opposing this weakening effect there is the strengthening effect of increased donation from the 5σ orbital, but from the magnitude of the changes in Table III it is clear that the weakening effect of the increased π back-bonding will predominate. The overall effect is the familiar "trans influence"[10] which generally has been attributed to π back-bonding only.[1] In our previous work,[9,10] the factors affecting the degree of trans influence have been discussed in detail.

In changing the halogen from Cl to Br to I, the most apparent trend in the carbonyl force constants is the weakening of the carbon to oxygen bond of the cis carbonyl. The reason for this trend has been pointed out previously.[10] Using the manganese complexes as

an example, we see from Table III that the only cause for the weakening in the cis carbonyl is an increase in its $2\pi_y$ occupancy. An examination of the eigenvectors suggests that the increase in the $2\pi_y$ occupation is due to increasing participation of the $2\pi_y$ orbital in the 9a₁ halogen–metal bond. As we go from Cl to I the energy of the halogen p orbitals rises closer to that of the carbonyl, enhancing the overall interaction between the halogen p_z orbital and the $2\pi_y$ orbitals and increasing the participation of the $2\pi_y$ orbitals in the 9a₁ MO. This whole process can be described as the direct donation of electron density from the p_z halogen orbital to the $2\pi_y$ carbonyl orbitals.

The increase in the direct donation in going from Cl to Br to I is even more apparent in the disubstituted species. For example, the shift in the cis CO's force constant in going from Br to I for $Mn(CO)_5X$ is 0.10 mdyn/Å while the corresponding shift for $Mn(CO)_4X_2^-$ is 0.16 mdyn/Å. In Table III we see a correspondingly larger shift in the total cis 2π occupancies. The reason for this larger shift is simply that there are now two halogens which can donate electron density directly from their p_z orbital to the 2π orbitals.

Another aspect of the direct donation effect which has not been previously mentioned is that the importance of this effect depends on the central metal. In fact, the direct donation is amplified in going from Cr to Mn to Fe. The reason is that chromium has the largest covalent radius, for which the halogen p_z is furthest from the carbonyl 2π and will interact least with it. As the covalent radius decreases in going to manganese and then to iron, the halogen p_z carbonyl 2π interaction will increase. Thus, we would expect, for example, the shift in the cis force constant which arises from replacing Cl by Br to be least for chromium complexes and to be greatest for iron complexes. The force constants in Table III confirm this expectation with the one exception of the iron monohalides. We feel that this anomaly is a result of the fact that the data for the iron monohalides were obtained in a laboratory different from that where the data on the other complexes were obtained. It seems very possible that the effects of different solvents and instrumentation would be sufficient to bring about the change in the force constants of about 0.15 mdyn/Å which would be necessary to bring the iron monohalides into agreement with the trend.

The trends in the trans carbonyl are much more subtle than those in the cis. Because there are inherent errors in the CK approach and because the actual bond distances are unknown for most of the complexes, the trends must be interpreted with a note of caution. In the manganese monohalide complexes the force constants for the trans CO increase from Cl to Br to I. The occupancies in Table III suggest that this trend is due primarily to decreasing occupation of the 5σ orbital; the 2π occupation remains relatively constant. However, in the case of chromium and iron there are also small 2π changes. For chromium the change in 2π reinforces the 5σ change, but for iron the 2π change is in the opposite direction and results in a reversal of the trend in the force constants. Owing to the problems cited above, these results could be subject to some modification by a variation in the trans CO's bond distance and by improved force constants. However, we feel that the general conclusion that the changes in

(31) S. Evans, J. C. Green, M. L. H. Green, A. F. Orchard, and D. W. Turner, *Discuss. Faraday Soc.*, **No. 47** (1969).

the 5σ play an important role in determining the trans CO's force constant will remain true.

The trend in the trans CO of the disubstituted species allows us to compare two opposing trends in the occupancies. The replacement of two bromine atoms by two iodine atoms causes the 5σ occupation to decrease, a change which tends to strengthen the CO bond, just as in the manganese monohalide complexes. However, because the species is disubstituted, each CO trans to one halogen is cis to another. Thus, there will be an increase in the occupancy of the 2π orbital in going from bromine to iodine due to increased direct donation. The results in Table III show that for $Mn(CO)_4X_2^-$ these two effects cancel each other to produce similar force constants, but, in $Fe(CO)_4X_2$ the increase in 2π occupation dominates because of the iron's smaller covalent radius; the overall effect is to produce considerably weaker force constants for the iodide.

Distributions.—In the previous two sections we have discussed both the mono- and disubstituted species with respect to changes in the metal and in the halogen; in this section we will discuss the specific changes which occur when a second halide is substituted for a carbonyl. From the force constants in Table III we can see that both the trans and cis CO bonds are weaker in the dihalide than in the corresponding monohalide. There are two major reasons for this trend. First, the replacement of a neutral carbonyl by a negative halide causes an increase in the energy of the 3d diagonal term relative to the 5σ and 2π terms. This increase in

the 3d energy is due mainly to the crystal field of the additional halide and not to any additional electron donation to the metal. As the 3d level rises in energy, fewer electrons are donated to the 3d from the 5σ orbital and more are donated from the 3d to the 2π orbital. The overall effect is an increase in both the 5σ and 2π occupations, which results in a weaker CO bond and a lower force constant.

The second important effect is that of direct donation from the halogen p_z orbitals. Because these complexes are disubstituted with the halogens cis to each other, the cis carbonyl now has two halogens capable of donating to it, while the trans carbonyl now has one. Thus, we would expect a larger increase in the occupancy of those 2π orbitals which can receive electron density directly from the halogen. We may compare the occupancies of $Mn(CO)_4Br_2^-$ with those of $Mn(CO)_5)Br$ (Table III). The small increase, average 0.015, in the $2\pi_x$ of the trans carbonyl and in the $2\pi_y$ of the cis carbonyl is due to the increased energy of the 3d metal orbital, but the larger increase, average 0.034, in the $2\pi_y$ of the trans carbonyl and in the $2\pi_x$ of the cis carbonyl is due to the combined effect of the direct donation and the higher 3d energy. Thus, direct donation is responsible for more than half of the increase in the 2π occupancy in the latter pair of orbitals.

1,2-Dimethylhydrazinochloro- and -fluorodiphosphines

BY MARY D. HAVLICEK AND JOHN W. GILJE*

$P(NCH_3NCH_3)_3P$ and $ClP(NCH_3NCH_3)_2PCl$ react with PCl_3 to form $Cl_2PNCH_3NCH_3PCl_2$. The latter compound can also be prepared by hydrazinolysis of PCl_3 with $HNCH_3NCH_3H$. The corresponding 1,2-dimethylhydrazinofluorodiphosphines can be synthesized from the chloro derivatives by fluorination with SbF_3. These compounds form complexes with simple BX_3 Lewis acids. Direct reaction with B_2H_6 yields the bis-borane derivatives of each of these compounds except $Cl_2PNCH_3NCH_3PCl_2$, which undergoes decomposition. In the case of $F_2PNCH_3NCH_3PF_2$ a mono-borane adduct could also be isolated. In each of the compounds, BH_3 addition occurs exclusively at the phosphorus. With BF_3 unstable complexes form whose properties are reminiscent of the nitrogen-bonded BF_3 complexes of the aminohalophosphines.

While the aminolysis of PCl_3 was reported over 75 years ago[1] and the aminohalophosphines have received much attention since their first preparation 15 years ago,[2,3] little is known about halophosphine derivatives of other nitrogenous bases. The preparations of some hydrazino- and hydroxylaminochloro- and -fluorophosphines have been reported.[4] The reaction of PCl_3 with 1,1-dimethylhydrazine has been investigated,[5]

and closely related trifluoromethyl-,[6] alkyl-,[7,8] and alkylaminophosphino[9] derivatives of several hydrazines have been synthesized and studied.

In a communication Payne, Noth, and Henniger reported[10] that $P[N(CH_3)_2]_3$ reacts with $HNCH_3NHCH_3 \cdot 2HCl$ to form $P(NCH_3NCH_3)_3P$, whose cage structure

(1) A. Michaelis and G. Schroeter, *Ber.*, **27**, 490 (1895).
(2) A. B. Burg and P. J. Slota, *J. Amer. Chem. Soc.*, **80**, 1107 (1958).
(3) E. Fluck, *Top. Phosphorus Chem.*, **4**, 291 (1967).
(4) A. E. Goya, M. D. Rosario, and J. W. Gilje, *Inorg. Chem.*, **8**, 725 (1969).
(5) D. B. Whigan, J. W. Gilje, and A. E. Goya, *ibid.*, **9**, 1279 (1970).

(6) E. W. Ainscough, L. K. Peterson, and D. E. Sabourin, *Can. J. Chem.*, **48**, 401 (1970), and references therein.
(7) J. M. Kanamueller and H. H. Sisler, *Inorg. Chem.*, **6**, 1765 (1967), and references therein.
(8) S. F. Spangenberg and H. H. Sisler, *ibid.*, **8**, 1004 (1969).
(9) O. J. Sherer and J. Wokulat, *Z. Naturforsch. B*, **22**, 474 (1967).
(10) D. S. Payne, H. Noth, and G. Henniger, *Chem. Commun.*, 327 (1965).