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Electronic Interaction of Ligands with Carbonyl Groups in Transition-Metal Complexes of the Types $LMn(CO)_5$ and $LMo(CO)_5$

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The Mn $2p_{3/2}$, C 1s, and O 1s binding energies of $LMn(CO)_5$ compounds are linearly related to each other and to the inductive constant σ_I and the Pauling electronegativity x_P of the group L. The binding energies show little correlation with the mesomeric constant $\sigma_R°$. Apparently only the σ-donor ability of L is important in determining the degree of back-bonding to the CO groups in $LMn(CO)_5$. The Mo $3d_{5/2}$, C 1s, and O 1s binding energies of $LMo(CO)_5$ compounds ($L = PX_3$ or CO) are linearly related to each other and to the phosphorus lone-pair ionization potential of the free PX_3. The data indicate that both the σ-donor and π-acceptor abilities of PX_3 are important in determining the degree of back-bonding to the CO groups in $X_3PMo(CO)_5$. The π-acceptor ability of PF_3 appears to be slightly greater than that of CO.

Introduction

In recent years much attention has been given to the electronic interaction of various ligands, L, with carbonyl groups in transition-metal complexes of the type $L_xM(CO)_y$.[1-10] No general consensus has been reached regarding the nature of the interaction. Thus, the influence of the group L on the C–O stretching force constants has been variously explained—entirely in terms of the π-acceptor character of L,[3,4] entirely in terms of the σ-donor character of L,[5,6] and in terms of both the π-acceptor and σ-donor characters of L.[1,2,7-9]

We have used X-ray photoelectron spectroscopy to study the problem because this technique yields information not readily obtained by any other method—that is, information about the charges of individual atoms in compounds. It has been previously shown that the carbon 1s and oxygen 1s binding energies of a carbonyl group are a good measure of the $d\pi \rightarrow \pi^*$ back-bonding to the carbonyl group.[11,12] We restricted this study to volatile $LM(CO)_5$ compounds of manganese and molybdenum and determined gas-phase core binding energies of the metal, carbon, and oxygen atoms, as well as of the atoms in the ligands L. Only three of the 20 compounds we studied have been previously studied by other workers as gases by using X-ray photoelectron spectroscopy.[13-16]

Results and Discussion

Manganese Compounds. The core binding energies of the manganese compounds are presented in Table I. Figures 1 and 2, which are plots of E_B(Mn $2p_{3/2}$) vs. E_B(C 1s) and E_B(O 1s), show that the manganese binding energies are linearly related to the carbon and oxygen binding energies. We had not expected this result. When we began this research, we thought that perhaps, because of the delocalized nature of the $d\pi-\pi^*$ bonding, changes in the π-acceptor character of the ligands would cause the charges of the metal, carbon, and oxygen atoms to change by similar amounts but that, because of the well-known attentuation of electronegativity effects in σ-bonded systems, changes in the σ-donor character of the ligands would principally affect the charge of the metal atom. We do not believe that the σ-donor and π-acceptor properties of the ligands in the $LMn(CO)_5$ series are correlated in any simple or obvious way. Thus although both Cl and SiF_3 are poor σ donors, Cl is generally considered to be a π donor and SiF_3 is generally considered to be a good π acceptor. Because of the variation in the character of the ligands, we believed that measurement of effective atomic charges (by determining core binding energies) would allow us to distinguish and to evaluate the π and σ characteristics of the ligands. However, the fact that changes in the metal, carbon, and oxygen binding energies are of similar magnitude and proportional to one another, even though the ligands range widely in σ-donor character, shows that our initial reasoning was wrong and that the binding energy data alone cannot be used to determine both the relative π-acceptor and σ-donor characters of the ligands

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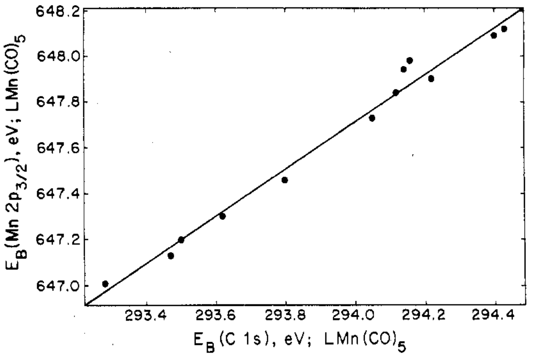

Figure 1. Plot of manganese $2p_{3/2}$ binding energies vs. carbon 1s binding energies for $LMn(CO)_5$ complexes. Data are given in Table I. The straight line corresponds to $E_B(Mn) = 1.001E_B(C) + 353.49$.

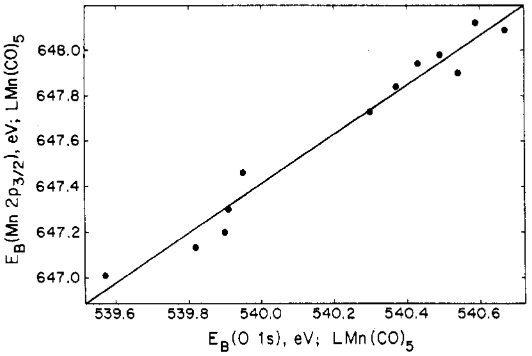

Figure 2. Plot of manganese $2p_{3/2}$ binding energies vs. oxygen 1s binding energies for $LMn(CO)_5$ complexes. Data are given in Table I. The straight line corresponds to $E_B(Mn) = 1.071E_B(O) + 69.21$.

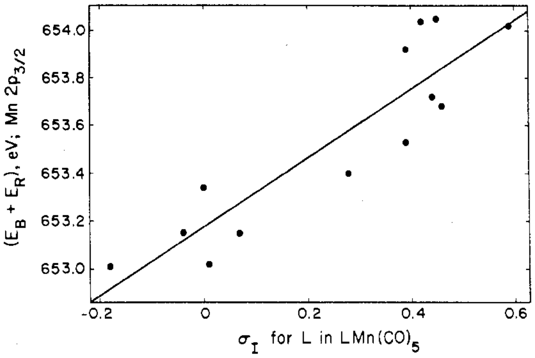

Figure 3. Plot of $(E_B + E_R)$ for Mn $2p_{3/2}$ ionization of $LMn(CO)_5$ complexes vs. the inductive constant σ_I of the L groups. Data are given in Table II. The straight line corresponds to $E_B + E_R = 1.4422\sigma_I + 653.18$.

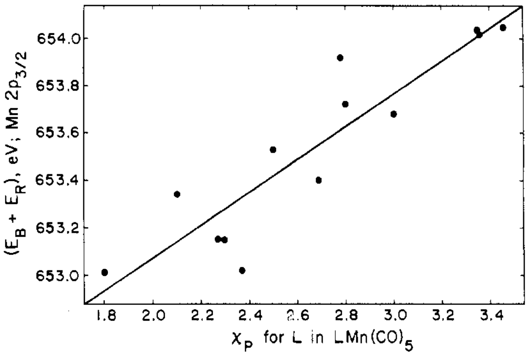

Figure 4. Plot of $(E_B + E_R)$ for Mn $2p_{3/2}$ ionization of $LMn(CO)_5$ complexes vs. the Pauling electronegativity x_P of the L groups. Data are given in Table II. The straight line corresponds to $E_B + E_R = 0.6928x_P + 651.69$.

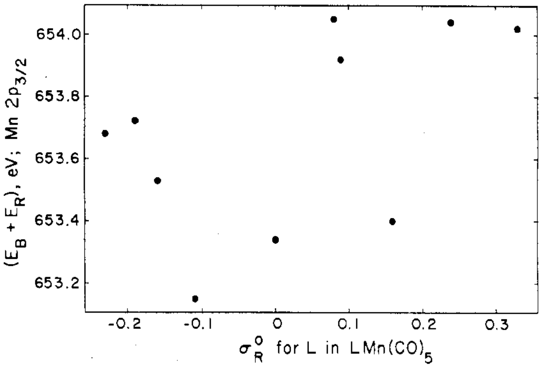

Figure 5. Plot of $(E_B + E_R)$ for Mn $2p_{3/2}$ ionization of $LMn(CO)_5$ complexes vs. the mesomeric constant $\sigma_R°$ of the L groups, showing the poor correlation between these quantities. Data are given in Table II.

without making further assumptions.

The mutual proportionality of the manganese, carbon, and oxygen binding energies can be rationalized if we assume that, in the $LMn(CO)_5$ compounds, only one property of the ligand (that is, either its σ-donor character alone or its π-acceptor character alone) is important in determining the degree of back-bonding to the carbonyl groups. To determine which of these is the important factor, we have studied the correlation of the data with different sets of ligand parameters which are believed to be measures of either σ-donor ability or π-acceptor ability. The parameters which we have used as measures of σ-donor character are the inductive constant, σ_I, derived from equilibrium and kinetic data of organic systems,[17] and the electronegativity on the Pauling scale, x_P, derived from thermochemical data[18] and valence orbital energies.[19] The parameter which we have used as a measure of π-acceptor character is the mesomeric constant, $\sigma_R°$, derived from equilibrium and kinetic data of aromatic compounds.[17]

A core binding energy can be equated to the sum of several energy terms, as shown by eq 1.[20] Here k is a constant

$$E_B = kQ + V - E_R + l \tag{1}$$

characteristic of the core-ionizing atom, Q is the charge of the atom, V is the electrostatic potential due to the charges of all the other atoms in the molecule, E_R is the electronic relaxation energy associated with the core ionization, and l is a constant characteristic of the core level. On going from one compound to another, the change in the quantity $(kQ + V)$ is closely proportional to the change in charge of the atom under consideration (i.e., the metal atom or an atom of a carbonyl group).[21] Because l is constant for all the compounds, we can write eq 2. Hence in Figures 3–5 we have plotted, for the

$$\Delta Q \propto \Delta(kQ + V) = \Delta(E_B + E_R) \tag{2}$$

Mn $2p_{3/2}$ ionizations, the quantity $(E_B + E_R)$ vs. σ_I, x_p, and $\sigma_R°$, respectively. The relaxation energies were estimated by using the transition-state concept[22-24] combined with the

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(20) Gelius, U. *Phys. Scr.* **1974**, *9*, 133.

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Table I. Core Binding Energies of the $Mn(CO)_5$ Groups in $LMn(CO)_5$ Complexes (eV)

compd	Mn $2p_{3/2}$		C 1s		O 1s	
	E_B	FWHM[a]	E_B	FWHM	E_B	FWHM
$(CH_3)_3SnMn(CO)_5$[b]	647.0 (1)[c]	1.3 (1)[c]				
$Mn_2(CO)_{10}$[b]	647.01 (3)	1.02 (9)	293.28 (3)	1.12 (6)	539.57 (7)	1.44 (4)
$CH_2{=}CHCH_2Mn(CO)_5$	647.13 (3)	1.32 (7)	293.47 (4)	1.58 (6)	539.82 (3)	1.65 (5)
$CH_3COMn(CO)_5$[d]	647.23 (4)	1.3 (1)	293.44 (8)	1.5 (1)	539.86 (5)	1.5 (1)
$CH_3Mn(CO)_5$[d]	647.30 (5)	1.1 (1)	293.62 (7)	1.22 (7)	539.91 (7)	1.51 (8)
$HMn(CO)_5$[b]	647.46 (4)	1.1 (1)	293.80 (4)	1.2 (1)	539.95 (3)	1.46 (8)
$IMn(CO)_5$[e]	647.73 (3)	1.0 (1)	294.05 (3)	1.29 (7)	540.30 (3)	1.61 (8)
$Cl_3SiMn(CO)_5$[e]	647.84 (4)	1.0 (1)	294.12 (3)	1.22 (8)	540.37 (3)	1.42 (7)
$CF_3COMn(CO)_5$[d]	647.90 (5)	1.0 (1)	294.22 (5)	1.15 (9)	540.54 (3)	1.51 (6)
$BrMn(CO)_5$[e]	647.94 (3)	0.91 (9)	294.14 (4)	1.33 (9)	540.43 (3)	1.61 (7)
$ClMn(CO)_5$[e]	647.98 (3)	1.1 (1)	294.16 (4)	1.28 (9)	540.49 (3)	1.55 (8)
$F_3CMn(CO)_5$[d]	648.09 (2)	1.05 (7)	294.40 (2)	1.24 (4)	540.67 (2)	1.52 (4)
$F_3SiMn(CO)_5$[d]	648.12 (3)	1.01 (8)	294.43 (3)	1.22 (5)	540.59 (3)	1.45 (6)

[a] Full width at half-maximum. [b] Data for these compounds were determined previously and appear in: Avanzino, S. C.; Jolly, W. L. *J. Electron Spectrosc. Relat. Phenom.* 1976, *8*, 15; *J. Am. Chem. Soc.* 1976, *98*, 6505; Chen, H. W.; Jolly, W. L.; Kopf, J.; Lee, T. H. *Ibid.* 1979, *101*, 2607. When necessary, the values were corrected to an Ar $2p_{3/2}$ reference of 248.62 eV. [c] The uncertainty in the last digit (estimated as twice the standard deviation determined by the least-squares fit) is indicated parenthetically. [d] Binding energies for these compounds are calibrated against the Ne 1s, Ne 2s, and N_2 1s lines. [e] Binding energies for these compounds are calibrated against the Ne 1s, N_2 1s, and Ar $2p_{3/2}$ lines.

Table II. Calculated Relaxation Energies for Manganese Core Ionization in $LMn(CO)_5$ Complexes and Ligand Parameters

L	E_R,[a] eV	(E_B + E_R), eV	σ_I[b]	x_P[c]	$\sigma_R{}^\circ$[b]
$(CH_3)_3Sn$	6.15	653.15	(0.07)[d]	2.30	
$(CO)_5Mn$	6.00	653.01	(−0.18)[d]	1.8	
$CH_2{=}CHCH_2$	5.89	653.02	0.01	2.37	
CH_3CO	6.20	653.40	0.28	2.69	0.16
CH_3	5.85	653.15	−0.04	2.27	−0.11
H	5.88	653.34	0.0	2.1	0.0
I	5.80	653.53	0.39	2.5	−0.16
Cl_3Si	6.08	653.92	0.39	2.78	0.09
CF_3CO	6.12	654.02	0.59	(3.36)[d]	0.33
Br	5.78	653.72	0.44	2.8	−0.19
Cl	5.70	653.68	0.46	3.0	−0.23
F_3C	5.96	654.05	0.45	3.46	0.08
F_3Si	5.92	654.04	0.42	3.35	0.24

[a] See Experimental Section for method of calculation. [b] Reference 17. [c] References 18 and 19. [d] Estimated from a plot of σ_I vs. x_P.

equivalent cores approximation[25] and CNDO/2 wave functions. The data plotted in Figures 3, 4, and 5 are given in Table II, and the methods used for their estimation are described in the Experimental Section.

It is significant that the quantity (E_B + E_R) for manganese is well correlated with σ_I and x_P (correlation coefficients 0.904 and 0.911, respectively) and poorly correlated with $\sigma_R{}^\circ$ (correlation coefficient 0.501).[26] We conclude that, on going from one $LMn(CO)_5$ compound to another (at least in the set which we have studied), changes in the degree of back-bonding to the CO groups are determined principally by changes in the σ-donor character of the ligands L. Changes in the π-acceptor or π-donor character of these ligands appear to have little effect on the CO groups. Perhaps the relative unimportance of L–Mn π bonding in the $LMn(CO)_5$ compounds which we studied is simply due to the fact that the π-acceptor and π-donor abilities of the 13 ligands involved are all very weak compared to the relatively strong π-acceptor ability of a CO group. The theoretical rationale for an increase in back-bonding to the CO groups being associated with an increase in the σ-donor character of L has been described in the literature.[7,8] Briefly, it is based on the idea that an increase in electron density on the metal atom raises the energy of the metal dπ electrons and causes them to drift toward the CO π^* orbitals.

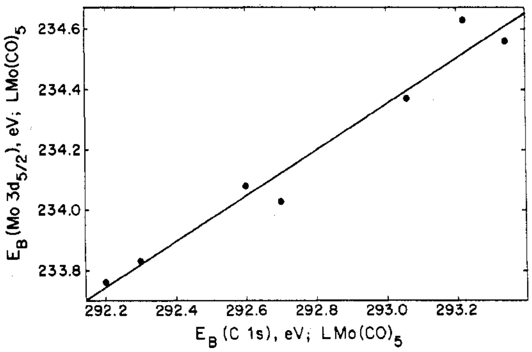

Figure 6. Plot of molybdenum $3d_{5/2}$ binding energies vs. carbon 1s binding energies for $LMo(CO)_5$ complexes. Data are given in Table III. The straight line corresponds to $E_B(Mo) = 0.7604E_B(C) + 11.55$.

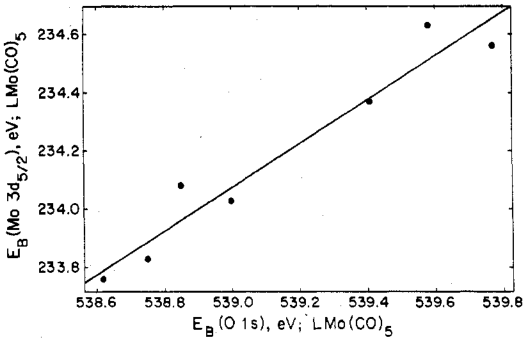

Figure 7. Plot of molybdenum $3d_{5/2}$ binding energies vs. oxygen 1s binding energies for $LMo(CO)_5$ complexes. Data are given in Table III. The straight line corresponds to $E_B(Mo) = 0.7515E_B(O) - 170.96$.

Other workers have studied the relationships between valence-shell ionization potentials of $LMn(CO)_5$ complexes (determined by UPS) and various physical properties. For example, it has been shown that the ionization potentials of the b_2 (Mn d_{xy}) levels of such compounds are correlated with the corresponding C–O stretching frequencies.[9] The vertical ionization potentials of the e(Mn $d_{xz,yz}$) levels of $LMn(CO)_5$ for L = I,[10] Br,[10] Cl,[10] H,[9] and CH_3[9] are linearly correlated with our E_B(Mn $2p_{3/2}$) values (correlation coefficient 0.985).

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(24) Davis, D. W.; Shirley, D. A. *Chem. Phys. Lett.* **1972**, *15*, 185.

(25) The equivalent cores approximation is reviewed by: Jolly, W. L. In "Electron Spectroscopy: Theory, Techniques and Applications"; Brundle, C. R., Baker, A. D., Eds.; Academic Press: London, 1977; Vol. I, p 119.

(26) Some degree of correlation between (E_B + E_R) and $\sigma_R{}^\circ$ is expected because of the correlation of (E_B + E_R) with σ_I and the fact that the values of σ_I and $\sigma_R{}^\circ$ are weakly correlated (correlation coefficient 0.27).

Table III. Core Binding Energies of $Mo(CO)_5PX_3$ Complexes and $Mo(CO)_6$ (eV)

	Mo $3d_{5/2}$		C 1s		O 1s		P $2p_{3/2}$	
compd	E_B	FWHM[a]	E_B	FWHM	E_B	FWHM	E_B	FWHM
$Mo(CO)_5P(NMe_2)_3$	233.76 (5)[b]	1.56 (10)[b]	292.2 (1)	1.62 (50)	538.62 (8)	1.98 (22)	137.7 (4)	1.7 (6)
$Mo(CO)_5PMe_3$	233.83 (5)	1.54 (11)	292.30 (6)	1.83 (12)	538.75 (4)	1.80 (8)	137.05 (9)	1.39 (24)
$Mo(CO)_5P(OMe)_3$	234.03 (3)	1.13 (6)	292.7 (2)	1.27 (6)	539.0 (2)	1.48 (9)	138.81 (4)	1.06 (8)
$Mo(CO)_5P(OEt)_3$	234.08 (4)	1.05 (8)	292.6 (2)	1.09 (14)	538.85 (20)	1.60 (8)	138.93 (5)	1.27 (12)
$Mo(CO)_5PCl_3$	234.37 (4)	1.11 (10)	293.06 (4)	1.12 (8)	539.41 (4)	1.47 (9)	139.41 (8)	1.18 (20)
$Mo(CO)_5PF_3$	234.56 (5)	1.18 (7)	293.34 (5)	1.23 (11)	539.77 (4)	1.35 (9)	140.67 (6)	1.25 (17)
$Mo(CO)_6$	234.63 (3)	1.13 (6)	293.22 (4)	1.18 (10)	539.58 (3)	1.42 (6)		

[a] Full width at half-maximum. [b] The uncertainty in the last digit (estimated as twice the standard deviation determined by the least-squares fit) is indicated parenthetically.

This correlation suggests that core binding energy data can aid in the assignment of UPS peaks.[27]

Molybdenum Compounds. The core binding energies of the molybdenum compounds are presented in Table III. Just as in the case of the $LMn(CO)_5$ compounds, the metal binding energies are linearly related to the carbon and oxygen binding energies. These correlations are shown in Figures 6 and 7, which are plots of E_B(Mo $3d_{5/2}$) vs. E_B(C 1s) and E_B(O 1s).

In the case of the $LMo(CO)_5$ compounds, the mutual proportionality of the molybdenum, carbon, and oxygen binding energies probably should have been anticipated. Except for $Mo(CO)_6$, the ligand L in each compound is a substituted phosphine, PX_3. An increase in the electronegativity of X causes the phosphine to become a poorer σ donor and a better π acceptor. That is, the σ-donor and π-acceptor properties of the ligands are correlated, and without further information one cannot tell whether a shift in binding energy is mainly due to a change in one property or the other.

The data in Table III show that the carbon and oxygen binding energies of $Mo(CO)_5PF_3$ are greater than those of $Mo(CO)_6$, although the molybdenum binding energy of $Mo(CO)_5PF_3$ is slightly smaller than, or of similar magnitude to, that of $Mo(CO)_6$. Surely the σ-donor ability of PF_3 is somewhat greater than, or at least approximately the same as, that of CO. (The proton affinities of PF_3 and CO are 160 and 143 kcal/mol, respectively.[28,29]) If we assume that both the σ and π properties of L are important in determining the CO back-bonding in this series, then the fact that replacement of one CO group in $Mo(CO)_6$ by PF_3 causes a slight decrease in back-bonding to the remaining CO groups indicates that PF_3 is a somewhat better π acceptor than CO. The same conclusion was reached by Corderman and Beauchamp on the basis of the observed displacement of CO from $C_5H_5CoCO^-$ by PF_3.[30] It is interesting that the molybdenum binding energy of $Mo(CO)_5PF_3$ is slightly lower than that of $Mo(CO)_6$, consistent with a greater σ-donor character in PF_3 than in CO. However, the uncertainity of the data is such that this observed difference is almost insignificant.

The phosphorus binding energies of the coordinated PX_3 ligands are closely correlated with the phosphorus binding energies of the corresponding free PX_3 ligands,[31a] as shown in Figure 8. It is interesting that, in the case of PX_3 ligands which are relatively strong bases, the phosphorus binding energies of the coordinated ligands are greater than those of the free ligands, whereas, in the case of PX_3 ligands which are weak bases, the reverse is true. The tendency toward lower-than-expected phosphorus binding energies on going to the complexes with the weaker bases is probably due to a gradual increase in metal $d\pi \rightarrow$ligand π^* back-bonding. Such back-bonding would be expected to increase on going from the strong bases to the weak bases. It does not appear likely that the effect is due to an increase in relaxation energy on going from the strong bases to the weak bases; in fact it has been calculated that the relaxation energy for the P $2p_{3/2}$ ionization of PF_3 is *less* than that of PMe_3.[31a]

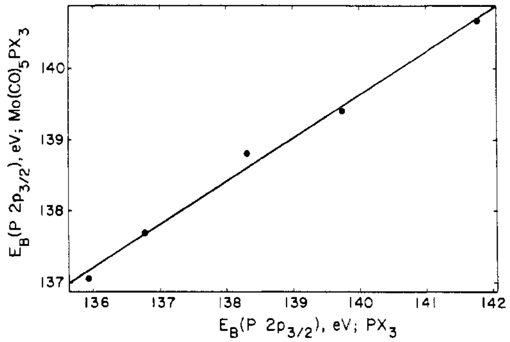

Figure 8. Plot of phosphorus $2p_{3/2}$ binding energies of $Mo(CO)_5PX_3$ complexes vs. phosphorus $2p_{3/2}$ binding energies of free PX_3 ligands. Data for free PX_3 ligands are from ref 31a. The straight line corresponds to E_B(complex) = 0.6063E_B(free) + 54.74.

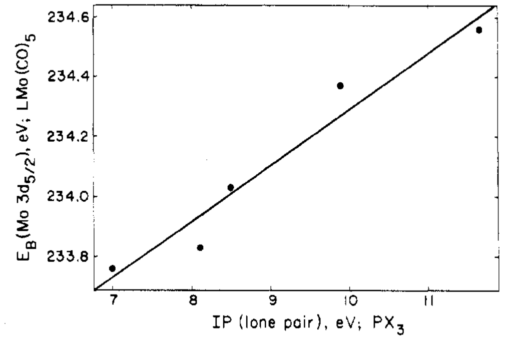

Figure 9. Plot of molybdenum $3d_{5/2}$ binding energies of $Mo(CO)_5PX_3$ complexes vs. phosphorus lone-pair ionization potentials for free PX_3 ligands. The adiabatic lone-pair potential of $P(NMe_2)_3$ is taken from: Lappert, M. F.; Pedley, J. B.; Wilkins, B. T.; Stelzer, O.; Unger, E. *J. Chem. Soc., Dalton Trans.* **1975**, 1207; other values are from ref 31c. The straight line corresponds to E_B = 0.1773IP + 232.48.

The molybdenum binding energies of the $Mo(CO)_5PX_3$ complexes are linearly related to the phosphorus lone-pair ionization potentials of the free PX_3 molecules, as shown in Figure 9. It has been shown that lone-pair ionization potentials are linearly related to proton affinities,[31] and therefore the molybdenum (and carbon and oxygen) binding energies

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(27) There is considerable uncertainity in the assignment of $LMn(CO)_5$ UPS peaks. [See: DeKock, R. L. In "Electron Spectroscopy"; Brundle, C. R., Baker, A. D., Eds.; Academic Press: London, 1977; Vol. 1, p 293.] Our correlation of E_B(Mn $2p_{3/2}$ with e(Mn $d_{xz,yz}$) suggests that the e(Mn $d_{xz,yz}$) ionization potential of $CF_3Mn(CO)_5$ may be 10.53 eV rather than, as usually assumed, around 9.3 eV.

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are linearly related to the PX_3 proton affinities. This correlation cannot be taken as evidence that CO back-bonding is mainly due to the σ-donor character of PX_3 because, as we have already pointed out, the σ-donor and π-acceptor characters of PX_3 molecules are inversely correlated.

As a whole, the data for the $Mo(CO)_5L$ compounds indicate that back-bonding to the CO groups depends on both the σ-donor and π-acceptor abilities of the ligands L. It appears that, on going from $P(NMe_2)_3$ to PF_3, there is a marked increase in π-acceptor ability. In the $LMn(CO)_5$ series, the lack of dependence of CO back-bonding on the π-acceptor abilities of the ligands is probably due to the fact that, on going from the weakest π acceptor (perhaps Cl) to the strongest (perhaps CF_3CO), the *change* in π-acceptor ability is relatively small.

Experimental Section

The core binding energies were determined by using the X-ray photoelectron spectrometer and procedures previously described.[32] The methods of synthesis and characterization of the compounds have also been described.[12] Various binding energies of ligand atoms, not given in Tables I and III, were measured. These and the corresponding line widths (with the uncertainty in the last digit indicated parenthetically) are listed here. $CH_2{=}CHCH_2Mn(CO)_5$: C 1s 289.85 (5), 1.84 (12). $CH_3COMn(CO)_5$: C 1s 291.9 (3), 1.6 (3) (>C=O); 290.4 (1), 1.2 (3) ($-CH_3$); O 1s 537.4 (1), 1.2 (3). $CH_3Mn(CO)_5$: C 1s 289.5 (1), 1.5 (3). $IMn(CO)_5$: I $3d_{5/2}$ 625.27 (3), 1.27 (7). $Cl_3SiMn(CO)_5$: Cl $2p_{3/2}$ 205.64 (4), 1.31 (7); Cl $2p_{1/2}$ 207.28 (6), 1.31 (7); Si 2p 108.38 (4), 1.36 (9). $CF_3COMn(CO)_5$: C 1s 293.1 (1), 1.1 (2) (>C=O); 297.9 (1), 1.4 (2) ($-CF_3$); O 1s 538.21 (6), 1.3 (2); F 1s 694.13 (3), 1.74 (8). $BrMn(CO)_5$: Br $3d_{5/2}$ 74.30 (3), 1.27 (8); Br $3d_{3/2}$ 75.39 (3), 1.27 (8). $ClMn(CO)_5$: Cl $2p_{3/2}$ 203.84 (3), 1.16 (7); Cl $2p_{1/2}$ 205.43 (7), 1.16 (7). $F_3CMn(CO)_5$: C 1s 296.48 (4), 1.14 (9); F 1s 692.98 (4), 1.78 (9). $F_3SiMn(CO)_5$: F 1s 692.86 (3), 1.46 (6); Si 2p 109.0 (1), 1.3 (2) (unresolved spin–orbit doublet fit to one peak). $Mo(CO)_5P(NMe_2)_3$: C 1s 291.2 (16), 1.5 (4). $Mo(CO)_5PMe_3$: C 1s 290.57 (11), 1.12 (23). $Mo(CO)_5P(OEt)_3$: C 1s 291.08 (5), 6 (1) (CH_3). $Mo(CO)_5PCl_3$: Cl $2p_{3/2}$ 206.21 (4), 1.30 (9); Cl $2p_{1/2}$ 207.87 (8), 1.23 (13). $Mo(CO)_5PF_3$: F 1s 693.80 (4), 1.69 (4).

The binding energy of an atom A can be expressed in the following ways:

$$\begin{aligned} E_B &= kQ_A + V - E_R + l \\ &= c\Phi_{val}(A) - E_R + l \\ &= c[\Phi_{val}(A) + \Phi_{val}(B^+)]/2 + l \qquad (3) \end{aligned}$$

We have already defined the terms in the first line. The function $\Phi_{val}(A)$ refers to the potential at the nucleus of atom A due to the valence electrons of the molecule. We follow the method of Schwartz,[33] in which the populations of the various atomic orbitals on A and the atomic charges of all the other atoms in the molecule are used to calculate the potential. The function $\Phi_{val}(B^+)$ is the potential calculated for the isoelectronic cation obtained by substituting the core of atom A with the core of atom B, the next element in the periodic table. The term $[\Phi_{val}(A) + \Phi_{val}(B^+)]/2$ is the potential for the hypothetical transition state, and c is a parameter which compensates for the approximate CNDO/2 method used to estimate Φ_{val}. In a previous study[34] we have found that values of c in the range 0.38–0.78 give good correlations. In this work we have chosen the intermediate value $c = 0.5$, corresponding to the following equation for E_R: $E_R = 0.25[\Phi_{val}(A) - \Phi_{val}(B^+)]$. Changes in the assumed value of c as great as ±30% cause no significant change in the results and conclusions. The CNDO/2 calculations were performed by using the program as modified by Sherwood.[35] The bond distances and angles of the $Mn(CO)_5$ moiety were assumed to be constant in the $LMn(CO)_5$ series. The Mn–C and C–O bond distances used were 1.83 and 1.147 Å, respectively; these are the average bond distances in $HMn(CO)_5$[36] and $Mn_2(CO)_{10}$.[37] The C–Mn–C angles were assumed to be 90°. The metal–ligand and intraligand bond distances and the ligand bond angles were taken from the literature for the molecules $Mn_2(CO)_{10}$,[37] $CH_3COMn(CO)_5$,[38] $CH_3Mn(CO)_5$,[39] $HMn(CO)_5$,[36] $IMn(CO)_5$,[18] $Cl_3SiMn(CO)_5$,[40,41] $CF_3COMn(CO)_5$,[38,42] $BrMn(CO)_5$,[43] $ClMn(CO)_5$,[43] $CF_3Mn(CO)_5$,[39] $F_3SiMn(CO)_5$,[41] $C_3H_5Mn(CO)_5$,[39,44] and $Me_3SnMn(CO)_5$.[45]

The Pauling electronegativity for the $Mn(CO)_5$ group was calculated from thermochemical data given by Connor.[46]

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Registry No. $CH_2{=}CHCH_2Mn(CO)_5$, 14057-83-1; $CH_3Mn(CO)_5$, 13601-24-6; $IMn(CO)_5$, 14879-42-6; $Cl_3SiMn(CO)_5$, 38194-30-8; $CF_3COMn(CO)_5$, 14099-62-8; $BrMn(CO)_5$, 14516-54-2; $ClMn(CO)_5$, 14100-30-2; $F_3CMn(CO)_5$, 13601-14-4; $F_3SiMn(CO)_5$, 39945-25-0; $(CH_3)_3SnMn(CO)_5$, 14126-94-4; $Mn_2(CO)_{10}$, 10170-69-1; $Mo(CO)_5PF_3$, 15322-05-1; $Mo(CO)_6$, 13939-06-5; $CH_3COMn(CO)_5$, 13963-91-2; $HMn(CO)_5$, 16972-33-1; $Mo(CO)_5P(NMe_2)_3$, 14971-43-8; $Mo(CO)_5PMe_3$, 16917-96-7; $Mo(CO)_5P(OMe)_3$, 15631-20-6; $Mo(CO)_5P(OEt)_3$, 15603-75-5; $Mo(CO)_5PCl_3$, 19212-18-1.

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