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Ligand Additivity in the Valence Photoelectron Spectroscopy of Phosphine-Substituted Molybdenum Carbonyls

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The He I valence photoelectron spectra in the 6–9-eV ionization region are reported for the following complexes: $Mo(CO)_5PMe_3$, *cis*-$Mo(CO)_4(PMe_3)_2$, *trans*-$Mo(CO)_4(PMe_3)_2$, *fac*-$Mo(CO)_3(PMe_3)_3$, $Mo(CO)_5PEt_3$, *trans*-$Mo(CO)_4(PEt_3)_2$, $Mo(CO)_5P$-*n*-Bu_3, and *trans*-$Mo(CO)_4(P$-*n*-$Bu_3)_2$. The observation of vibrational structure due to excitation of a CO stretching mode in several of the spectra aids band assignment. These data are used to test the validity of the model of ligand additivity for determining the energetics of the d_π electrons in octahedral d^6 complexes. It is shown that the model successfully correlates the positions, intensities, and number of the ionization bands for the above compounds. A comparison of the results for the complexes of different phosphine ligands indicates that PMe_3, PEt_3, and P-*n*-Bu_3 are comparable π-acceptors, but that the σ-donor strength increases as $PMe_3 < PEt_3 <$ P-*n*-Bu_3.

Introduction

Photoelectron spectroscopy (PES) in concert with molecular orbital theory has proven invaluable in the elucidation of valence electronic structure.[2,3] For transition-metal systems, the ionization potentials of the primarily metal-localized d electrons are of particular interest. These generally occur at low ionization energy and are thus isolated from the often complex ionization bands of the ligands. The d-electron ionization potentials provide a direct energetic probe of the metal center, and several recent studies have used the shifts in these ionizations to infer the influence of various ligands on the metal orbital energetics.[4-11]

We recently proposed a simple model for evaluating the energetics of the three primarily d_π orbitals of low-spin octahedral d^6 transition-metal complexes of mixed-ligand types.[12] This model, which we call ligand additivity, postulates that these orbital energies are comprised of linear contributions from each ligand. Thus, for a complex of formulation $ML_nL'_{6-n}$ the orbital energy of each d_π orbital is given by

$$\epsilon_i = a_M{}^0 + nb_M{}^L + (6-n)b_M{}^{L'} + x_ic_M{}^L + (4-x_i)c_M{}^{L'} \quad (1)$$

where $a_M{}^0$ is a constant characteristic of the metal atom in its particular oxidation state, $b_M{}^L$ and $b_M{}^{L'}$ are constants describing the gross energetic effect of L and L′ upon the metal atom, $c_M{}^L$ and $c_M{}^{L'}$ are constants desribing the energetic effect upon the d_π orbital of interacting with L and L′, respectively, and x_i is the number of ligands L with which the d_π orbital can interact. Equation 1 can be simplified to

$$\epsilon_i = a + bn + cx_i \quad (2)$$

where $a = a_M{}^0 + 6b_M{}^{L'} + 4c_M{}^{L'}$, $b = b_M{}^L - b_M{}^{L'}$, and $c = c_M{}^L - c_M{}^{L'}$. The parameters b and c, which both measure differences in the effects of L and L′ upon M, can be used to compare the relative σ-donor and π-acceptor capabilities of L and L′.[12]

Equation 2 was found to apply very well to electrochemical data for mixed carbonyl–isocyanide complexes of Mn(I) and Cr(0) wherein the $E_{1/2}$ for oxidation was treated as a "solution ionization potential" of the highest occupied orbital.[12] A similar concept was found to be true in the core X-ray photoelectron spectroscopic (XPS) studies of Feltham and Brant.[13] In this case additive ligand group shifts were determined that could predict core ionization shifts of solid complexes within the uncertainity of the experiment (~0.2 eV). Clearly, if one is investigating neutral complexes, gas-phase PES provides a more direct probe of valence-orbital energetics than does electrochemistry and a more precise and informative probe than does core XPS of solids. PES allows the ionization potentials of all three d_π orbitals to be determined, rather than just the HOMO, and these results can be directly related to eq 2 by Koopmans' theorem.[14] With regard to the validity of ligand additivity, the probing of all three d_π orbital energies by PES provides a much more stringent test of the model as it not only should correlate the orbital energies of $ML_nL'_{6-n}$ systems for different values of n, or for different isomers with the same n, but also should hold consistently for all three d_π orbitals within a given compound.

In this paper we report the valence photoelectron spectra of a series of neutral d^6 complexes $Mo(CO)_n(PR_3)_{6-n}$ (n = 3, 4, 5, or 6) where R is an alkyl group. This is the first systematic investigation of the cumulative influence of repeated ligand substitution on the valence ionization potentials of metal complexes. It will be shown that the data strongly support the model of ligand additivity and that the model can be used to directly extract relative ligand bonding capabilities from the PES data.

Experimental Section

Photoelectron Spectra. All photoelectron spectra were collected on an extensively modified spectrometer built around a 36-cm hemispherical analyzer[15] by using He I mode techniques previously detailed.[6] The data were collected for the indicated compounds at the following ionization chamber temperatures: $Mo(CO)_6$, 25 °C; $Mo(CO)_5PMe_3$, 25 °C; *cis*-$Mo(CO)_4(PMe_3)_2$, 50 °C; *trans*-$Mo(CO)_4(PMe_3)_2$, 30 °C; *fac*-$Mo(CO)_3(PMe_3)_3$, 90 °C; $Mo(CO)_5(PEt_3)$, 25 °C; *trans*-$Mo(CO)_4(PEt_3)_2$, 55 °C; $Mo(CO)_5(P$-*n*-$Bu_3)$; 60 °C; *trans*-$Mo(CO)_4(P$-*n*-$Bu_3)_2$, 95 °C.

The photoelectron spectra were deconvoluted into asymmetric Gaussian bands by using the program GFIT.[16] In several cases,

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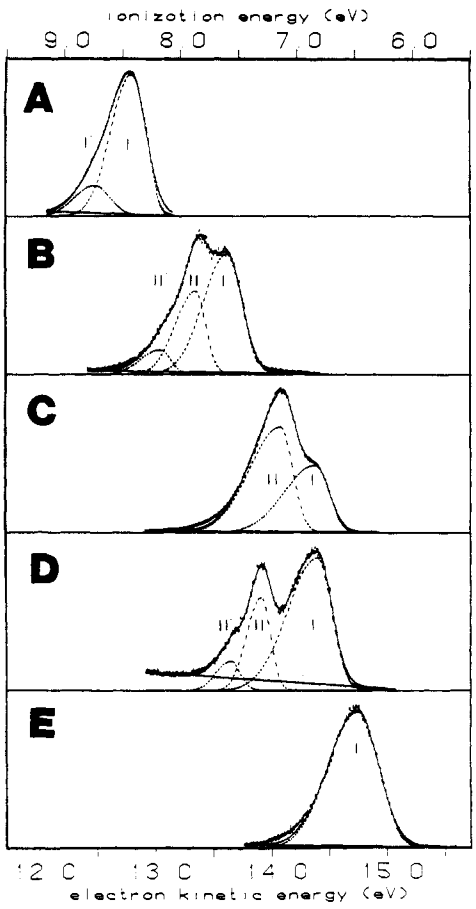

Figure 1. Low-ionization-energy region of the photoelectron spectra of $Mo(CO)_n(PMe_3)_{6-n}$ compounds: (a) $Mo(CO)_6$; (b) $Mo(CO)_5PMe_3$; (c) *cis*-$Mo(CO)_4(PMe_3)_2$; (d) *trans*-$Mo(CO)_4(PMe_3)_2$; (e) *fac*-$Mo(CO)_3(PMe_3)_3$.

vibrational fine structure due to the CO stretch was observed on the high-binding-energy side of the metal region. In these spectra a Gaussian band was included to fit the high-binding-energy shoulder, and this band was constrained to have the same left and right half-widths as the main ionization band component.

Sample Preparation. $Mo(CO)_5PMe_3$, $Mo(CO)_5PEt_3$, and $Mo(CO)_5P$-*n*-Bu_3 were synthesized by using published procedures.[17,18] *cis*-$Mo(CO)_4(PMe_3)_2$ was prepared in a procedure analogous to that used to prepare *cis*-$Mo(CO)_4(PR_3)_2$ (R = Et, *n*-Bu).[19] *trans*-$Mo(CO)_4(PMe_3)_2$ was prepared by thermal equilibration of *cis*-$Mo(CO)_4(PMe_3)_2$ to a cis/trans mixture.[20] A small sample (50 mg) of *cis*-$Mo(CO)_4(PMe_3)_2$ was dissolved in heptane in a 50-mL Schlenk vessel fitted with a water-cooled condenser. The vessel was submerged in an oil bath, and the temperature was gradually raised to 65 °C over a period of 72 h. The cis/trans mixture could be separated in situ on the spectrometer due to the difference in sublimation temperatures of the two isomers under high vacuum. At 30–40 °C a clean spectrum of the trans isomer was obtained. When the trans isomer was exhausted, the temperature was raised to 50–60 °C, giving a spectrum of the pure cis isomer.

fac-$Mo(CO)_3(PMe_3)_3$ was synthesized as follows: *fac*-$Mo(CO)_3(py)_3$ (py = pyridine) was generated by using the method of Hieber[21] by refluxing $Mo(CO)_6$ in pyridine. This solution was stirred with excess PMe_3 at room temperature for 2 h under N_2. The excess PMe_3 and pyridine solvent were removed under vacuum, and the crude product was recrystallized from methanol.

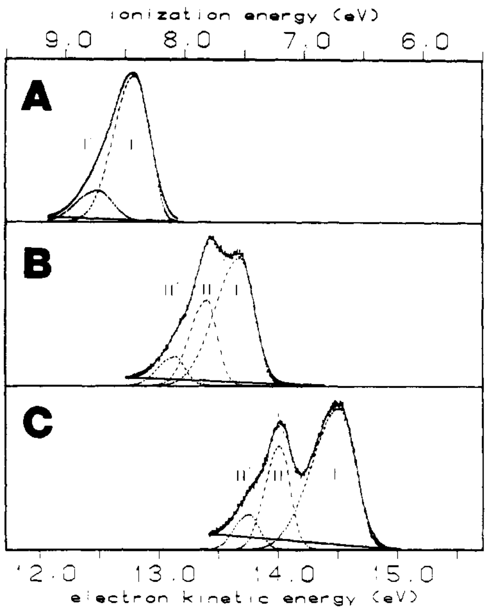

Figure 2. Low-ionization-energy region of the photoelectron spectra of $Mo(CO)_n(PEt_3)_{6-n}$ compounds: (a) $Mo(CO)_6$; (b) $Mo(CO)_5PEt_3$; (c) *trans*-$Mo(CO)_4(PEt_3)_2$.

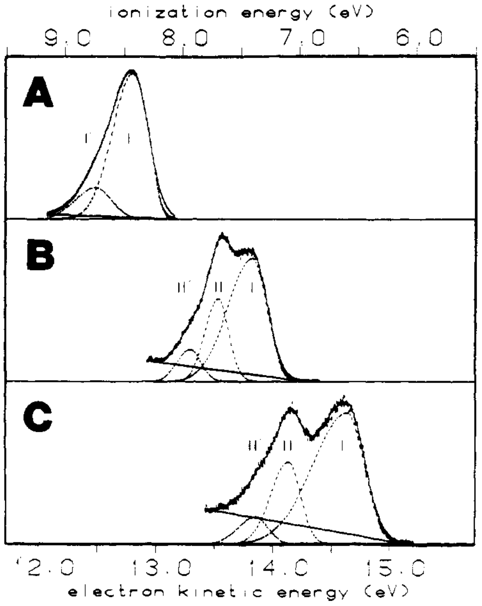

Figure 3. Low-ionization-energy region of the photoelectron spectra of $Mo(CO)_n(P$-*n*-$Bu_3)_{6-n}$ compounds: (a) $Mo(CO)_6$; (b) $Mo(CO)_5P$-*n*-Bu_3; (c) *trans*-$Mo(CO)_4(P$-*n*-$Bu_3)_2$.

trans-$Mo(CO)_4(PR_3)_2$ (R = Et, *n*-Bu) were generated from *cis*-$Mo(CO)_4(NHC_5H_{10})_2$ by using the published procedure.[19]

Results

None of the samples exhibited appreciable decomposition, and all spectra reported here are of stereochemically pure species in the gas phase; the large shifts in the position and intensity of the valence ionization bands make contaminant molecules or isomerizations easy to detect. Our ability to maintain stereochemical purity was demonstrated with a mixture sample of *cis*- and *trans*-$Mo(CO)_4(PMe_3)_2$. The trans component sublimed cleanly at a lower ionization chamber temperature than did the cis component, and the spectrum of each could be collected without contamination from the other. We also attempted to obtain spectra for *cis*-$Mo(CO)_4(PEt_3)_2$ and *cis*-$Mo(CO)_4(P$-*n*-$Bu_3)_2$. However, at the necessary ionization chamber temperature the cis $\rightleftarrows$ trans equilibrium constant is quite large for both of these[19] and each displayed

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Table I. Band Positions, Half-Widths, and Intensities for the d_π Ionizations of $Mo(CO)_n(PR_3)_{6-n}$ Complexes

complex	band[a]	position, eV	half-width		rel intens
			left	right	
$Mo(CO)_6$ [b]	I	8.42	0.38	0.29	1.00
	I′	8.68			
$Mo(CO)_5(PMe_3)$	I	7.60	0.48	0.30	1.00
	II	7.87	0.40	0.21	0.69
	II′	8.17			
cis-$Mo(CO)_4(PMe_3)_2$	I	6.84	0.62	0.29	1.00
	II	7.14	0.62	0.25	1.51
trans-$Mo(CO)_4(PMe_3)_2$	I	6.82	0.60	0.29	1.00
	II	7.31	0.29	0.19	0.50
	II′	7.57			
fac-$Mo(CO)_3(PMe_3)_3$	I	6.48	0.59	0.42	1.00
$Mo(CO)_5(PEt_3)$	I	7.54	0.50	0.28	1.00
	II	7.82	0.33	0.21	0.62
	II′	8.09			
trans-$Mo(CO)_4(PEt_3)_2$	I	6.71	0.54	0.32	1.00
	II	7.21	0.29	0.21	0.57
	II′	7.47			
$Mo(CO)_5(PBu_3)$	I	7.40	0.49	0.29	1.00
	II	7.69	0.26	0.22	0.56
	II′	7.93			
trans-$Mo(CO)_4(PBu_3)_2$	I	6.59	0.69	0.36	1.00
	II	7.09	0.35	0.25	0.48
	II′	7.36			

[a] The primed bands are due to vibrational fine structure (CO stretch) on the unprimed band. [b] From ref 9.

the characteristic trans spectrum.

Figure 1 displays close-up scans for the He I ionization of the predominantly Mo 4d electrons for the $Mo(CO)_n(PMe_3)_{6-n}$ series of molecules. This series contains $Mo(CO)_6$, $Mo(CO)_5PMe_3$, *cis*-$Mo(CO)_4(PMe_3)_2$, *trans*-$Mo(CO)_4(PMe_3)_2$, and *fac*-$Mo(CO)_3(PMe_3)_3$. Figures 2 and 3 present the data for $Mo(CO)_6$, $Mo(CO)_5PR_3$, and *trans*-$Mo(CO)_4(PR_3)_2$ with R = Et and *n*-Bu, respectively.

Several of the ionization bands exhibit prominent vibrational structure. The high-binding-energy edge of the spectra for $Mo(CO)_6$, $Mo(CO)_5PR_3$, and *trans*-$Mo(CO)_4(PR_3)_2$ display a distinctive shoulder corresponding to the ionization from an orbital with strong back-bonding to CO ligands.[9] As will be discussed below, these shoulders are diagnostic of an orbital bonded to four CO ligands. In the fitting of the spectra with asymmetric Gaussians, these vibrational shoulders were constrained to have the same left and right half-widths as their origin bands.

The results of fitting the spectra of Figures 1–3 to asymmetric Gaussians are summarized in Table I. For $Mo(CO)_6$, *fac*-$Mo(CO)_3(PMe_3)_3$, and the *trans*-$Mo(CO)_4(PR_3)_2$ compounds, the estimated confidence limit in the band positions is ±0.01 eV. For *cis*-$Mo(CO)_4(PMe_3)_2$ and the $Mo(CO)_5PR_3$ compounds there is greater overlap of the ionization bands and the uncertainty in fitting is estimated as ±0.03 eV. The "primed" bands are vibrational fine structure on the "unprimed" main bands.

The PE spectra of $Mo(CO)_5PMe_3$ and $Mo(CO)_5PEt_3$ have been previously reported by Yarbrough and Hall.[22] Although the band positions of the primarily Mo 4d ionizations are not reported, the splittings between the two ionizations are, and these are in excellent agreement (±0.02 eV) with those reported here.

Discussion

Validity of the Ligand Additivity Model. As shown previously,[12] the application of ligand additivity, in conjunction with Koopmans' theorem, leads to predicted patterns among the ionization potentials of a series of compounds such as $Mo(CO)_n(PR_3)_{6-n}$. The predicted ionization potentials are given in terms of the parameters *a*, *b*, and *c* in Table II.[23] In order to test the validity of the ligand additivity model as applied to PES data, the experimental data of Table I were least squares fit to the ligand additivity expressions given in Table II. Each band was given unit weight. The resulting *a*, *b*, and *c* parameters and predicted ionization potentials are given in Table III.

Table II. Predicted Ionization Potentials for the Series $ML_nL'_{6-n}$ in Terms of the Ligand Additivity Parameters *a*, *b*, and *c*[a]

compd	first IP	second IP	third IP
ML_6	$a + 6b + 4c$ (3)		
ML_5L'	$a + 5b + 3c$ (2)	$a + 5b + 4c$ (1)	
cis-$ML_4L'_2$	$a + 4b + 2c$ (1)	$a + 4b + 3c$ (2)	
trans-$ML_4L'_2$	$a + 4b + 2c$ (2)	$a + 4b + 4c$ (1)	
fac-$ML_3L'_3$	$a + 3b + 2c$ (3)		
mer-$ML_3L'_3$	$a + 3b + c$ (1)	$a + 3b + 2c$ (1)	$a + 3b + 3c$ (1)
cis-$ML_2L'_4$	$a + 2b + c$ (2)	$a + 2b + 2c$ (1)	
trans-$ML_2L'_4$	$a + 2b$ (1)	$a + 2b + 2c$ (2)	
MLL'_5	$a + b$ (1)	$a + b + c$ (2)	
ML'_6	a (3)		

[a] L′ is assumed to be a poorer π-acceptor than L. The degeneracies of each ionization are given in parentheses.

Table III. Least-Squares Fit of the Ionization Data for $Mo(CO)_nL'_{6-n}$ to the Ligand Additivity Model and Predicted Ionization Potentials

	L′		
	PMe_3	PEt_3	P-*n*-Bu_3
	Fit of Ionization Data		
a, eV	4.401	3.787	3.446
b, eV	0.497	0.601	0.649
c, eV	0.246	0.256	0.258
	Predicted (Experimental) Ionization Potentials (eV)		
$n = 6$	8.37 (8.42)	8.41 (8.42)	8.37 (8.42)
$n = 5$	7.62 (7.60)	7.56 (7.54)	7.46 (7.40)
	7.87 (7.87)	7.81 (7.82)	7.72 (7.69)
$n = 4$ (*cis*)	6.88 (6.84)		
	7.13 (7.14)		
$n = 4$ (*trans*)	6.88 (6.82)	6.70 (6.71)	6.56 (6.59)
	7.37 (7.31)	7.21 (7.21)	7.07 (7.09)
$n = 3$ (*fac*)	6.38 (6.48)		
mean dev	0.04	0.01	0.03

Since three data points are necessary to uniquely determine *a*, *b*, and *c*, a test of the validity of the model should ideally involve many more than three ionization potentials. It is for this reason that the high degrees of substitution and stereospecificity available for L′ = PMe_3 make the $Mo(CO)_n(PMe_3)_{6-n}$ series the best one for testing the model. This series has a total of eight unique ionization bands (not including those due to vibrational structure). The agreement between the fitted and observed ionization potentials for this series is remarkably good. The largest deviation, observed for *fac*-$Mo(CO)_3(PMe_3)_3$, is 0.10 eV, and the mean deviation over the series is only 0.04 eV. For L′ = PEt_3, the fit is even better although, with only five ionization bands in the series, the least-squares analysis is not as overdetermined as for L′ = PMe_3. The agreement is not quite as good for L′ = P-*n*-Bu_3 but is still quite satisfactory.

The intensities of the observed bands are also consistent with the predictions of the model. If it is crudely assumed that all three d_π orbitals of these systems will have equal ionization

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[22] Yarbrough, L. W., II; Hall, M. B. *Inorg. Chem.* **1978**, *17*, 2269–2275.

[23] Since, according to Koopmans' theorem, the ionization potential is equal to the negative of the orbital energy, the parameters *a*, *b*, and *c* in Tables II and III are formally opposite in sign (but equal in magnitude) from those of eq 2.

cross sections throughout each series, then the ratios of band intensities for those complexes with more than one ionization band would be equal to the ratios of the degeneracies for each band, given in Table II. Thus, for $Mo(CO)_5PR_3$, *cis*-$Mo(CO)_4(PR_3)_2$, and *trans*-$Mo(CO)_4(PR_3)_2$, the predicted ratio of the intensities of the first to the second bands would be approximately 2:1, 1:2, and 2:1, respectively. It can be clearly seen that the spectra display this general pattern. The assumption of equal cross section is not generally valid,[3] and there is some uncertainty in determining the exact relative areas of overlapping bands. Nonetheless, the intensity ratios that are found are in good accord with the above predictions. For example, $Mo(CO)_5PMe_3$, *cis*-$Mo(CO)_4(PMe_3)_2$, and *trans*-$Mo(CO)_4(PMe_3)_2$ give first:second intensity ratios of 2:1.37, 1.32:2, and 2:1.00, respectively, and similar agreement is seen for the $Mo(CO)_5PR_3$ and *trans*-$Mo(CO)_4(PR_3)_2$ series for R = Et, *n*-Bu.

One of the crucial assumptions of the ligand additivity model is that the d_π orbitals do not rehybridize when the symmetry of the complex is lowered from O_h. A ramification of this assumption is the prediction of accidental degeneracies in the ionization of the *cis*-$Mo(CO)_4L'_2$ and *fac*-$Mo(CO)_3L'_3$ complexes. The former has C_{2v} symmetry under which no degeneracy is mandated, yet the model predicts that, since two of the d_π orbitals interact with three CO ligands and one L′ ligand, only two ionization bands should be observed. Similarly, the *fac* complexes are predicted to have but one triply degenerate ionization even though the d_π orbitals transform as $a_1 + e$ under C_{3v} symmetry. The predictions of both of these degeneracies are verified by the PE spectra of *cis*-$Mo(CO)_4(PMe_3)_2$ and *fac*-$Mo(CO)_3(PMe_3)_3$, which indicate two and one ionization bands, respectively. The spectrum of the latter provides especially compelling support for the assumption of retained octahedral hybridization; the band is well represented by a single Gaussian and is peaked sharply at the top.

It is clear that, despite its simplicity, the ligand additivity model successfully explains the positions, intensities, and number of ionizations in the $Mo(CO)_n(PR_3)_{6-n}$ systems. The data presented here provide excellent experimental verification of the model for this class of complexes.

Vibrational Fine Structure. As noted above, several of the ionization bands have shoulders on the high-energy side that correspond to the excitation of a predominantly CO stretch upon ionization. Similar vibrational fine structure has been observed and discussed in detail for $M(CO)_6$ (M = Mo, W).[9] With the fitting procedures employed here, the separation between the vertical ionization band and the high-energy shoulder is 2200 ± 100 cm^{-1} for all of the observed progressions. These numbers are too imprecise to indicate any trends within the series. The high mean value for the progessional frequency is consistent with the expected result of ionizing a d_π electron; the loss of a metal electron participating in back-bonding should result in a weakening of the M–C bonds and a concomitant strengthening of the C–O bonds. Thus it is reasonable that the mean progressional frequency, which corresponds to a CO stretch in the 17-electron cations, is higher than that for the CO stretching modes of the 18-electron neutral molecules.

Structure is observed only for the ionization band of $Mo(CO)_6$ and for the second ionization bands of $Mo(CO)_5L'$ and *trans*-$Mo(CO)_4L'_2$. This is consistent with the rules we have listed previously for the observation of this structure.[24] On the basis of previous work, we expect this structure to be most clearly observed when a single normal mode dominates the progression and particularly when a totally symmetric stretching mode is activated by the ionization process. According to the ligand additivity model, each of the bands that show vibrational structure in this study should result from the ionization of a d_π electron that is symmetrically π-bonded to four CO ligands. None of the bands resulting from an orbital interacting with a phosphine ligand displays the vibrational structure. The observation of vibrational structure appears to be diagnostic of an orbital bonded to four carbonyls in these systems and, in this sense, provides further support for the ligand additivity model.

Bonding Capability of PR_3 Ligands. The *b* and *c* parameters of eq 2 provide measures of the donor/acceptor properties of the ligands L′ relative to CO.[12] *b* compares the total donor ability (σ-donation − π-acceptance) of L′ to that of CO while *c* is a measure of the difference in π-accepting ability between L′ and CO; it is important to note that *c* has no dependence on the σ-donor ability of the ligands.[12] In the convention used here, a ligand L′ with positive *b* and *c* values in Table III is both a stronger overall donor and a weaker π-acceptor than CO, and the magnitudes of *b* and *c* increase as these differences between L′ and CO increase.

The *b* and *c* parameters for the $Mo(CO)_n(PR_3)_{6-n}$ series are given in Table III. The *c* parameters for all three phosphines are positive, indicating, as expected, that all three are weaker π-acceptors than is CO. In addition, the values of *c* are very similar for all three (0.25 ± 0.01), indicating that, relative to CO, the three PR_3 ligands have essentially the same π-bonding capability. This is not surprising since alkylphosphines are generally considered to be very weak π-acids. Inspection of the *b* parameters shows a distinct difference in the donor abilities of the three. All the *b* parameters as positive, indicating that all three phosphines are more effective overall donors than is CO. The magnitudes of the *b* parameters vary appreciably, however, from 0.50 for L′ = PMe_3 to 0.60 for L′ = PEt_3 to 0.65 for L′ = P-*n*-Bu_3. From this it can be concluded that the donor abilities of the phosphines follow the order PMe_3 < PEt_3 < P-*n*-Bu_3 and that PEt_3 is closer to P-*n*-Bu_3 than to PMe_3 in overall donor ability.

The shift of the valence metal ionizations caused by the total donor ability of L′ in comparison to that of CO, as represented by the *b* parameter, should also be experienced by the core ionizations.[6,25] The ligand-group shift for PR_3 in comparison to that for CO was found by Feltham and Brant to be 0.6 ± 0.2 eV for a large class of complexes.[13] This is in excellent agreement with the *b* parameters we find for the complexes discussed here. The XPS studies of solids are not sufficiently precise to allow differentiation between the different phosphine ligands or to determine the exact correlation of core ionizations with valence ionizations. We are currently completing a definitive gas-phase XPS investigation of multiply phosphine-substituted transition-metal complexes.[26]

The above conclusions are in accord with those reached by Tolman in his seminal study of substituent effects upon the CO stretching frequencies of $(CO)_3NiPX_1X_2X_3$ complexes.[27] The A_1 ν_{CO} values of $Ni(CO)_3PMe_3$, $Ni(CO)_3PEt_3$, and $Ni(CO)_3P$-*n*-Bu_3 in CH_2Cl_2 solution are 2064.1, 2061.7, and 2060.3 cm^{-1}, respectively, and although the differences are small, they are consistent with the notion that P-*n*-Bu_3 is the strongest overall donor and PMe_3 the weakest. It was not possible in that study to partition the influences into σ and π effects. Graham[28] used CO stretching frequencies in conjunction with the Cotton–Kraihanzel model[29] to assign σ and

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π parameters in $LM(CO)_5$ systems, but of the compounds discussed here, only $Mo(CO)_5P$-*n*-Bu_3 was studied. Bodner and co-workers[30] have inferred relative donor:acceptor abilities for a number of ligands by examining the carbonyl ^{13}C chemical shifts of a large number of $LM(CO)_n$ complexes. Their results are in accord with those presented here; i.e., the donor-acceptor ratios of alkylphosphines increases in the order $PMe_3 < PEt_3 <$ P-*n*-Bu_3.

The parameter *a* listed in Table III for each series should correspond to the first ionization potential of the homoleptic hexakis(phosphine) complex $Mo(PR_3)_6$. Although it is likely that these would not be stable for alkylphosphines, it is of interest to note that P-*n*-Bu_3 is a stronger enough donor than PMe_3 that the ionization potential of Mo(P-*n*-$Bu_3)_6$ is predicted to be nearly 1 eV lower than that of $Mo(PMe_3)_6$.

Future Considerations. The application of the ligand additivity model to PES data allows, in principle, the direct determination of ligand bonding capabilities by using the energetic effects of ligands upon d orbitals. As the observed magnitudes of change in the ionization potentials indicate, this is more sensitive than investigating a ligand's influence indirectly by, for example, observing the change in CO stretching frequency induced by the ligand. In addition, it is not necessary to have homologous systems for different ligands; the ligand additivity parameters *a*, *b*, and *c* can be uniquely determined from several different combinations of substituted systems. As an example, a comparison of the PE spectra of ML_6 and ML_5L' would directly yield *b* and *b* + *c*, from which all these parameters can be derived.

The model will achieve even greater utility when the relationship between *b* and *c* is determined. Since *b* represents a combined σ and π influence whereas *c* is π only, it should be possible to achieve true separation of σ and π effects through the proper comparison of *b* and *c*. Our efforts to achieve this are ongoing.

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Note Added in Proof. A recent communication by Bancroft et al.[31] reports the PE spectra of $W(CO)_6$, $W(CO)_5PMe_3$, $W(CO)_5PEt_3$, *cis*-$W(CO)_4(PMe_3)_2$, *trans*-$W(CO)_4(PMe_3)_2$, *trans*-$W(CO)_4(PEt_3)_2$, and *fac*-$W(CO)_3(PMe_3)_3$ and the correlation of these within the ligand additivity model. Their results provide further strong experimental support for the validity of the model.

Registry No. $Mo(CO)_6$, 13939-06-5; $Mo(CO)_5(PMe_3)$, 16917-96-7; *cis*-$Mo(CO)_4(PMe_3)_2$, 16027-45-5; *trans*-$Mo(CO)_4(PMe_3)_2$, 30513-03-2; *fac*-$Mo(CO)_3(PMe_3)_3$, 19195-94-9; $Mo(CO)_5(PEt_3)$, 19217-79-9; *trans*-$Mo(CO)_4(PEt_3)_2$, 19217-81-3; $Mo(CO)_5(PBu_3)$, 15680-62-3; *trans*-$Mo(CO)_4(PBu_3)_2$, 17652-79-8.

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Gas-Phase Reactions. 44.[1] The $P_4 \rightleftarrows 2P_2$ Equilibrium Visualized[2,3]

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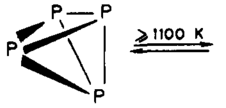
Photoelectron spectroscopic molecular fingerprints and their intensity variations during reactions have been used to determine the temperature dependence of the $P_4 \rightleftarrows 2P_2$ equilibrium constant, $\ln K_P = -27870(1/T) + 12.90$, with a correlation coefficient $R = 0.995$. A MNDO total energy hypersurface helps to further visualize the $T_d \rightarrow D_{2d}$ symmetry-forbidden dissociation into $2P_2$ and their reverse combination to white phosphorus.

Introduction

In the gas phase, the P_4 tetrahedron decomposes at temperatures above 1100 K into two P_2 fragments[5] (eq 1). The



(1)

dissociation energy, $D_0 = 217$ kJ/mol,[6] is used to produce the then stable diatomic species P_2, iso(valence)-electronic to the nitrogen molecule, by formally breaking four PP bonds while two are shortened from 221 pm[5] to 189 pm.[6]

Both element modifications (eq 1) have been investigated repeatedly by photoelectron (PE) spectroscopy,[7–12] and the observed ionization patterns are assigned to the radical-cat-

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