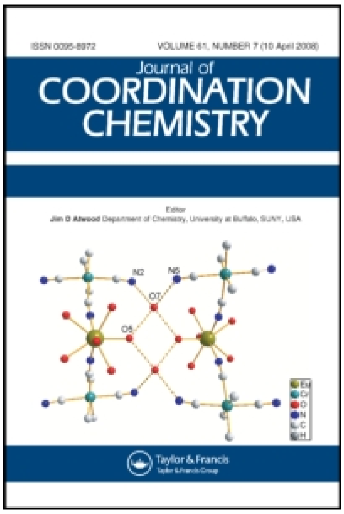

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STERIC AND ELECTRONIC BALANCE IN METAL-PHOSPHINE COORDINATION: THE PHOSPHINE TWIST

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STERIC AND ELECTRONIC BALANCE IN METAL-PHOSPHINE COORDINATION: THE PHOSPHINE TWIST

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The relationship between the bite angles of *cis* phosphines and the electron distribution and bonding to the metal is studied by gas phase valence photoelectron spectroscopy. The complexes selected for the electronic structure comparison are *cis*-$Mo(CO)_4(PMe_3)_2$, $Mo(CO)_4$DMPE (DMPE = 1,2-bis dimethylphosphinotethane), $Mo(CO)_4$DMPM (DMPM = bis(dimethylphosphino) methane), *cis*-$W(CO)_4(PMe_3)_2$, $W(CO)_4$DMPE, and *cis*-$W(CO)_4$DMPM. The Mo carbonyl complexes give simple photoelectron spectra with the valence ionizations originating from the phosphine lone pairs bonding to the metals and from the metal d^6 configurations. The W complexes give similar spectra, but have an additional electronic spin-orbit perturbation. The ionizations from the phosphine lone pairs that donate to the metals in σ bond formation show the effects of the different bite angles of the ligands. However, the total interaction and charge distribution of the phosphines with the metals look very similar in each case. The metal-based ionizations also show very similar bonding and charge distribution in each case. The similarity of the *cis*-$(PMe_3)_2$ and DMPE spectra is interesting in light of the ≈15° difference in P-M-P angles. The metal-based ionizations of the DMPM complexes are slightly different from those of the other complexes, primarily because of through-space interactions with the methylene carbon in the phosphine backbone. The similarity in electronic interactions with the metal in these complexes is traced to a *twist* of the phosphine coordination to the metal which adjusts for the steric or bite angle constraints of the ligands with a minimum effect on the bonding to the metal. This results in slightly bent metal-phosphorus bonds.

KEYWORDS: phosphine ligand bonding, photoelectron spectra, *cis*-complexes

INTRODUCTION

Phosphine ligands have an important place in both transition metal coordination chemistry and organometallic chemistry. The principles of bonding in terms of electron pair donation and π electron acceptance by the phosphine, and the consequences of steric effects for bulky phosphines and chelate effects for multidentate phosphines, have become common textbook material. Nonetheless, there has been little investigation of the interrelationships between the factors of electronic structure and bonding and the constraints of steric or chelate effects. In a previous paper we examined the photoelectron spectra, bonding, and electron distribution of diphosphine ligands ($R_2P(CH_2)_xPR_2$; x = 1 or 2; R = CH_3) that were

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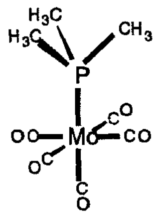
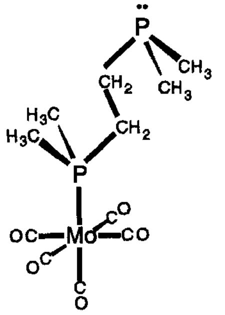
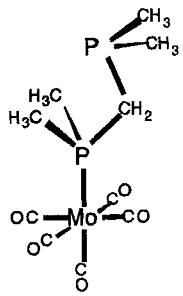


PMe_3

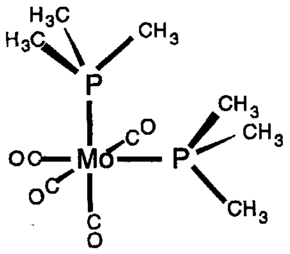


η^1- DMPE

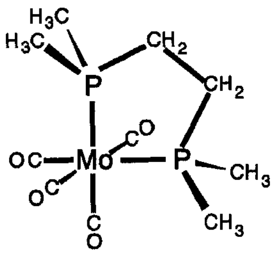


η^1- DMPM

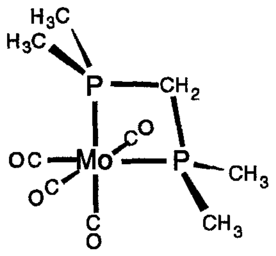
bound to the metal center through only one of the two phosphorus atoms, as shown below.[1] This study allowed comparison of very subtle differences in the electron distribution and bonding of potentially bidentate phosphines and the corresponding monodentate trialkylphosphine without concern for major differences in the metal-phosphine geometries. The overall conclusion from the study was that the bonding of these three ligands was extremely similar. In the present study we compare the bonding of these ligands in chelating geometries to the bonding of *cis*-trimethylphosphine in $L_2Mo(CO)_4$ and $L_2W(CO)_4$ complexes. In these cases there are significant steric and chelate effects on the geometry of the complexes. For instance, the P-M-P angle in *cis*-(trimethylphosphine)$_2$ complexes ranges from 94–98°,[2] but is only about 78–82° for DMPE complexes[3,4] and falls to as low as 67° for a DMPM complex.[5] One important point that emerges from this investigation is the identification of a phosphine *twist* mechanism that helps accommodate the geometric constraints while maintaining as much of the metal-phosphine bond as possible. The phosphine twist that occurs with geometric constraints may be viewed as a slightly bent metal-phosphine bond.



cis-$(PMe_3)_2$



DMPE



DMPM

Despite numerous studies of chelating *versus* monodentate ligands, direct comparisons of the electron distribution and bonding are rare. In 1988 the heats of reaction, -ΔH, for coordination of monodentate phosphines and chelating diphosphines were compared.[6] These -ΔH values were determined for substitution of norbornadiene (NBD) by each phosphine as outlined in the following reactions:

$$Mo(CO)_4NBD + 2PR_3 \rightarrow cis\text{-}Mo(CO)_4(PR_3)_2 + NBD \quad (1)$$

$$Mo(CO)_4NBD + R_2P(CH_2)_xPR_2 \rightarrow Mo(CO)_4(R_2P(CH_2)_xPR_2) + NBD \quad (2)$$

$$x = 1, 2; R = Me, Ph.$$

For the three phosphines that are the focus of the present paper, PMe_3, DMPE, and DMPM, the $-\Delta H$ values are 32.9 ± 0.1, 32.4 ± 0.1, and 24.5 ± 0.5 kcal/mol, respectively. From the $-\Delta H$ values for each phosphine, the $-\Delta H$ for reaction of 2 CO's with $Mo(CO)_4NBD$, and the dissociation energy of the Mo-CO bond,[7,8] the Mo-P bond strengths were estimated. These are found to be 43.2, 42.9, and 39.0 kcal/mol for PMe_3, DMPE, and DMPM, respectively. The Mo-P bond energies for PMe_3 and DMPE are essentially identical, and the Mo-P bond energy for DMPM is about 4 kcal/mol less. A similar study of phosphine substitution to form $L_2Fe(CO)_3$ complexes reached similar conclusions.[9]

Photoelectron spectroscopy (PES) is ideally suited for experimentally investigating the electronic factors of the metal-phosphine interaction. In some cases, PES affords a direct probe of relative metal-ligand bond strengths, as well as a measure of the charge distribution at the metal center.[10] Previously in this laboratory, we have investigated the bonding of trimethylphosphine and demonstrated the ability to predict the electronic properties of metal complexes with multiple ligand substitutions by means of the principle of ligand additivity.[11-13] These studies revealed additive ligand electronic effects in both the valence and core ionizations for the series of molybdenum carbonyl complexes, $Mo(CO)_{6-n}(PMe_3)_n$, $n = 1,2,3$. The data show that substitution of one PMe_3 molecule for a CO destabilizes the Mo *4d* valence metal levels 0.50 ± 0.04 eV and the Mo $3d_{5/2}$ core levels 0.65 ± 0.10 eV for each phosphine substitution, $n = 1\text{-}3$. The trimethylphosphine ligand was found to be one-fourth as effective as a CO ligand at stabilizing the metal levels through π backbonding.

Expansion of this model to higher substitution numbers, $n = 4,5,6$, is difficult due to the instability of the PMe_3 complexes $n = 4\text{-}6$ in the gas phase and the question of steric effects on the additivity. It is important to examine the highly phosphine substituted carbonyl complexes in order to determine if the additive charge shift continues or saturates at higher substitution numbers. The study of these highly phosphine substituted complexes requires a phosphine that has similar electronic properties to PMe_3, but also reduces steric crowding and gives a metal complex with greater stability in the gas phase. Substitution of the chelating phosphines, DMPE or DMPM for *cis*-$(PMe_3)_2$ is the next step for greater gas phase stability of these more highly substituted complexes. Thus, the study of ligand additivity at high phosphine substitution (*i.e.* *cis*-$Mo(CO)_2(DMPE)_2$, $n = 4$ and $Mo(DMPE)_3$, $n = 6$) can be continued. Before the PES data from these chelating diphosphine complexes can be used in conjunction with the previous PMe_3 additivity studies, both the electronic capabilities and the geometric structure differences of the three ligand sets need to be examined to identify the best electronic analogue to the *cis*-$(PMe_3)_2$ fragment.

EXPERIMENTAL

Synthesis

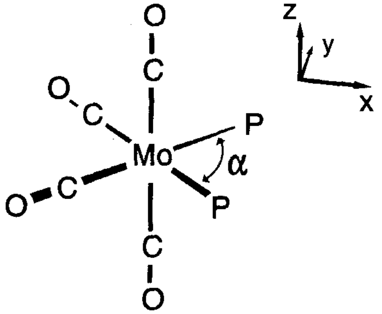
The complexes $Mo(CO)_4DMPM$,[14] $Mo(CO)_4DMPE$,[14,15] *cis*-$Mo(CO)_4(PMe_3)_2$,[14,15] $W(CO)_4DMPM$,[14] $W(CO)_4DMPE$,[15] and *cis*-$W(CO)_4(PMe_3)_2$[15] were prepared by the referenced procedures. The laboratory methods of preparation and characterization were as described in the previous paper.[1]

Photoelectron Spectra

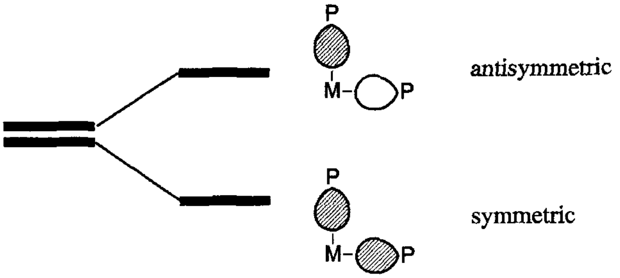
The photoelectron instrumentation and methods of collection were as described previous.[1] The spectra were obtained for each compound at the following cell temperatures (±4°C): $Mo(CO)_4DMPM$, 95 °C; $Mo(CO)_4DMPE$, 100 °C; *cis*-$Mo(CO)_4(PMe_3)_2$, 80 °C; $W(CO)_4DMPM$, 110 °C; $W(CO)_4DMPE$, 120 °C; *cis*-$W(CO)_4(PMe_3)_2$, 100 °C. The independent collections show no evidence of sample decomposition at the given temperatures. The data are represented analytically in terms of asymmetric Gaussian peaks. Each peak is defined by parameters representing the position of the peak, the halfwidths on the high (W_h) and low (W_l) binding energy sides of the peak, and the amplitude of the peak as determined by the program GFIT.[16,17] Within the constraints of this model, the ionization potentials for the single ionization bands can have a reproducibility as good as ±0.005 eV. The ionization energies reported for the overlapping metal ionizations are reproducible in these methods to about ±0.02 eV.

PRELIMINARY CONSIDERATIONS

Before introducing the photoelectron data, it is helpful to consider qualitatively the expected electronic effects of the P-M-P distortions from O_h symmetry. Hoffman and Kubáček have discussed the electronic structure consequence of *cis*-carbonyl (π-acceptor) and *cis*-chloride (π-donor) deformations in octahedral geometry for d^4 transition metal complexes.[18] Their results can be applied easily to phosphine distortions in these d^6 systems. The Hoffman paper uses a coordinate system in which the x-axis bisects the P-M-P angle and the z-axis is directed at a CO that is *cis* to both phosphines, as shown below. In this coordinate system, the occupied metal d orbitals that derive from the t_{2g} set of octahedral symmetry are the $d_{x^2-y^2}$, d_{xz} and d_{yz}.



The metal orbitals that are available for bonding to the phosphines are the d_{xy}, $5s$, $5p_x$ and $5p_y$. The phosphine lone pairs will hereafter be referred to as the PLPs. The two phosphines are in a *cis* conformation and the PLPs form the symmetric and antisymmetric combinations. The energy separation of these combinations is dependent on their direct through-space overlap interaction, and the energy of the corresponding orbitals of the complex is dependent on the different interactions of these combinations with the metal and carbonyl orbitals. The effect of distortions in the P-M-P angle, α, are examined here in terms of changes in overlap between the PLPs and each of the metal orbitals.



The PLP interaction with the metal *d* orbitals is shown in Figure 1. The antisymmetric combination of the PLPs is involved in σ bonding to the d_{xy}, and $5p_y$, orbitals and the symmetric combination of the PLPs is involved in σ bonding to the $5s$ and $5p_x$ orbitals. The bonding to the d_{xy} orbital will be dominant, but it is not known if this is sufficient to reverse the order of the symmetric and antisymmetric PLP-based orbitals in the complex. The PLP-d_{xy} overlaps will be affected by changes in the P-M-P angle as depicted in Figure 1. Movement of the lone pairs off the d_{xy} lobes will decrease overlap for either $\alpha > 90°$ or $\alpha < 90°$. This has the effect of destabilizing the orbital of the complex that results from the overlap of the antisymmetric combination of the PLPs with the d_{xy} orbital.

Considering the occupied metal *d* orbitals, the d_{xz} and d_{yz} orbitals should not be affected by overlap interactions through distortion of the angle α because the PLPs lie in the nodal plane of these orbitals. The PLPs are also on the nodes of the $d_{x^2-y^2}$ orbital when the angle between the lone pairs is 90°. The symmetric combination of the PLPs can interact with the $d_{x^2-y^2}$ orbital if the angle α is greater or smaller than 90°. This is a filled-filled interaction which will destabilize the resulting metal $d_{x^2-y^2}$-based orbital of the complex. The PLPs can also have a direct through-space interaction with the CO π* orbitals. This is a donor/acceptor interaction which places charge from the PLPs into the CO π* orbitals. These CO π* orbitals are involved in stabilizing the $d_{x^2-y^2}$ orbital, thus this interaction will also be destablizing to the resulting $d_{x^2-y^2}$-based orbital of the complex.

The coordination geometries of *cis*-$(PMe_3)_2$, DMPE, and DMPM from the X-ray structures given in the introduction show the P-Mo-P angles to be ≈94°, ≈80°, and ≈67° for the three ligands, respectively. Changes in the splitting between the metal-based ionizations will reflect the changes in interactions of the phosphines with the metal *d* orbitals. The ionization correlating to the $d_{x^2-y^2}$ orbital will be sensitive to the PLP-$d_{x^2-y^2}$ interaction. General shifts of the ionizations will reflect the different donor, acceptor, and overlap interactions of the geometrically constrained phosphines.

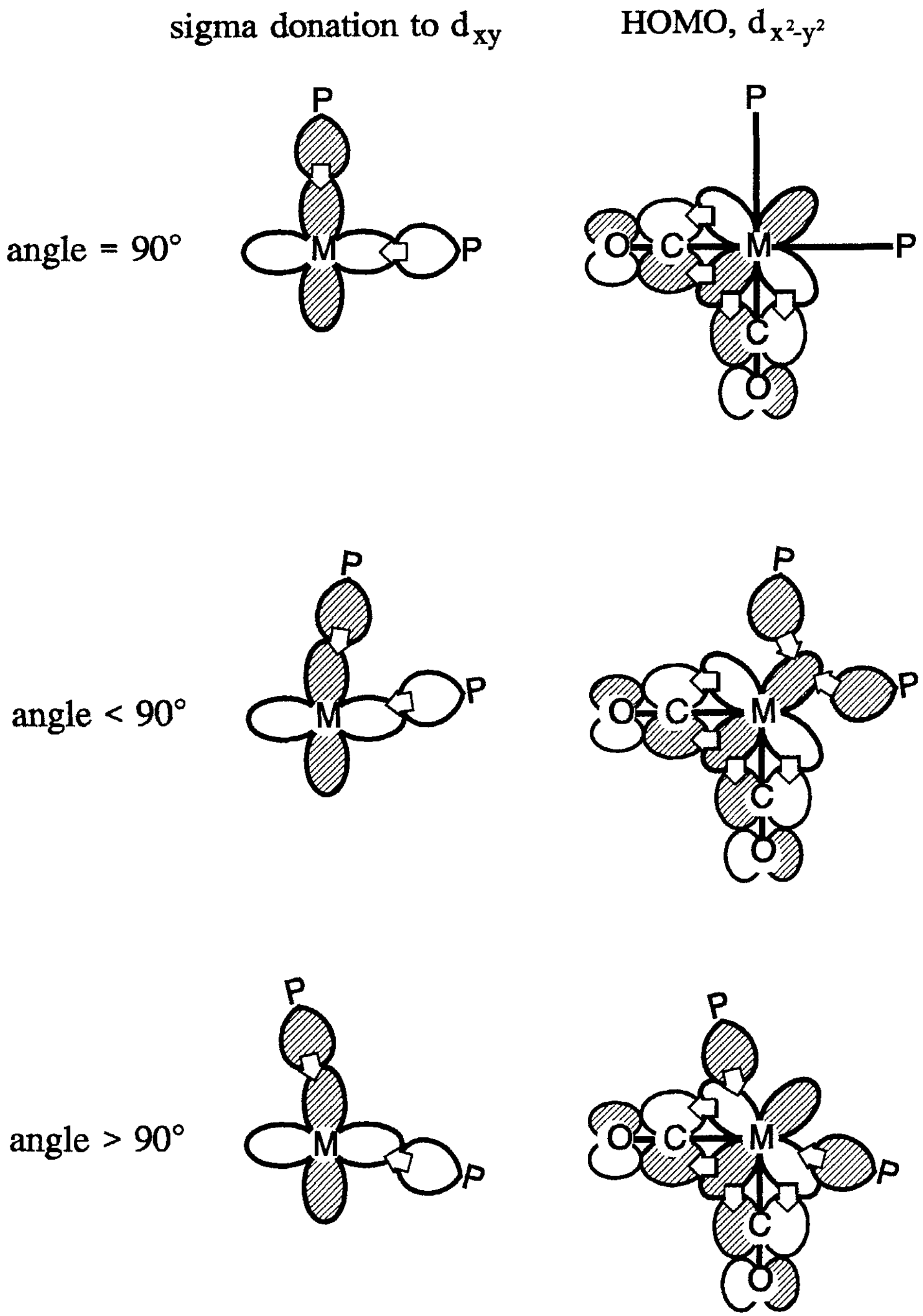


Figure 1 The phosphine lone pair donor and HOMO($d_{x^2-y^2}$) interactions at $\alpha < 90°$ and $\alpha > 90°$.

RESULTS

Molybdenum Complexes

HeI PES data for *cis*-Mo(CO)$_4$(PMe$_3$)$_2$, Mo(CO)$_4$DMPE, and Mo(CO)$_4$DMPM are shown in Figure 2 and Figure 3. Figure 2 depicts the 6–11 eV binding energy region, which includes the ionizations from the three metal-based orbitals and the

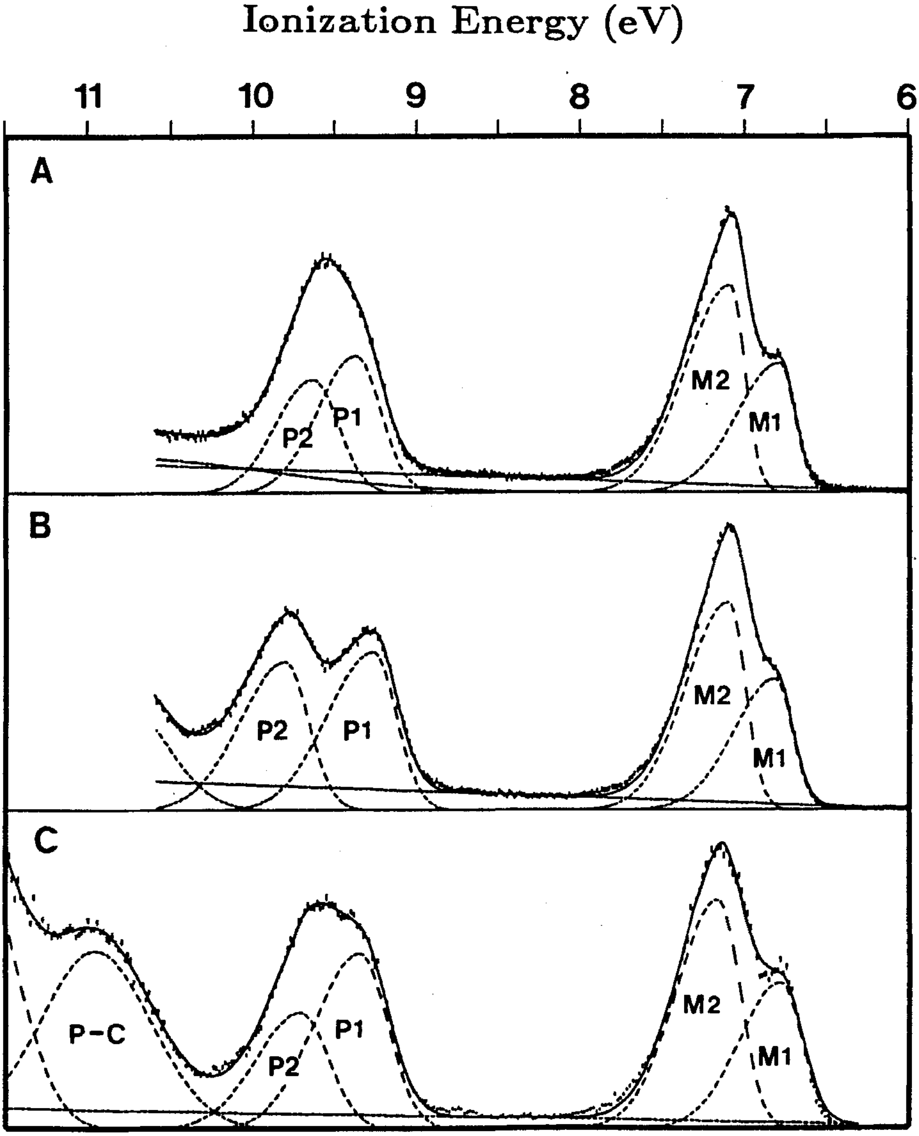


Figure 2 HeI Spectra (6-11 eV) of *cis*-Mo(CO)$_4$(PMe$_3$)$_2$ (**A**), *cis*-Mo(CO)$_4$DMPE (**B**), and *cis*-Mo(CO)$_4$DMPM (**C**).

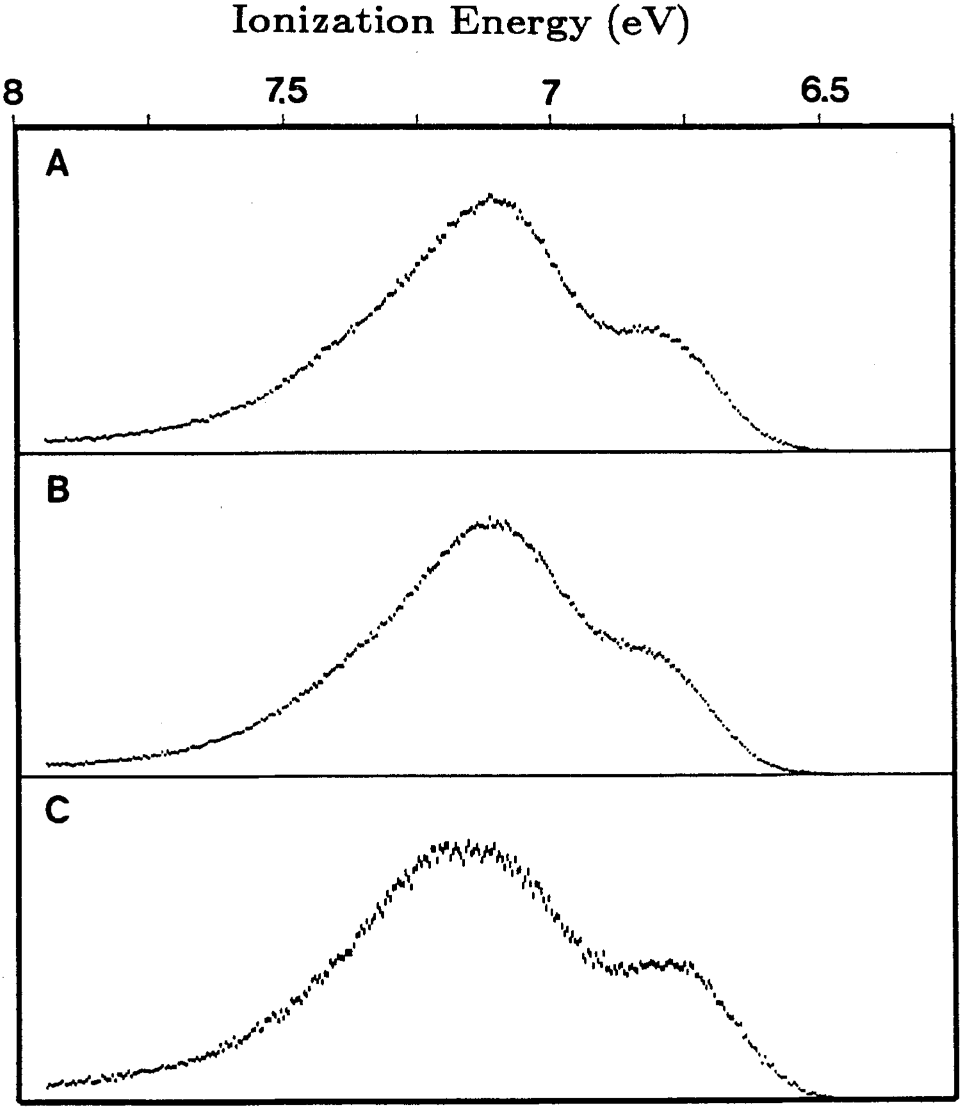


Figure 3 HeI Close-Up Spectra of Mo 4*d*-based ionizations for *cis*-$Mo(CO)_4(PMe_3)_2$ (**A**), *cis*-$Mo(CO)_4$DMPE (**B**), and *cis*-$Mo(CO)_4$DMPM (**C**).

ionizations from the phosphine lone pair (PLP) based orbitals. Figure 3 shows more detail for the Mo-based ionizations of the three complexes. The ionization features in Figure 2 are represented analytically by asymmetric Gaussian peaks as described in the experimental section. The results are listed in Table 1.

The assignments of the predominantly ligand or metal-based orbital character of the valence ionizations are straightforward and have been presented in previous

Table 1 Ionization potentials and bandshape analysis for the $Mo(CO)_4(P)_2$ complexes

complex	band	IP(eV)	W_h	W_l	rel area
cis-$Mo(CO)_4(PMe_3)_2$	M1	6.80	0.62	0.22	1.00
	M2	7.11	0.62	0.22	1.61
	P1	9.38	0.54	0.36	1.14
	P2	9.63	0.54	0.36	0.94
cis-$Mo(CO)_4$DMPE	M1	6.83	0.59	0.25	1.00
	M2	7.12	0.59	0.25	1.58
	P1	9.27	0.65	0.34	1.40
	P2	9.80	0.65	0.34	1.32
cis-$Mo(CO)_4$DMPM	M1	6.78	0.59	0.31	1.00
	M2	7.17	0.59	0.31	1.56
	P1	9.35	0.64	0.40	1.38
	P2	9.71	0.64	0.40	0.92

studies of these metal-phosphine complexes.[12,13] The ionizations near 9.5 eV are due primarily to the symmetric and antisymmetric combinations of the phosphine lone pair orbitals and correspond to the Mo-P bonds. One can see large differences in these ionizations between the three molybdenum tetracarbonyl complexes. The two PLP ionizations are split by 0.25 eV in the *cis*-$(PMe_3)_2$ complex, by 0.53 eV in the DMPE complex, and by 0.36 eV in the DMPM complex. The origin and importance of this splitting will be discussed later.

The ionizations near 7 eV are primarily from the Mo 4*d* orbitals. The 1:2 intensity pattern results from the splitting of the t_{2g} set of the parent $Mo(CO)_6$ complex by the C_{2v} symmetry of the formally Mo(0), d^6 metal as described in the discussion section. The primary conclusion to be drawn from this figure is that the metal-based ionizations of these complexes are extremely similar. Careful visual comparison of the spectra of the Mo 4*d* ionizations in Figure 3 shows that ionization band M1 shifts only slightly in these three complexes. The visible trend in IP for band M1 is DMPE > *cis*-$(PMe_3)_2$ > DMPM. Table 1 shows nearly identical ionization energies for both band M1 and band M2 of the *cis*-$(PMe_3)_2$ and DMPE complexes. Only a very small 0.03 eV stabilization of band M1 of the DMPE complex relative to that of the *cis*-$(PMe_3)_2$ complex is obtained. Comparison of the $Mo(CO)_4$DMPM metal ionizations shows a 0.05 eV destabilization of band M1 from the DMPE complex and a 0.05 eV stabilization of band M2.

The relative error in fitting a single ionization band is ±0.005 eV, but for fitting the overlapping metal ionizations of Figure 3 the error increases to ±0.02 eV. Since the differences between the IP's of band M1 are close to the experimental uncertainty, little emphasis can be placed on the absolute values of these shifts, even though the shifts are visually discernable. These shifts become more clear for the corresponding tungsten complexes discussed in the next section.

Close examination of Figure 3 also reveals a small difference in bandshape between the spectra of the *cis*-$(PMe_3)_2$, DMPE, and DMPM complexes for bands M1 and M2. The bands in each spectrum were constrained to have the same widths on the low (W_l) and the high (W_h) binding energy sides because of the extensive overlap. The average of W_l and W_h for bands M1 and M2 in the *cis*-$(PMe_3)_2$ complex is slightly smaller (due to a smaller W_l) than in the DMPE complex (Table 1). In the DMPM spectrum, the average of W_l and W_h is broadened compared to the other two specta. Also, band M2 in the DMPM spectrum has lost the sharp peak top evident in the *cis*-$(PMe_3)_2$ and DMPE spectra. Both of these features indicate a small splitting under band M2. The 7.17 eV IP reported for band M2 in the DMPM complex represents the average energy of the two split ionizations under this band.

Tungsten Complexes

Ionization data have been obtained for some *cis*-$W(CO)_4(PR_3)_2$ and $W(CO)_4(R_2P(CH_2)_xPR_2)$ complexes previously.[19] However, the previous work was not concerned with direct comparison of the ionizations between chelating *vs.* *cis*-$(PR_3)_2$ complexes. We find some significant differences from the spectra that have been published previously. HeI photoelectron spectra for *cis*-$W(CO)_4(PMe_3)_2$, $W(Co)_4$DMPE, and $W(CO)_4$DMPM in the 5.9–10.8 eV binding energy region are shown in Figure 4. Close-up spectra comparing the W 5*d* ionizations for *cis*-$W(Co)_4(PMe_3)_2$, $W(CO)_4$DMPE, and $W(CO)_4$DMPM are shown in Figure 5. An asymmetric Gaussian fit analogous to the Mo data was performed and the results are given in Table 2.

The phosphine lone pair ionizations are at ≈9.7 eV for the tungsten complexes. The splittings between the symmetric and antisymmetric combinations are 0.33, 0.58, and 0.46 eV for the *cis*-$(PMe_3)_2$, DMPE, and DMPM complexes, respectively. These results are similar to the separations for Mo complexes both in magnitude and in the trend DMPE>DMPM>PMe_3. These separations and the measured IP's will be discussed in more detail later.

The ionization envelopes for the metal band spectra in Figure 5 are fit with four asymmetric Gaussians representing the first IP (band M1), the spin-orbit split second IP (bands M2 and M2*)[20], and one CO vibrational spacing. Ionization band M1 is also affected by spin-orbit coupling as this ion-state has J = 1/2 and interacts with one of the J = 1/2 ion-states under band M2.[21,22] This band is well separated from bands M2 and M2* in the three complexes and allows a more accurate

Table 2 Ionization potentials and bandshape analysis for the $W(CO)_4(P)_2$ complexes

complex	band	IP(ev)	W_h	W_l	rel. area
cis-$W(CO)_4(PMe_3)_2$	M1	6.80	0.30	0.24	1.00
	M2	7.10	0.43	0.22	1.15
	M2*	7.27	0.43	0.32	1.35
	M2'	7.56	0.43	0.32	0.33
	P1	9.53	0.84	0.47	NA
	P2	9.86	0.84	0.47	NA
cis-$W(CO)_4$DMPE	M1	6.84	0.30	0.23	1.00
	M2	7.12	0.31	0.22	1.20
	M2*	7.30	0.36	0.27	1.49
	M2'	7.57	0.36	0.27	0.31
	P1	9.42	0.59	0.36	NA
	P2	10.00	0.68	0.34	NA
cis-$W(Co)_4$DMPM	M1	6.75	0.33	0.23	1.00
	M2	7.10	0.31	0.23	1.25
	M2*	7.32	0.31	0.23	1.15
	M2'	7.57	0.31	0.23	0.31
	P1	9.46	0.63	0.39	1.69
	P2	9.92	0.63	0.39	1.45

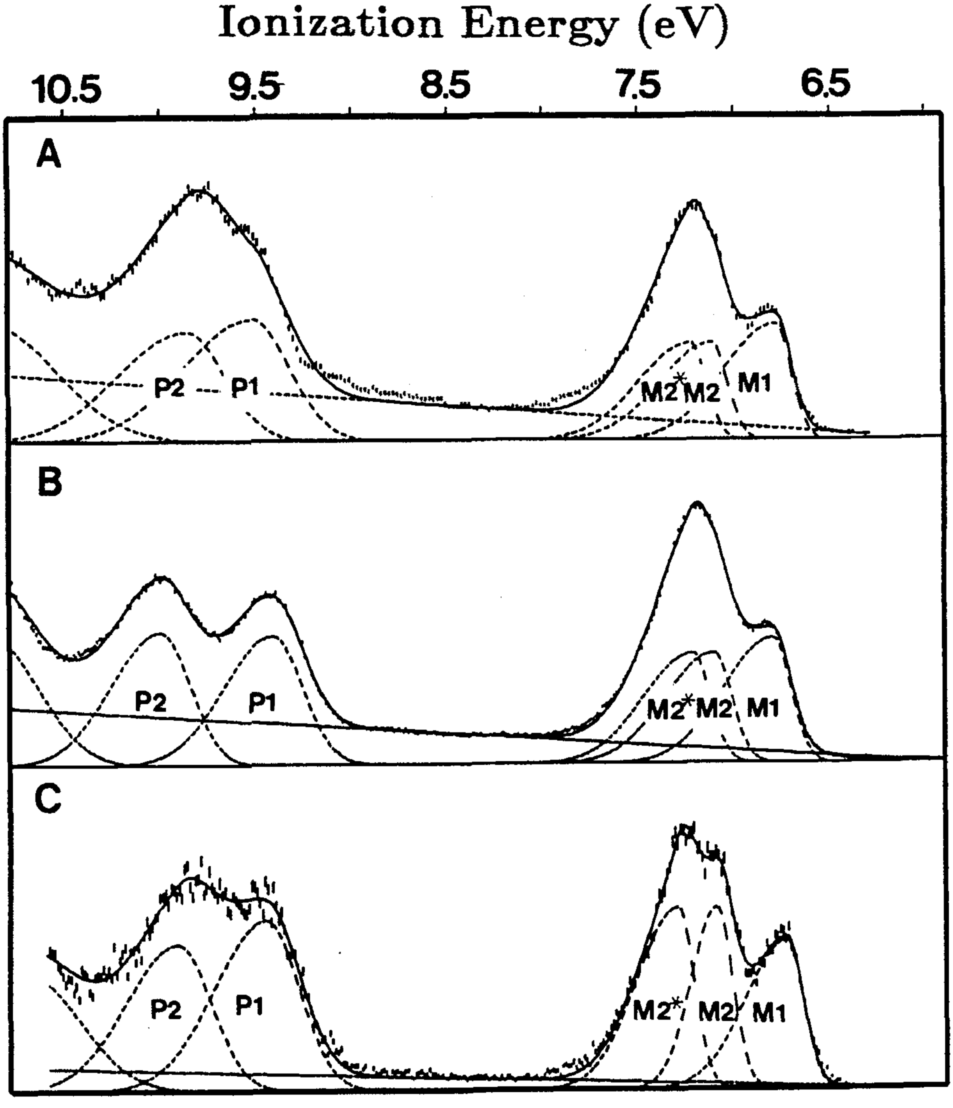


Figure 4 HeI Spectra 6-11 eV for *cis*-$W(CO)_4(PMe_3)_2$ (A), *cis*-$W(CO)_4$DMPE (B), *cis*-$W(CO)_4$DMPM (C).

comparison of the first IP for each complex than in the Mo data (fit error ±0.005 eV for single ionization bands). The reported IP's for band M1 are 6.80, 6.84, and 6.75 eV for the *cis*-$(PMe_3)_2$, DMPE, and DMPM complexes, respectively. These IP's reflect the same trend in the band M1 observed in the Mo complexes. The importance of these IP's will be examined in the discussion section.

The data and IP's for the W 5*d* ionizations of *cis*-$W(CO)_4(PMe_3)_2$, $W(CO)_4$DMPE, and $W(CO)_4$DMPM complexes have been published previously.[19,23] The results in

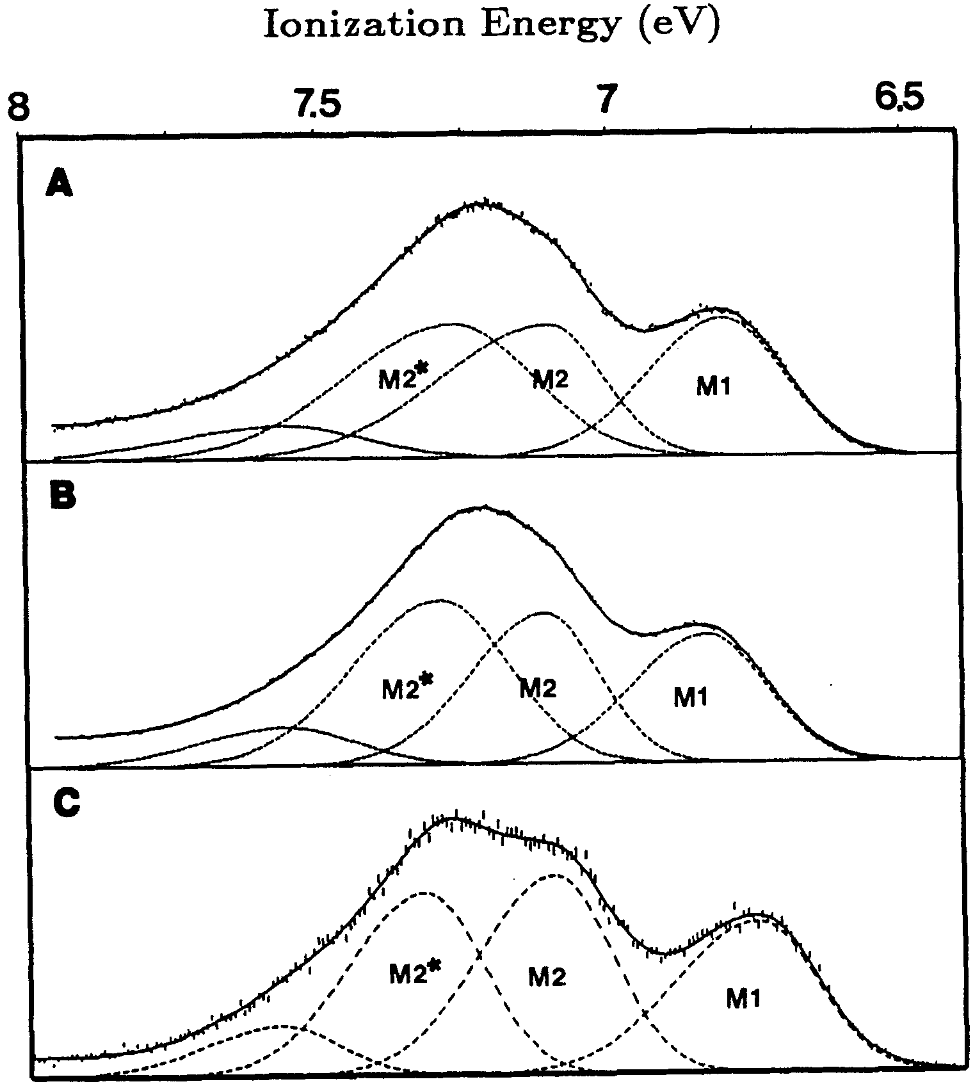


Figure 5 HeI Close-up Spectra of the W 5*d* Ionizations for *cis*-W(CO)$_4$(PMe$_3$)$_2$ (**A**), *cis*-W(CO)$_4$DMPE (**B**), and *cis*-W(CO)$_4$DMPM (**C**).

Table 2, differ significantly from previous values. The reported IP's in references 19 and 23 (with the present ones in parentheses) are 6.72(6.80), 7.00(7.10), and 7.25(7.27) eV for *cis*-W(CO)$_4$(PMe$_3$)$_2$; 6.74(6.84) and 7.15(7.12,7.30) eV for W(CO)$_4$DMPE; and 6.69(6.75), 7.19(7.10, 7.32) eV for W(CO)$_4$DMPM. The latter two spectra were not fit with spin-orbit splitting under band M2 in the previous work.

Asymmetric Gaussian bandshapes were used to model the PES data in the present study, whereas the previous work was constrained to symmetric Gaussian shapes. Theoretically, the high-binding energy half-width will always be larger than the low-binding energy side due to the accessibility of unresolved vibrational states.[24] We have shown that attempts to model PES data with symmetric Gaussians will usually result in higher ionization energies and will lose the important information present in the bandshapes and relative intensities. Since the previously published ionization energies are always lower than those reported here, the choice of bandshape does not explain the differences in the observed values. A second possible reason for the differences in ionization energies is the external calibration of the energy scale. This calibration is performed in our research by fixing the separation between the argon $^2P_{3/2}$ ionization (15.759 eV) and CH_3I $^2E_{1/2}$ ionization (9.538 eV). The calibration is not reported for the previous data. It is noteworthy that the previously reported energies and those presented here show the same trend in the first IP. The IP of band M1 decreases in the order DMPE > *cis*-$(PMe_3)_2$ > DMPM. Thus, the primary reason for the difference in IP's must lie in the different calibrations of the energy scale and will not affect the comparisons that are to be made.

An additional complication exists for the spectra and energies reported for *cis*-$W(CO)_4(PMe_3)_2$. The published spectrum and the fit of the data are not consistent with the spectrum given in Figure 5. The intensity of the second IP relative to the first IP also is not the same as in the spectrum reported here. We believe the previous spectrum is a mixture of *cis* and *trans* isomers. From our experience, the *trans* isomer is always present in small amounts and sublimes first. Further heating of the sample brings the pure *cis* isomer into the gas phase. If the temperature is raised 20°C or higher than the initial sublimation temperature of the *cis* isomer, a small change in the relative band intensities is seen indicating a small percentage of the *trans* isomer is present. Gas phase equilibrium mixtures of *cis* to *trans* have been observed previously in the PES spectra of *cis*-$Mo(CO)_4(PEt_3)_2$ and *cis*-$Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2$.[12] In addition, kinetic measurements on the *cis/trans* isomerization rates have also been performed.[25] The gas phase *cis/trans* ratio will depend upon the ionization cell temperature at the time of data collection and this temperature is not known for the previously published spectrum. Our data were collected in a 5° range above the initial sublimation temperature and has little or no *trans* isomer present.

An indication of the expected relative intensity between first and second IP's is evident by examination of the DMPE spectrum in Figure 5. Since this molecule is locked into the *cis* configuration, this spectrum reflects the relative intensity to be expected for the first and second ionization bands. The M1:(M2 + M2*) ratio is the same in both the *cis*-$(PMe_3)_2$ and DMPE spectra presented here, supporting the validity of the present data.

DISCUSSION

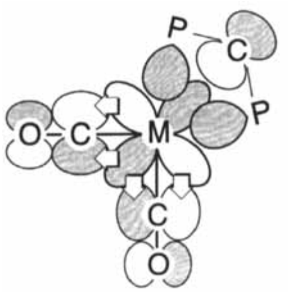
Phosphine Lone Pair Ionizations

The major differences in the spectra of *cis*-$Mo(CO)_4(PMe_3)_2$, $Mo(CO)_4$DMPE, and $Mo(CO)_4$DMPM in Figure 2 occur in the ionizations between 9-10 eV. These ionizations are predominately phosphine lone pair in character and originate from the symmetric and antisymmetric combinations of the lone pairs which contribute to the M-P σ bonds. The symmetric combination is stabilized in comparison to the antisymmetric combination by the through-space overlap interaction, but the antisymmetric combination is favorably stabilized by overlap interaction with the metal *d* orbitals. The splittings observed in the spectra of the molybdenum complexes for the DMPE and the *cis*-$(PMe_3)_2$ ligands are 0.53 and 0.25 eV, respectively. Since the splitting is larger for the DMPE complex, it is natural to assign the higher ionization potential (more stable orbital energy) to the symmetric combination. The shorter P-P distance in the DMPE complex (due to a smaller P-Mo—P bite angle) leads to a larger lone pair-lone pair through space interaction, which stabilizes the symmetric combination and destabilizes the antisymmetric combination.

In the *cis*-$(PMe_3)_2$ complex, the P-Mo-P angle is larger, resulting in a weaker through-space interaction. The symmetric combination is now less stable than the corresponding orbital in the DMPE case, and the antisymmetric combination is more stable. It is conceivable that the orbitals "cross over", placing the antisymmetric combination below the symmetric, because the antisymmetric combination has the stronger bonding interaction with the metal *d* orbitals. However, it is most probable that the ionizations have simply moved 0.25 eV closer together and have not moved the 0.75 eV necessary to "cross over". Thus the ionizations are assigned similarly for the *cis*-$(PMe_3)_2$ complex.

Based on through-space analysis, the splitting of the symmetric and antisymmetric combinations of the PLP ionizations of the DMPM complex presents a curious problem. The P-Mo-P angle in a chelating DMPM molecule is approximated at 67°.[5] Thus, a larger symmetric/antisymmetric splitting should result. This is not seen for either for the Mo or W DMPM complexes.

The answer to this problem lies in the planarity of the metal-P-CH_2-P metallocycle. The bridging CH_2 group contains a filled symmetric C-H bonding orbital that is situated in the plane between the two phosphorus atoms. This orbital interacts directly with the PLP symmetric combination. This important interaction is shown below. The PLP symmetric combination is destabilized by this filled-filled interac-



tion and is pushed closer in energy to the PLP antisymmetric combination. Thus, the separation is smaller than expected from the phosphine lone pair-lone pair through-space interaction alone. This interaction also has implications for the metal-based ionizations which are discussed later.

Bancroft, *et al.* have reported a measure of the relative W-P bond strengths for tungsten carbonyl complexes in a previous publication.[19] The measurement involves the shift of the PLP-metal bond ionizations in the complexes from the free phosphine lone pair ionization energies. This determination is complicated for *cis* phosphines because the lone pair ionizations are split and shifted by the through-space orbital interactions. There is an additional problem in this comparison for chelating DMPE and DMPM ligands. These ligands are "locked" into a chelating geometry with eclipsed lone pairs in the complexes, whereas the free ligand spectra are obtained from the staggered conformations. The ionizations of the two phosphine lone pairs in the free ligands are degenerate and do not show either a through-space or through-bond splitting.[1] Changing from staggered to eclipsed geometry causes differences in the intraligand bond angles. The extent of 3*s* and 3*p* mixing is governed by these intraligand angles and this affects the energy of the phosphine lone pair. The result is a different phosphine lone pair energy for the staggered *vs.* eclipsed geometries. Furthermore, the phosphine lone pair ionizations of the DMPM complex have additional interaction with the CH_2 backbone in the eclipsed geometry. All of these ionization shifts are a consequence of the intraligand overlap differences which accompany the metal-phosphine bonding. Thus, the ionization energy changes with coordination to the metal do not solely reflect the bonding to the metal.

With these considerations in mind, it is interesting to compare the averages for the phosphine lone pair ionizations for each of the complexes. For the molybdenum complexes, the averages for the *cis*-$(PMe_3)_2$, DMPE, and DMPM PLP ionizations are 9.50, 9.53, and 9.53 eV, respectively. These averages indicate the charge and overlap effects at the coordinated phosphorus atoms to be nearly identical for the three complexes. The 0.03 eV difference is within the error associated with fitting the severely overlapping PLP bands of the *cis*-$(PMe_3)_2$ and DMPM complexes. Interestingly, the average of the PLP IP's of *trans*-$Mo(CO)_4(PMe_3)_2$ is 9.57 eV (8.92 and 10.22 eV).[12] This value is slightly more stable than the averages found for the three *cis* complexes, and is probably due to achieving maximum metal-phosphine lone pair bonding overlap in the *trans* isomer. For the *cis*-$(PMe_3)_2$, DMPE, and DMPM complexes of tungsten, these three average values are 9.69, 9.71, and 9.69 eV respectively. As for the molybdenum complexes, these values indicate essentially identical charge and overlap effects at the coordinated phosphorus atoms. These averages are 0.18 eV more stable than the values for the molybdenum complexes, reflecting the stronger interaction between the phosphine lone pair and the tungsten atom.

The equivalent charge and overlap effects at the phosphorus atoms in each ligand geometry are a paradox as one would expect different metal-phosphine lone pair overlaps for the three P-M-P coordination geometries. This unexpected observation is made at this point solely on the basis of the phosphine lone pair ionizations. The metal-based ionizations provide additional information.

Molybdenum-Based Ionizations

Comparison of the metal-based ionizations in Figure 3 reveals a striking similarity between the spectra for the *cis*-$(PMe_3)_2$ and DMPE complexes. The ligand field charge potential felt at the metal has a strong effect on the position of the metal bands, and this result is consistent with the identical charge and overlap effects at the coordinated phosphorus atoms in each complex as indicated in the previous section.

The 1:2 intensity pattern results from the splitting of the filled *d* orbitals in C_{2v} symmetry. The splitting pattern can be related to the number of CO ligands *versus* phosphines backbonding into each t_{2g} orbital.[12] Two of these orbitals are stabilized by backbonding to three CO's and one phosphine, while the remaining t_{2g} orbital is stabilized by backbonding to only two CO's and two phosphines. Thus, the splitting between the first and second IP's is the difference in backbonding stabilization between CO and each phosphine. This splitting is nearly identical in the *cis*-$(PMe_3)_2$ and DMPE complexes at 0.31 and 0.29 eV. A similar comparison has been made for the mono-phosphine complexes $(CO)_5MoPMe_3$,$(CO)_5MoDMPE$, and $(CO)_5MoDMPM$, where the diphosphines are coordinated through only a single phosphorus atom.[1] Here one of the metal-based orbitals is backbonding to four carbonyls while the other two meal-based orbitals are backbonding to three carbonyls and one phosphine. Thus the difference is again the difference in backbonding stabilization between one carbonyl and one phosphine. The splitting for these three complexes is again 0.29 ± 0.02 eV. The identical splitting of the metal-based ionizations for these complexes shows that the π-backbonding stabilization of all of these ligands is essentially the same. From further comparison to a hydride ligand, which has no π interactions with the metal, it was found that these phosphines are one-fourth as effective as CO at π-backbonding stabilization of the metal.[1]

The 0.40 eV M1-M2 separation in the chelating DMPM complex is significantly greater than that for the *cis*-$(PMe_3)_2$ or DMPE complexes. It is not expected that the change in this M1-M2 separation is a difference in π-acceptor ability for the DMPM ligand, because the three phosphines have similar π-acceptor properties in the monodentate complexes. Some other overlap effect must give rise to the M1-M2 separation in the DMPM complex. Two possibilities exist. First, the CH_2 bonding orbital, in addition to interaction with the symmetric PLP combination, points directly at the metal orbital assigned to ionization band M1 (see the previous section). As mentioned, this is a filled-filled interaction that results in destabilization of that *d* orbital which lies between the two P atoms ($d_{x^2-y^2}$). Band M1 correlates to ionization from this orbital. The destabilization of band M1 can also be explained by the PLP-$d_{x^2-y^2}$ filled-filled interaction that is allowed because the DMPM bite angle is very small (≈67°).

The splitting under band M2 in the spectrum of the DMPM complex is more curious. Theory predicts both of these metal-based IP's are unaffected by distortions in the P-Mo-P angles because the phosphine lies in the nodal plane. However, distortions in the local CO coordination geometry could perturb these two ionizations. If the normally 90° OC-metal-CO angle *trans* to the chelating phosphines undergoes a distortion, this would most affect the ionization energy of band M1. If the 180° OC-metal-CO angle *cis* to the chelating phosphine distorts, the ionizations under band M2 would be most affected. Thus, the spectrum of the DMPM complex suggests a possible change in CO coordination geometry for the 180° OC-metal-CO angle. X-ray structures of a methylene bridged chelating phosphine with both phosphorus atoms coordinated to the same metal are rare and a DMPM structure could not be located. The structure of $Mo(CO)_4DPPM$,[5] where DPPM is *bis*(diphenylphosphino)methane, is examined for comparison. The P-Mo-P angle is 67.3(1)° in this structure. The OC-Mo-CO angle for the carbonyls that are *trans* to the phosphines is 94.0(4)°. This distortion does not significantly affect the electronic structure. However, the DPPM structure also has a distortion in the

OC-Mo-CO angle for the CO's *cis* to the phosphines and *trans* to each other. This angle is 167.9° and is 12.1° distorted from the optimum 180°. These CO's are involved in backbonding to the two orbitals assigned to the ionizations under band M2. This distortion, if present in the DMPM complex, would account for the splitting under band M2.

Tungsten-Based Ionizations

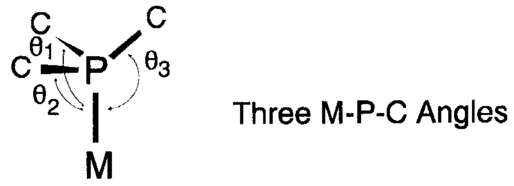
The PES spectra in Figure 5 compare the W 5*d* ionizations for *cis*-$W(CO)_4(PMe_3)_2$, $W(CO)_4$DMPE, and $W(CO)_4$DMPM. These spectra are more complex due to the spin-orbit coupling between the resulting ion-states.[20] Band M2 is most visibly affected (broadened) and is fit with two similar asymmetric Gaussians representing two ion-states (bands M2 and M2*). This splitting is most evident in the DMPM spectrum. The splittings between bands M2, M2*, and M1 in each complex reflect the magnitude of the spin-orbit interaction, however, the broad nature of band M2 does not leave sufficient features to clearly determine accurate IP's of the two spin-orbit split ion-states under this broad band. For this reason, and because of the additional orbital mixing described earlier, there is not sufficient information to carry out a detailed analysis of the spin-orbit coupling parameters.

Comparison of the first IP for each of the complexes gives a similar observation to the one made in the Mo analogues. Band M1 in the complex spectrum of the DMPE is 0.04 eV more stable than that of the *cis*-$(PMe_3)_2$ complex and 0.09eV more stable than band M1 in the DMPM complex. The 0.04 eV difference is more significant in these tungsten complexes as the reproducibility in fitting the single ionization band M1 is ±0.005 eV. The spin-orbit coupling in these W analogues increases the separation of the first and second IP's and has allowed for more accurate comparison of the first IP's of each complex.

The Phosphine Twist

The point that has emerged thus far is that complexes with these three *cis* phosphine systems *cis*-$(PMe_3)_2$, DMPE, and DMPM have very different P-M-P bond angles because of steric or geometric constraints, but that the electron distribution and bonding at the metal is still very much the same in all cases. This is consistent with the essentially identical bond strengths which were observed by de la Vega, *et al.*[6] in the thermochemistry of the *cis*-$(PMe_3)_2$ and DMPE complexes. The DMPM complex was found to have a somewhat smaller ΔH of coordination, and the photoelectron studies show the presence of additional destabilizing filled-filled interactions. How is the similar bonding understood in view of the different geometries? In 1972, Krüger and Tsay published an X-ray structure in *Acta. Cryst. B.* for pseudo-tetrahedral $Ni(DCPM)_2$ (DCPM = *bis*(dicyclohexylphosphino)-methane).[26] In this paper it was briefly mentioned that the local geometry about the phosphorus atoms was distorted due to the 77° P-Ni-P chelate angle (109.5° for a normal tetrahedron). This distortion was observed as inequivalent Ni-P-C(ligand) angles. They first suggested the metal-phosphorus interaction proceeded through a "bent" Ni-P bond. A search for later publications from these two authors concerning this subject revealed nothing further has been written discussing the electronic and steric consequences of this bent bond. In this section, the idea of the bent metal-P bond will be developed and discussed in terms of the electronic and steric considerations.

The bent metal-phosphine bond may be identified by examining the three metal-P-C angles of the trialkylphosphine. If these three angles are equal the phosphine lone pair is pointing directly at the metal. If these angles are different, the phosphine lone pair is directed to a point away from the metal center. This arrangement is referred to here for the first time as the *phosphine twist*. The twist is shown schematically in Figure 6 for the *cis*-$(PMe_3)_2$ and DMPM coordination geometries. The geometrical distortion may by viewed as a pivot of the phosphine about a point along the bond between the metal and the phosphine. In each case, the phosphine is twisted so that the phosphine lone pair is directed at the vacant bonding site rather than at the metal center.



A search for X-ray structures containing *cis*-$(PMe_3)_2$, DMPE, or DMPM was performed to evaluate the consistency of the twist and to determine the "normal" M-P-C angles for an unstrained coordinated PMe_3 ligand. Over 200 structures containing either DMPE or *cis*-$(PMe_3)_2$ ligands were found.[27] No structures of chelating DMPM could be located. For the PMe_3 structures, the *cis*-$(PMe_3)_2$ molecules could be found in both a sterically constrained geometry such as

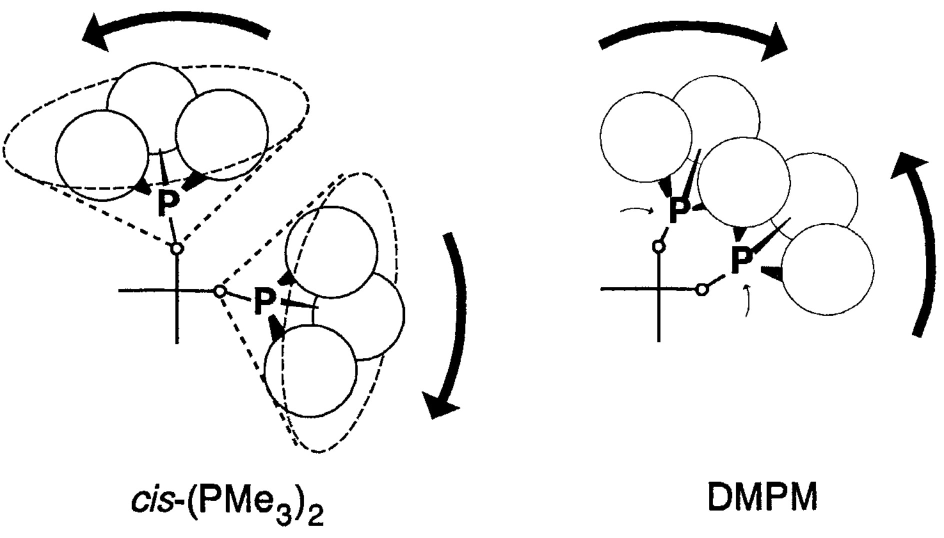


Figure 6 Representation of the phosphine twist distortion.

octahedral or trigonal bipyramidal, but also in non-constrained geometries like tetrahedral or as octahedral *trans*-$(PMe_3)_2$. The latter non-strained example will give the metal-P-C angles free of the twist. The twist was found to be present in each DMPE structure and in only those *cis*-$(PMe_3)_2$ structures having close steric contacts. Of these, several of the most pertinent structures containing both ligand sets are reviewed here. An example of each type of phosphine X-ray structure and the important angles appears in Table 3.

The standard deviation of each M-P-C angle from the average M-P-C angle was chosen as an approximate indication of the twist. The real twist is actually the amount the phosphine lone pair has rotated off the normal bonding axis. The standard deviation of the M-P-C angles was chosen as an indication of the twist because it is derived from numbers that are commonly reported for the structure. Also, the 3σ values for the structures could be used when referring to the significance of the magnitude of the twist value when it is small. The average of all three M-P-C angles is consistently between 115°–117° for all the structures presented. Thus, the standard deviation will express the relative difference in twist value between those phosphines that are twisted and those that are not. The evalution of the twist in terms of these angles is given in Table 4.

Table 3 Structure comparisons for selected metal-phosphines

structure	geometry	P(1)-M-P(2)°	M-P(1)-C°	M-P(2)-C°
$Ni(NO_2)(NO)(PMe_3)_2$	T_d	105.1(1)	116.1(2)	115.6(3)
			114.7(2)	114.3(2)
			115.7(3)	116.2(3)
$W(CO)_5PMe_3$	O_h	NA	116.8(4)	
			116.0(4)	
			113.9(4)	
cis-$W(CO)_4(PMe_3)_2$	O_h	97.44(6)	114.1(4)	a
			112.5(4)	
			123.1(3)	
$[Ni(CH_3)(PMe_3)_4]BPh_4$	TBP	94.4(9)	124.7(3)	116.4(3)
			116.8(3)	116.6(3)
			112.8(3)	118.1(3)
		96.4(9)	123.4(3)	*b*
			118.3(3)	
			111.7(3)	
		97.8(9)	121.4(3)	*b*
			118.1(3)	
			114.2(3)	
cis-$W(CO)_4$DMPE	O_h	80.10(6)	118.2(3)	118.1(3)
			119.4(3)	118.9(3)
			108.7(3)	107.5(3)
cis-$Cr(CO)_2(DMPE)_2$	O_h	82.60(5)	117.8(3)	117.3(3)
			121.6(3)	126.8(3)
			112.0(3)	108.9(3)
trans-$Ti(CH_3)_2(DMPE)_2$	O_h	78.8(1)	123.7(3)	122.8(3)
			117.4(3)	119.1(3)
			110.2(3)	109.2(2)
cis-$Mo(CO)_4$DPPM	O_h	67.3(1)	96.3(3)	97.5(3)
			121.8(4)	120.4(3)
			122.5(3)	123.2(3)

[a] Not used due to disorder in the methyl groups of P(2).

[b] These angles are of the axial PMe_3 given above.

Table 4 Analysis of the phosphine twist.

complex	average M-P-C°	twist value°
$Ni(NO_2)(NO)(PMe_3)_2$	115.4(2)	0.8(2)
$W(CO)_5(PMe_3)$	115.6(4)	1.5(4)
$[Ni(CH_3)(PMe_3)_4]BPh_4$		
equatorial	117.9(3)	4.6(3)
axial	117.0(3)	0.9(3)
cis-$Cr(CO)_2(DMPE)_2$	117.4(3)	6.4(3)
trans-$Ti(CH_3)_2(DMPE)_2$	117.0(3)	6.2(3)
cis-$W(CO)_4DMPE$	115.1(3)	5.5(3)
cis-$Mo(CO)_4DPPM$	113.6(3)	13.0(3)

The $Ni(NO_2)(NO)(PMe_3)_2$ structure[28] has a slightly distorted tetrahedral geometry. The P-Ni-P angle is consistent with the distorted T_d geometry at 105.1(1)°. This angle is large enough that negligible steric contact occurs between the two PMe_3 ligands. As a result, very symmetric Ni-P-C angles are found. For six Ni-P-C angles, the average and standard deviation are $115.4(2) \pm 0.8(2)$°. The phosphines are not considered to be twisted in this molecule.

The $W(CO)_5PMe_3$ structure[29] represents an octahedral geometry. From Table 3, the W-P-C angles are 116.0(4)°, 116.8(4)°, and 113.9(4)°. The latter angle is slightly smaller due to the arrangement of the methyl groups relative to the four *cis* W-CO bonds. The methyl group with the smallest W-P-C angle points out into a OC-W-CO quadrant while the others are more directly over W-CO bonds. Even without another PMe_3 molecule, steric contacts between the C≡O or W-CO bonds twists the phosphine. The methyl group centered into a OC-W-CO quadrant, which has small steric contacts with the C≡O or W-CO bonds, can twist in between the OC-W-CO angle decreasing this W-P-C(methyl) angle and increasing the other two W-P-C(methyl) angles. The average W-P-C angle is 115.6(4) and has a larger twist value equal to 1.5(4)°.

The $[Ni(CH_3)(PMe_3)_4]BPh_4$ structure[2] depicts a trigonal bipyramidal geometry with three equatorial PMe_3 ligands in steric contact with the one axial PMe_3 ligand. The P(axial)-Ni-P(equatorial) angles are all greater than 90° indicating strong steric interaction. The Ni-P(equatorial)-C angles are all severely distorted, twisting in a direction that points the phosphine lone pairs back toward the equatorial coordination sites on the metal. The twist value is 4.6(3)°. The axial PMe_3 has nearly equal Ni-P-C angles. A slight twist may occur due to asymmetric contacts with the methyl groups of the equatorial PMe_3's. However, the twist value is within the 3σ limit. The average Ni-P-C angle is 117.0(3)° with a negligible twist value of 0.9(3)°.

The two DMPE examples, *trans*-$Ti(CH_3)_2(DMPE)_2$[3] and *cis* $Cr(CO)_2(DMPE)_2$,[4] contain twist values that are typical of the DMPE structures we have found. As an example, the average Ti-P-C angle in *trans*-$Ti(CH_3)_2(DMPE)_2$ is 117.0(3) and the twist value is very large at 6.2(3)°. The lone pairs of DMPE ligand are "reaching out" for the vacant coordination sites on the metal even though the bite angle is less than 90°.

The last example is of the *cis*-$Mo(CO)_4DPPM$ structure, which is the source of the estimate for the P-M-P angle in the DMPM complexes. The phosphines is *cis*-$Mo(CO)_4DPPM$ are very severely twisted. The average Mo-P-C angle is 113.6(3)° (out of the normal 115-117° range) and the twist value is a very large 13.0(3)°.

Significance of the Twist to Metal-Phosphine Bonding

In either a *cis*-$(PMe_3)_2$ or chelating diphosphine geometry, the phosphine lone pairs are rotated in the proper direction to achieve the optimum d_{xy}-PLP bonding overlap. According to experiment, the overalp that is achieved is nearly equivalent to that in the 90° P-M-P geometry. This is depicted in Figure 7B for either DMPE or DMPM and in Figure 7C for the *cis*-$(PMe_3)_2$ interaction of the antisymmetric phosphine lone pair combination with the d_{xy} orbital. The optimum overlap is determined by how much the phosphine must twist for a *cis*-$(PMe_3)_2$, DMPE, or DMPM coordination geometry. The magnitude of the phosphine twist is variable and depends upon the extent of the phosphine steric interaction or ring strain. Thus, twisting the phosphine lone pair produces nearly equivalent PLP-d_{xy} overlaps, nearly equal charge on the coordinated phosphorus atoms, and nearly equal M-P bond strengths.

At the metal, deviations in α can cause the lone pairs to interact with the filled $d_{x^2-y^2}$ orbital. This destabilizes this orbital through a filled-filled interaction. At large P-Mo-P angles, the lone pairs can interact with each $d_{x^2-y^2}$ lobe adjacent to the CO ligands. However, in the PMe_3 coordination geometry, the lone pairs are twisted back toward each other and toward the node of the $d_{x^2-y^2}$ orbital, thus minimizing this interaction. In the DMPE case, the lone pairs are twisted away from the lobe of the $d_{x^2-y^2}$ orbital centered between the phosphine lone pairs. This also decreases the interaction between the metal $d_{x^2-y^2}$ and the phosphine lone pairs. Therefore, in either coordination geometry, the phosphine twist can decrease the filled-filled interaction between the metal orbital and the lone pairs. The small shifts in the spectra indicate these filled-filled interactions are negligible, giving the same metal band splitting as for the monodentate complexes where no distortions are present. The DMPM spectra show the largest differences in the metal ionizations compared to the PMe_3 and DMPE spectra. Band M1 becomes destabilized due to interactions of the phosphine lone pair with the lobe of the $d_{x^2-y^2}$ centered between the two phosphine lone pairs or due to interaction with the CH_2 bonding orbital.

CONCLUSIONS

The substitution of monodentate phosphines with chelating analogues has become increasingly more common in the study of metal complexes. The results reported in this manuscript indicate substitution of DMPE for a *cis*-$(PMe_3)_2$ unit can be performed with only a small change in the metal-based ionizations. Substitution of *cis*-$(PMe_3)_2$ with the DMPM chelate causes more significant (but still small) shifts in the first ionization energy because of filled-filled interactions and a break in the degeneracy of the ionizations under band M2 due to changes in the CO coordination geometry. Thus, DMPE is the better chelating analogue when substituting for a *cis*-$(PMe_3)_2$ fragment and will be used in future studies of ligand additivity.

In addition, the process of evaluating the electronic structure of *cis*-monodentate vs. chelate phosphines has revealed that the phosphine is capable of local twisting to relieve the ring strain and steric demands created by DMPE, DMPM, or *cis*-$(PMe_3)_2$ ligands. From an electronic standpoint the result of the phosphine twist, whether in a *cis*-$(PMe_3)_2$, DMPE, or DMPM geometry, can create two "bent" metal-phosphorus bonds with nearly equal metal-P bonding overlap. This twist is in the direction which points the lone pair back toward the metal *d*-bonding orbital.

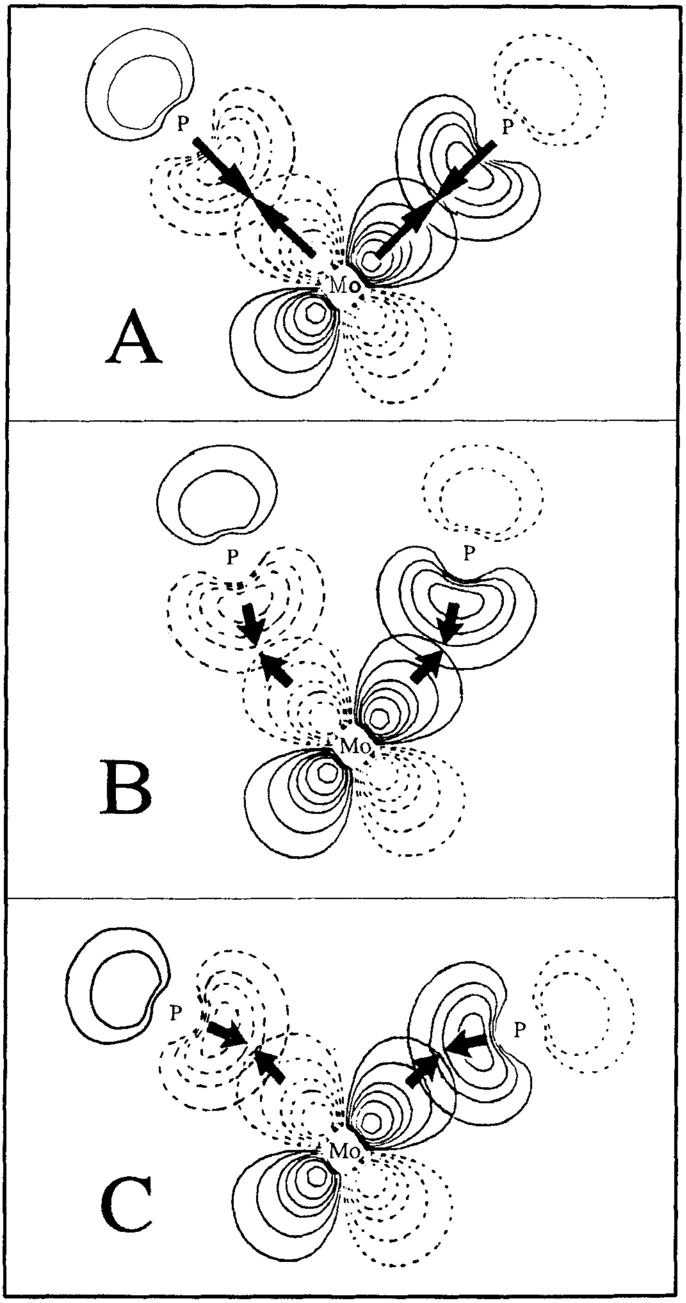


Figure 7 Illustration of the phosphine lone pair alignment with the metal for **A**, P-Mo-P angle idealized to 90°; **B**, P-Mo-P angle less than 90° and with phosphine twist as in DMPM and DMPE coordination; and **C**, P-Mo-P angle greater than 90° and with phosphine twist as in *cis*-$(PMe_3)_2$ coordination.

This is observed in each structure examined. Because the twisted phosphine is off the normal bonding axis, the lone pair orbital no longer points directly at the metal atom, but at a point along the coordination site. These results show that metal-phosphine bonds are not rigid, but can "bend" to accommodate steric interactions or ring strain without large sacrifices in thermodynamic stability.

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