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Electronic Structure of Monodentate-Coordinated Diphosphine Complexes. Photoelectron Spectra of $Mo(CO)_5(P(CH_3)_2CH_2P(CH_3)_2)$ and $Mo(CO)_5(P(CH_3)_2CH_2CH_2P(CH_3)_2)$

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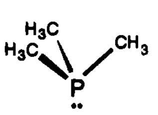
Photoelectron spectroscopy is used to study the electronic structure of molybdenum carbonyl complexes that contain diphosphine ligands bound to the metal through only one of the two phosphorus atoms. This represents the first examination of the relative bonding capabilities of diphosphine ligands in the absence of chelating geometries, which is important for understanding many chelate effects. Photoelectron spectra are reported for $Mo(CO)_5DMPE$ and $Mo(CO)_5DMPM$ and compared to the spectra of $Mo(CO)_5PMe_3$ and the corresponding free phosphine and diphosphine ligands (PMe_3 is trimethylphosphine, DMPE is 1,2-bis(dimethylphosphino)ethane, and DMPM is bis(dimethylphosphino)methane). The energy splittings between the d^6 metal-based ionizations of these complexes indicate that the π-back-bonding ability is the same for each of these phosphine ligands and is relatively small, about 25% that of carbon monoxide. The metal-based ionizations shift only slightly to lower binding energy from the PMe_3 to the DMPE to the DMPM complex (total shift = 0.10 eV) due to a slightly increasing negative charge potential at the metal along this series. This would normally be interpreted as slightly increasing σ-donor strength in the order PMe_3 < DMPE < DMPM. However, the difference between the ionization energy of the coordinated lone pair (CLP) of the phosphine and the ionization energy of the lone pair of the free ligand indicates an opposite trend in σ-donor strength with PMe_3 (1.28 eV) > DMPE (1.27 eV) > DMPM (1.23 eV). The shift of the uncoordinated phosphine lone-pair ionization (ULP) of the monocoordinated diphosphine complexes, which is affected primarily by charge potential effects, reveals that the important factor is a transfer of negative charge from the uncoordinated end of the phosphine through the alkyl linkage to the coordinated phosphine. This transfer is more important for the DMPM ligand because of the shorter alkyl chain between the phosphorus atoms. Aside from these subtle details of charge distribution, the primary conclusion is that the diphosphine ligands, DMPE and DMPM, have σ-donor and π-acceptor strengths extremely similar to those of PMe_3.

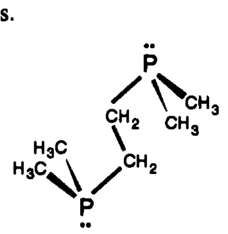
Introduction

The extensive use of phosphine ligands in inorganic and organometallic chemistry has prompted many investigations into the structure, reactivity, and bonding of phosphines (PR_3) to transition-metal centers.[1-7] These investigations have evaluated the phosphines (with differing R groups) in terms of both the electronic interactions and steric size (Tolman cone angles).[8] The electronic capabilities of phosphines, which are the primary focus of this study, are characterized by the σ-donor and π-acceptor strengths. Phosphines with strong electron-withdrawing groups are considered good π acceptors and weak σ donors (i.e. PX_3; X = F, Cl).[9] On the other hand, good inductive donor groups create strong σ donors and weak π acceptors (i.e. $P(alkyl)_3$; alkyl = CH_3, *tert*-butyl, cyclohexyl, etc.). Steric size is equally important in proposed reaction schemes, influencing both associative and dissociative reaction mechanisms in solution or in the gas phase.

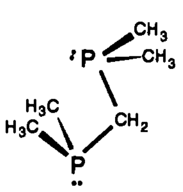
Diphosphines have special significance in the study of metal–phosphine complexes.



PMe_3



DMPE



DMPM

Diphosphines are capable of bonding to the metal center with only one of the two phosphine ends, chelating to the same metal center using the two phosphine ends, or bridging between two metal centers. The use of a chelating diphosphine in place of two cis-PR_3 groups gives the metal complex greater kinetic stability (reducing dissociative decomposition mechanisms), which may assist certain chemical or spectroscopic investigations. This feature of the diphosphines has prompted our interest into their electronic structure in relation to the additive electronic effects of successive phosphine substitution on metals, as revealed previously by gas-phase photoelectron spectroscopy.[10-17] In place of complexes with two cis-PMe_3 groups, we can examine metal complexes containing chelating diphosphines with the general formula $Me_2P(CH_2)_xPMe_2$ (x = 1, 2) and extend the range of phosphine-substituted com-

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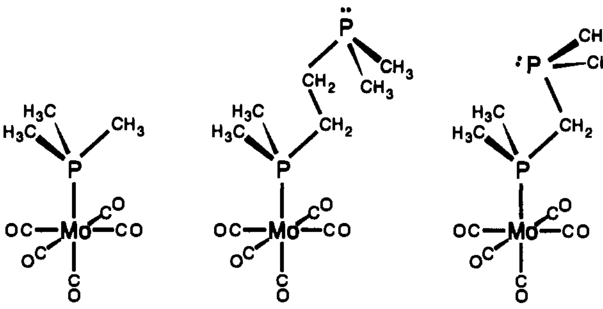
plexes suitable for gas-phase investigation (i.e. $M(CO)_2(diphosphine)_2$ or $M(diphosphine)_3$). The common assumption in the substitution of a chelating diphosphine in place of two cis-PR_3 groups is that the bond strengths and electronic interactions (σ and π) of the diphosphine unit in the chelating geometry are essentially identical to those of the two cis monodentate phosphines. However, the extent that this assumption is valid has not been put to a rigorous test.

Separation of the σ and π effects of a ligand on the basis of an observed chemical or physical (spectroscopic) property of a transition-metal complex is not always clear. This is because of the synergistic relationship of σ-donation and π-acceptance, both of which alter properties related to the charge potential at the metal center. Photoelectron spectroscopy (PES) has been shown to be particularly useful for the separation of ligand σ- and π-bonding effects because the valence ionizations are separately dependent on the σ- and π-symmetry interactions.[14,15] These principles have been illustrated in the study of additive ligand electronic effects in the series $Mo(CO)_{6-n}(PMe_3)_n$ ($n = 1, 2, 3$).[12,13] In these d^6 metal complexes, the energy splitting between the metal-based ionizations gives a measure of the relative π-back-bonding ability of CO vs PMe_3, and the overall shift of individual metal-based ionizations gives a measure of the total charge distribution effects.

The ionizations from the coordinated phosphine ligand are also sensitive to the ligand donor and acceptor properties.[18] Most important here is the ionization of the phosphine lone pair, which forms the metal–phosphorus σ bond through donation to the metal center. The combination of metal-based and ligand-based ionization energies gives direct information on the relative metal–phosphorus bond strengths of different phosphines with the same metal complex fragment.[10–17,19] These previous photoelectron studies of metal–phosphine complexes provide the foundation for the study of metal–diphosphine complexes presented here.

The precise electronic effects of substituting a chelating diphosphine for two cis phosphines, and the choice of a chelating diphosphine with the most similar electronic and bonding properties to the pair of phosphines, is one subject of this research. The initial study reported in this paper compares the metal and ligand electronic structure of molybdenum pentacarbonyl complexes for two diphosphines, bis(dimethylphosphino)methane (DMPM) and 1,2-bis(dimethylphosphino)ethane (DMPE). These potentially bidentate diphosphines are bound to the metal by only one of the phosphines in these $Mo(CO)_5$(phosphine) complexes, allowing direct electronic structure comparison with the monocoordinated analogue, $Mo(CO)_5PMe_3$ (A). Subsequently, we will show the effects of the chelating geometry and steric factors.



A B C

Experimental Section

Synthesis. The complexes $Mo(CO)_5DMPM$, $Mo(CO)_5DMPE$, and $Mo(CO)_5PMe_2$ were prepared by the published procedure involving Et_3OBF_4 addition to $[Mo(CO)_5Br]NEt_4$ in the presence of the appropriate phosphine.[20,21] The preparations of the complexes were performed in a Vacuum Atmospheres drybox. Following the reactions, the solvents were removed on a high-vacuum synthesis line at 1×10^{-6} Torr and the diphosphine complexes were obtained as oils. The complexes were characterized by IR spectroscopy in the CO stretching region (1800–2100 cm^{-1}). The IR spectra of $Mo(CO)_5DMPE$ and $Mo(CO)_5PMe_3$ correspond with the reported literature values.[22] The IR spectrum of $Mo(CO)_5DMPM$ has not been reported previously. It gives a spectrum with intensity pattern and stretching frequencies essentially identical to that of the DMPE and PMe_3 complexes [$Mo(CO)_5DMPM$: 2072 cm^{-1} (w) and 1942 cm^{-1} (vs multiple bands)]. All solvents were distilled from the appropriate drying agent and degassed with nitrogen before use. DMPE and DMPM were purchased from Strem Chemical and were used as received. PMe_3 was prepared by the method of Sattleberger et al.[23] and was characterized by ^{31}P and ^1H NMR spectroscopy.

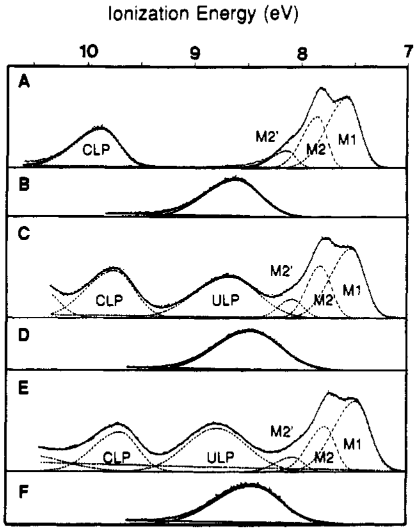


Figure 1. He I spectra for $Mo(CO)_5PMe_3$ (A), PMe_3 (B), $Mo(CO)_5DMPE$ (C), DMPE (D), $Mo(CO)_5DMPM$ (E), and DMPM (F).

Photoelectron Spectra. The photoelectron spectra were measured on an instrument built around a McPherson 36-cm radius hemispherical analyzer with specially designed photon sources, ionization cells, power supplies, counter interface, and collection methods that have been described elsewhere.[24–26] The argon $^2P_{3/2}$ ionization at 15.759 eV was used as an internal calibration lock of the energy, and the CH_3I $^2E_{1/2}$ ionization at 9.538 eV (both ±0.003 eV) provided an external calibration of the energy scale. The spectra were obtained for each compound within the range of the following cell temperatures: $Mo(CO)_5DMPM$, 50 ± 4 °C; $Mo(CO)_5DMPE$, 50 ± 4 °C; $Mo(CO)_5PMe_3$, 35 ± 4 °C (as measured via an Omega 2170A digital thermometer equipped with a K-type thermocouple passed through a vacuum feedthrough and attached directly to the ionization cell). The spectra for the free ligands, DMPM and DMPE, were obtained at room temperature. These liquids were introduced into the instrument via a glass tube regulated with a needle valve. 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 half-widths 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.[27–29] 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

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Table I. Ionization Potentials and Band Assignments for the $Mo(CO)_5P$ Complexes

complex	band	IP, eV	W_h	W_l	rel area	assgnt
$Mo(CO)_5PMe_3$	M1	7.57	0.45	0.27	1.85	^2E
	M2	7.85	0.34	0.19	1.00	$^2B_2$
	M2′	8.14	0.34	0.19	0.34	ν_1(CO)
	CLP	9.87	0.61	0.36	1.35	Mo–P
$Mo(CO)_5DMPE$	M1	7.52	0.46	0.29	1.87	^2E
	M2	7.81	0.29	0.24	1.00	$^2B_2$
	M2′	8.07	0.29	0.24	0.36	ν_1(CO)
	ULP	8.65	0.75	0.62	2.02	PLP
	CLP	9.72	0.60	0.44	1.76	Mo–P
$Mo(CO)_5DMPM$	M1	7.48	0.48	0.31	2.08	^2E
	M2	7.77	0.37	0.23	1.00	$^2B_2$
	M2′	8.06	0.37	0.23	0.33	ν_1(CO)
	ULP	8.76	0.66	0.66	2.13	PLP
	CLP	9.66	0.56	0.40	1.40	Mo–P
PMe_3		8.59	0.68	0.50		PLP
DMPE		8.45	0.76	0.64		PLP
DMPM		8.43	0.79	0.60		PLP

energies reported for the overlapping metal ionizations are reproducible in these methods to about ±0.02 eV.

Results

Photoelectron Spectra. The spectra of the metal–phosphine complexes and of the free phosphine ligands are compared in the region of 7–10.5-eV ionization energy in Figure 1. The analytical representation of the data is given in Table I.

The spectra of the free ligands PMe_3 (Figure 1B), DMPE (Figure 1D), and DMPM (Figure 1F) show a single band in the low-valence region, which correlates to ionization of the phosphine lone pairs. The free-molecule ionization energy of PMe_3 given in Table I was obtained in this laboratory previously.[12] The valence ionization energies of DMPE and DMPM have been reported previously by others,[19] and there are some small differences between the previous values and those presented here. The previously published values for the first ionization energies are 8.47 eV for DMPE and 8.51 eV for DMPM, in comparison to 8.45 eV for DMPE and 8.43 eV for DMPM from this work. These differences are most likely due to a combination of the lower signal-to-noise and the use of symmetric Gaussian band fits to estimate the vertical ionization potentials in the previous work. Asymmetric Gaussian shapes are used in this work. The theoretical rationale and practical consequences of asymmetric Gaussians for the representation of valence ionization data have been discussed in detail elsewhere.[28,29] When compared to estimates of the vertical ionization energies with the symmetric Gaussian approximation, the asymmetric Gaussian model gives slightly lower values. More importantly, the trend of slightly decreasing ionization energy from PMe_3 to DMPE to DMPM, as discussed later, is obtained in the present results.

For each of the complexes $Mo(CO)_5PMe_3$ (Figure 1A), $Mo(CO)_5DMPE$ (Figure 1C), and $Mo(CO)_5DMPM$ (Figure 1E), the assignments of the predominantly ligand-based and metal-based valence ionizations are straightforward and have been presented in previous PES studies of metal–phosphine complexes.[12,13] The band between 9.7 and 9.8 eV in the spectrum of each complex is due toionization from the coordinated phosphine lone-pair (CLP) orbital. This ionization is primarily phosphorus lone pair in character and correlates to the Mo–P σ bond in each complex. The ionizations in the 7.5–8-eV range originate from the formally Mo(0), d^6 metal center. The intensity pattern between bands M1 and M2 will be discussed later. Band M2′ represents CO vibrational fine structure associated with ionization from band M2. We have observed fine structure of this type previously in studies of molybdenum carbonyl complexes.[12] Table I shows a small 0.09-eV destabilization of the metal ionization energies from the PMe_3 complex to the DMPM complex, with the DMPE complex intermediate.

The spectra of the monocoordinated diphosphine complexes contain an additional band at 8.5–9.0 eV that is not present in the spectrum of $Mo(CO)_5PMe_3$. This band correlates to ionization from the uncoordinated phosphine lone pair (ULP) of each diphosphine ligand. The shift of the ULP ionization energies from the free-ligand ionization energies is key to understanding the charge distribution in each of the diphosphine complexes.

Discussion

As shown in previous photoelectron investigations of metal–phosphine complexes, the outer valence electronic structure leads to ionizations which correlate to the metal-based d orbitals and to the phosphine lone-pair orbitals. The significance of the shifts and splittings of these ionizations for understanding the electronic structure and bonding of these complexes has been discussed extensively elsewhere.[10–17] Focusing first on the metal-based ionizations, it is recognized that the metal $d\pi$ orbitals split into the e and b_2 symmetry sets in the local C_{4v} symmetry of the $Mo(CO)_5$(phosphine) complexes. The two $d\pi$ orbitals which form the e set each back-bond to three CO molecules and one phosphine. The remaining $d\pi$ orbital is b_2 symmetry and back-bonds to the four CO's which are cis to the phosphine. This gives rise to the 2:1 intensity patterns of the metal ionizations of Figure 1. The difference in the stabilization of the b_2 type orbital relative to the e types is just the difference in π-back-bonding interaction between a CO and the phosphine. CO is the more effective back-bonding ligand, and thus the b_2 ionization is at higher energy than the e ionization. The separation in energy between these ionizations is 0.29 ± 0.02 eV in each complex of this study, indicating that the π stabilization is the same by this technique for each phosphine ligand. For comparison, the separation between the corresponding metal ionizations of $Mn(CO)_5H$ and $Re(CO)_5H$ (after removal of Re spin–orbit splitting) is 0.40 ± 0.02 eV.[30] The hydride clearly has no π-acceptor ability, so this is the approximate splitting to expect if the phosphines also had no π-acceptor ability. It appears from this analysis that these phosphines are weak π-acceptor ligands, being about 25% as effective as carbonyl at π-back-bonding overlap stabilization of a metal d orbital.

The change in charge potential at an atom shifts an entire manifold of ionization bands equally if the orbital characters are all primarily based on the same atom. This is observed for the metal ionizations in this series. The metal-based ionizations of the DMPE complex (Figure 1C) are all 0.05 ± 0.02 eV destabilized from those of the PMe_3 complex (Figure 1A). The metal-based ionizations of the DMPM complex (Figure 1E) are all 0.09 ± 0.02 eV destabilized from those of the PMe_3 complex. These individual shifts are small, indicating that only subtle differences in negative charge potential are felt at the metal for these three ligands. In comparison, the charge potential shift for PMe_3 in place of CO is 0.50 ± 0.02 eV.[12]

The increase in negative charge potential at an atom may be due to an increase in electron density on that atom, an increase in negative charge on neighboring atoms, or both. These are termed the one-center and two-center charge effects, respectively. Changes in electron relaxation energies with ionization are also pertinent, although these are basically coupled to the charge distribution and flow and are not considered separately.[31] Interpretation of the metal ionization energy shifts in terms only of an increase in local, one-center electron density leads to the suggestion of slightly more negative charge on the metal in the order $Mo(CO)_5DMPM > Mo(CO)_5DMPE > Mo(CO)_5PMe_3$. This directly implies a similar order for the σ-donor abilities of the phosphine ligands.

However, the two-center charge effects must not be neglected. The energy of the metal orbitals will also be perturbed by changes in the magnitude of the charge on the coordinated phosphorus atom in either the phosphine or diphosphine ligands. A greater negative charge at the coordinated phosphorus atom in one complex will destabilize the filled metal levels due to the two-center effect. Additional experimental evidence is needed to identify which charge effect controls the destabilization of the metal ionizations and how this relates to the σ-donor abilities of the

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ligands. Further information on the two-center charge potential comes from analysis of the phosphine ligand-based ionizations.

Free-Ligand Ionizations. The ionization energies for all three free ligands are important, as they represent the starting ionization energies of the phosphorus lone pairs before interaction with the metal to form the Mo–P bond. The spectra of the free ligands, DMPE and DMPM, show only one low-valence band correlating to ionization from both of the phosphorus lone pairs of the diphosphine. It is possible for these two lone pairs of the diphosphines to interact through-space or through-bond in an intramolecular fashion. These interactions, if present, would create a splitting of the symmetric and antisymmetric combinations of the lone pair ionizations. In the gas phase, it is known that the DMPM molecule adopts a staggered conformation.[32] Since the P–P distance is smaller in DMPM than in DMPE (through-bond or through-space), these effects should be more prominent in the lone-pair ionization of DMPM.

No splitting is observed in the lone-pair ionizations of either free diphosphine molecule. Furthermore, the band shapes for DMPE and DMPM are similar. Comparison of the band shapes of all three free ligands shows that the lone-pair ionization of PMe_3 (W_l and W_h in Table I) is narrower by about 0.1 eV overall than the DMPE and DMPM bands. However, this broadening for DMPE and DMPM does not necessarily indicate through-space and through-bond contributions to the DMPE and DMPM band shapes. The broader ionization band of the diphosphines is most likely due to an increase in activated vibrational states upon ionization of the lone pair in the less symmetrical diphosphines. Regardless of the interpretation of these small bandshape differences, they do not influence the conclusions presented here.

The more important point is the energy of these free ligand ionizations. As shown in the results, the first ionization energies of DMPE and DMPM are very similar (within 0.02 eV) and about 0.15 eV less than the first ionization energy of PMe_3. The trend in ionization energies reflects the relative charge at that phosphorus atom, as determined by the donor strength of the substituent R groups in $(CH_3)_2PR$, where R is $-CH_2CH_2PMe_2$ for DMPE and R is $-CH_2PMe_2$ for DMPM. The alkyl chain is shorter for DMPM than for DMPE, bringing the PMe_2 donor group closer to the other phosphorus lone pair. The ionization energies for the analogous phenyl complexes 1,2-bis(diphenylphosphino)ethane (DPPE) and bis(diphenylphosphino)methane (DPPM) at 7.86 and 7.79 eV, respectively. These data show the trend that is expected on the basis of the R group donor strength.

Ligand Ionizations: Uncoordinated Lone Pair. Each of the monocoordinated diphosphine complexes contains an additional ionization in their spectra (at ≈8.7 eV) not present in the $Mo(CO)_5PMe_3$ spectrum (Figure 1). The additional ionization is from the uncoordinated phosphine lone-pair (ULP) orbital. This orbital has negligible direct overlap interaction with the metal. Thus, for each diphosphine, the difference between the ionization energy of the uncoordinated lone pair and the corresponding ionization energy of the free ligand is primarily a result of the difference in negative charge at these phosphorus atoms. The shifts to higher ionization energy of the uncoordinated lone pairs indicate a loss of negative charge on the uncoordinated phosphorus atom relative to the free ligands. This charge has most likely transferred toward the coordinated phosphorus atom through the CH_2 groups of the diphosphines. The energy of this ionization for the coordinated diphosphines is now significantly different ($Mo(CO)_5DMPE$, 8.65 (1) eV; $Mo(CO)_5DMPM$, 8.76 (1) eV), in contrast to the situation for the free diphosphines (DMPE, 8.45 eV; DMPM, 8.43 eV). The shift relative to the DMPM free-ligand value is 0.33 (1) eV compared to 0.20 (1) eV for the case of DMPE. The higher ionization energy for the DMPM uncoordinated lone pair indicates a greater shift of negative charge from this uncoordinated phosphorus atom relative to the same uncoordinated phosphorus atom in the DMPE complex. The shorter alkyl chain (methylene group) in DMPM apparently allows more charge transfer than the longer ethylene chain in DMPE. This is the most significant difference between the ionization energies of these complexes.

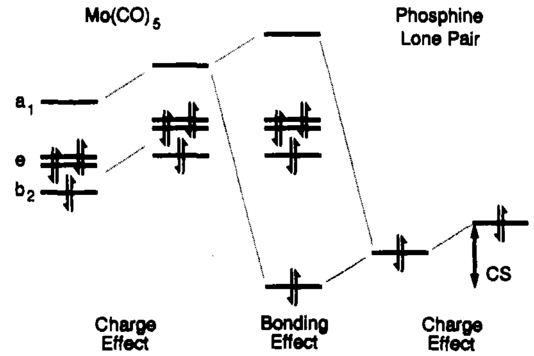

Figure 2. Orbital interaction diagram for PR_3 and an $M(CO)_5$ fragment.

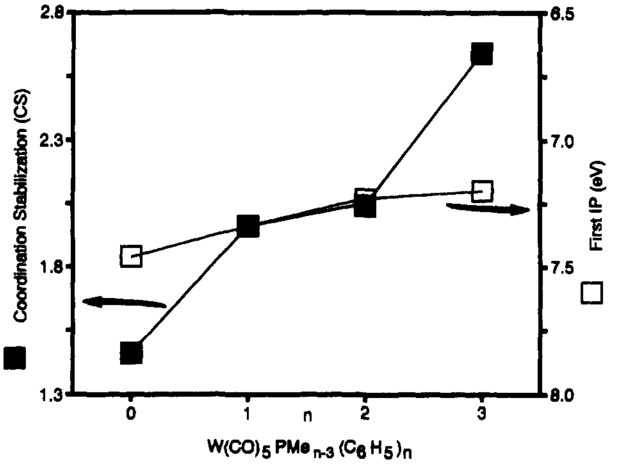

Figure 3. Coordination stabilizations and first ionization energies for $W(CO)_5PMe_{3-n}Ph_n$ (n = 0–3).

Ligand Ionizations: Coordinated Lone Pair. Each of the three complexes possesses an ionization near about 9.7 eV. This ionization correlates with the coordinated phosphorus lone-pair (CLP) orbital and corresponds to the Mo–P σ bond. Figure 2 shows an energy decomposition analysis of the interaction of a phosphine lone pair with a $M(CO)_5$ fragment. Upon coordination of the phosphine, the ionization stabilizes according to both the charge redistribution and bonding overlap between the metal and the phosphorus lone pair. The total shift of the ionization is termed the coordination stabilization (CS). The filled metal d block destabilizes in turn, as shown from the left of the figure, due solely to the charge transferred to the metal (one-center) and/or the phosphorus point charge felt by the metal (two-center), as described previously.

An estimation of the individual charge and overlap contributions to the CS depicted in Figure 2 is accomplished by comparison of valence UPS and core XPS data. The valence CS obtained in this study for $Mo(CO)_5PMe_3$ is 1.28 ± 0.01 eV and the core CS from a previous publication is 0.78 ± 0.1 eV.[13] The valence shift includes the contributions from both the change in charge potential at the atom and the change in bonding. The core shift includes only the change in charge potential. From Jolly's studies of the correlation of valence and core ionization energy shifts, the valence ionizations shift approximately 0.8 times as much as the core ionizations due to the change in charge potential.[33] Thus, the change in charge potential contribution to the valence shift is about 0.8 times 0.78 eV, or 0.64 eV. The bonding contribution to the valence shift is the remaining portion, which is about 1.28 − 0.64 eV, or 0.64 eV. Thus, the charge potential and the bonding contributions to the total valence coordination stabilization are about the same, as illustrated in Figure 2.

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(32) Rankin, D. A.; Robertson, H. E.; Karsch, H. H. *J. Mol. Struct.* **1981**, *77*, 121.

(33) Jolly, W. L. *Acc. Chem. Res.* **1983**, *16*, 370.

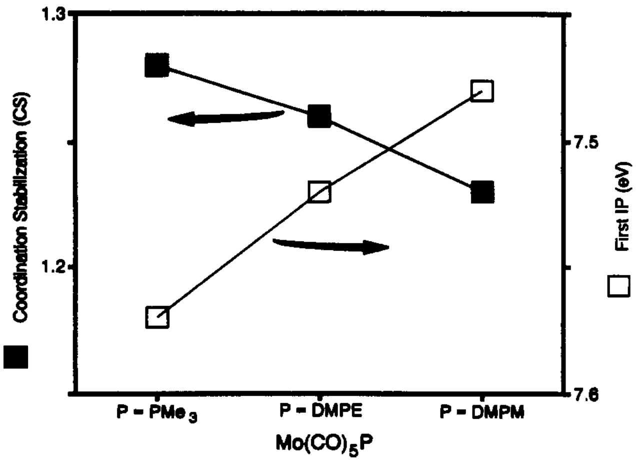

Figure 4. Coordination stabilizations and first ionization energies for $Mo(CO)_5P$ ($P = PMe_3$, DMPE, DMPM).

Bancroft has studied the W–P bond ionizations for a series of monophosphine- and diphosphine-substituted tungsten carbonyl complexes.[19] In that work, an increase in CS was interpreted as an increase in the σ-donor ability of a particular phosphine and hence an increase in the charge donated to the metal. The consistency in this interpretation can be tested by examining the trend in CS in comparison to the shifts in the metal-based ionization energies. This comparison is shown in Figure 3 for several phosphines in the series $W(CO)_5PMe_{3-n}Ph_n$ ($n = 0$–3, $Ph = C_6H_5$). The plot indicates PPh_3 is the best donor (largest CS). This complex also has the lowest first (metal-based) ionization energy, in agreement with the above assumption. The trend in first ionization energy tracks nearly linearly across the series from PMe_3 to PPh_3. The CS values are more erratic. This is because all CS values contain a contribution from bonding, and this contribution is different for different R groups. One factor in this case is that the successive substitution of phenyl groups for the methyl groups changes the R–P–R angles. Altering the R–P–R angles changes the moment of 3s vs 3p character mixed into the phosphorus lone-pair (PLP) orbital of the free ligand and changes the extent of overlap (metal d or p mixing) in the metal–P bond. Therefore, CS energies for phosphines with different R–P–R angles contain a variable bonding contribution. The correlation of the CS to charge potential effects (reflecting the relative σ-donor ability) therefore is less direct, although the general trend that is expected is maintained in this series.

The contribution of changes in R–P–R angles is less of a problem for the complexes in the present study because the R donor groups are all similar ($-CH_3$ or $-CH_2$). The individual diphosphine ligand R–P–R angles should be nearly identical, and any changes in the R–P–R angles upon coordination will be relatively constant. Subtraction of the free-ligand lone-pair ionization energy from the CLP ionization energy for each of the complexes gives the coordination stabilization energies 1.28 (1), 1.27 (1), and 1.23 (1) eV for the PMe_3, DMPE, and DMPM complexes, respectively. On the basis of the coordination stabilization/σ-donor correlation, this trend would predict the relative σ-donor strengths are quite similar, decreasing slightly in the order $PMe_3 >$ DMPE $>$ DMPM. However, the decreasing trend $PMe_3 >$ DMPE $>$ DMPM does not agree with the observed shift of the metal ionizations or with expectations based on the relative R donor strengths.

Figure 4 shows the trend in CS and first ionization energy for the three phosphines of this study, similar to Figure 3 for the phenyl phosphine complexes. In this case, the CS value decreases as the metal-based first ionization energy destabilizes. This result is opposite to the expected direct correlation discussed above and demonstrated by the tungsten series of $PMe_{3-n}Ph_n$ complexes. If the charge had been transferred to the metal via the Mo–P bond, the coordination stabilization shift should be largest for the DMPM complex, where the coordinated phosphorus arom is more negatively charged and has a closer energy match to the metal levels. However, the coordination stabilization shifts are in the opposite direction with DMPM, showing the smallest coordination stabilization.

These trends result from the compensation of charge provided by the uncoordinated end of the diphosphines. As the coordinated end of the diphosphine donates charge to the metal center, the charge is more effectively compensated in the DMPM complex because of the shorter alkyl chain between phosphorus atoms. The change in bonding contribution to the shift is diminished by this compensation of charge, and hence the coordination stabilization is decreased. The charge potential at the metal center is also increased by this electron redistribution. Thus, the coordination stabilization does not necessarily reflect the strength of bonding when this kind of charge compensation takes place. The shifts in charge potential apparently dominate the shifts in ionization energies. The differences in bonding contributions (σ-donor and π-acceptor) to the shifts are much less important and must be nearly the same for all three ligands.

Conclusions

The electronic structures of $Mo(CO)_5$DMPE and $Mo(CO)_5$DMPM have been compared to $Mo(CO)_5PMe_3$. We conclude that the σ-donor and π-acceptor properties of these three ligands are extremely similar. The small metal and ligand-based ionization shifts seen in these monocoordinated complexes can be attributed almost entirely to the charge imbalance present when one end of a diphosphine is uncoordinated. The shifts reflect the negative charge on the coordinated phosphorus atoms in the order DMPM $>$ DMPE $> PMe_3$ due to the charge transfer through the diphosphine alkyl chain. The metal ionizations of the DMPE and DMPM complexes are slightly shifted compared to the PMe_3 complex primarily by a two-center charge potential effect from the more negatively charged coordinated phosphorus atom. The shifts follow from the inductive nature of the R groups in Me_2PR ($R = -CH_3$, $-CH_2CH_2PMe_2$, or $-CH_2PMe_2$). The negative charge on the bound phosphorus atom increases in the order $-CH_3 < -CH_2CH_2PMe_2 < -CH_2PMe_2$.

These small effects should be even less significant when both ends of the diphosphine are coordinated to the same metal or bridging between two metal centers. In these geometries, charge compensation is not the same, as each end of the diphosphine contributes identical charge and overlap effects to the individual metal–P bonds. Further investigations which directly compare the electronic structure consequences of substituting a chelating DMPE and DMPM ligand for a cis-PMe_3 unit are underway. On the basis of the present study, it appears that the assumption that the bond strengths and electronic interactions of a chelating diphosphine are very similar to those of two cis-monodentate phosphines is quite reasonable, provided that geometric effects do not intervene.

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