Inorg. Chem. **1984**, *23*, 1545–1549

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Electronic Excited States of Arylphosphine Complexes of Copper(I) Halides

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Perturbation of the electronic transitions of aromatic phosphine ligands upon coordination to copper(I) has been investigated. The lowest electronic transition ($1 \rightarrow a_\pi$) of arylphosphines associated with an electron excitation from the lone electron pair of the phosphorus to an antibonding phenyl π orbital can be enhanced by coordination to copper(I). The phosphine–copper(I) electronic transition is classified as a σ,d $\rightarrow$ a_π transition. The transition is described as an electron excitation from the metal–phosphorus bond with a concerted donation of electron density from the metal to the phosphorus via d–d orbital back-bonding. The photophysical properties of the methyldiphenylphosphine complexes of the isoelectronic d^{10} metals Ni(0), Cu(I), and Zn(II) are shown to be consistent with the σ,d $\rightarrow$ a_π classification. The Ph$_3$P and MePh$_2$P complexes of CuX have phosphorescence lifetimes of 2–6 ms which are decreased from those of the free ligands where the lifetimes are 17 ms for Ph$_3$P and 40 ms for MePh$_2$P. By comparison, the phosphorescence lifetime of (MePh$_2$P)$_2$ZnCl$_2$ and (MePh$_2$P)HCl are 55 and 49 ms, respectively.

Introduction

Copper(I), having an electronic d^{10} structure, exhibits no low-energy ligand-field excited states.[1-3] Cuprous compounds are normally white[4] unless color results from an internal ligand or charge-transfer excitation band. The few articles that have suggested electronic transition assignments for phosphine–cuprous halide complexes[3,5-7] all seem to agree that the electronic transitions of the complexes are internal ligand processes that are only slightly perturbed by the bonding of the ligand to the metal. Since the electronic transitions are considered internal ligand processes, the same confusion recently described for the electronic transition assignments of the aromatic phosphines[8a,b] also appears in the literature for the arylphosphine–cuprous halide complexes. Our study of the solution dissociation properties of L$_3$CuX (L = Ph$_3$P, MePh$_2$P; X = Cl, Br, I) complexes[8a,c] indicated that the dissociation of the complexes has apparently masked a proper interpretation of the effect of metal coordination on the electronic transitions of the arylphosphines. The results of this study clearly show that coordination of arylphosphines to copper(I) halides has a pronounced effect on the lowest excited electronic state transition ($1 \rightarrow a_\pi$)[8a,b] of the ligands.

Experimental Procedures

Materials and Synthesis of Inorganic Complexes. Materials and the synthesis of the Ph$_3$P and MePh$_2$P complexes of CuX were the same as described previously,[8a,c]

[Ph$_2$P(CH$_2$)$_2$PPh$_2$]CuCl. The (diphos)CuCl complex, diphos = Ph$_2$P(CH$_2$)$_2$PPh$_2$, appears in the literature with the empirical formula given;[9] however, osmometry data indicate that the complex actually exists in the trimer form.[9a] The molecular weight of 1500 measured in benzene at 37 °C during this study (empirical formula weight equals 497) is in agreement with the literature. The exact structure of the trimer form is still not known. In order to be consistent with the current literature, the diphos complex will be referred to in this article by the empirical formula.

(MePh$_2$)$_2$ZnCl$_2$. This complex was prepared in the same manner as the copper complexes; mp 179–181 °C. Anal. calcd for C$_{26}$H$_{26}$P$_2$ZnCl$_2$: C, 58.30; H, 4.89; P, 11.56; Cl 13.24. Found: C, 58.43; H, 5.01; P, 11.69; Cl 13.03. (Ph$_3$P)$_2$ZnCl$_2$ has been reported and studied extensively;[10] however, no reference could be found for (MePh$_2$P)$_2$ZnCl$_2$.

(MePh$_2$)HCl. The protonated phosphine is assumed to be the product made by bubbling a 5–10-mL phosphine solution (benzene or EPA (ethyl ether–isopentane–ethanol)) with dry HCl for 1–2 min. The HCl was dried just prior to use by bubbling it through concentrated sulfuric acid. From the large change in the absorption spectra (see Results) essentially all of the phosphine was probably in a protonated form. No analysis or isolation of the salt was attempted. The phosphine solutions had to be rather dilute (less than approximately 5 × 10^{-4} M) or a white precipitate would be formed while the solution is bubbled with the dry HCl.

Spectra and Phosphorescence Lifetimes. The various spectra reported and phosphorescence lifetime measurements were accomplished with the same procedures as described for the arylphosphines.[8a,b] The 77 K absorption spectra were obtained by using the square quartz-tip

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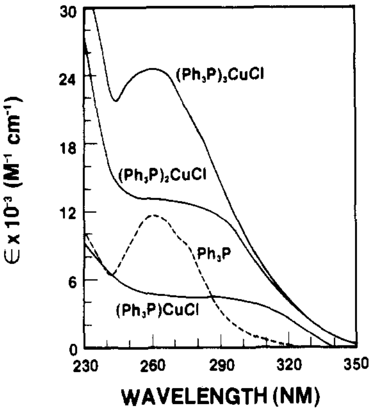

Figure 1. Absorption spectra of $(Ph_3P)_3CuCl$ (6.0×10^{-4} M CuCl, upper curve), $(Ph_3P)_2CuCl$ (5.8×10^{-4} M CuCl, middle curve), $(Ph_3P)CuCl$ (1.0×10^{-3} M CuCl, lower curve), and Ph_3P (----). The $(Ph_3P)_3CuCl$, $(Ph_3P)_2CuCl$, and $(Ph_3P)CuCl$ formulas indicate the ratio of Ph_3P to CuCl in solution and not the actual structures of the complexes that may exist in solution. Solvent: methylene chloride/cyclohexane in a 1:99 volume ratio.

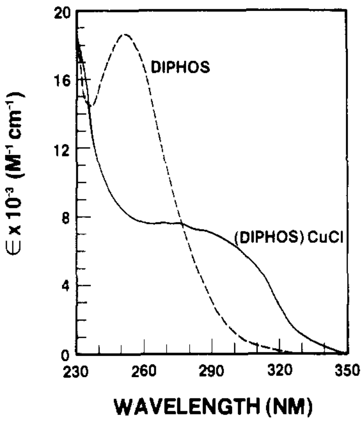

Figure 2. Absorption spectra of (diphos)CuCl (empirical formula) and diphos [diphos = $Ph_2P(CH_2)_2PPh_2$]. No significant change in the extinction coefficient noted for 4.4×10^{-4} to 4.4×10^{-6} M solutions of (diphos)CuCl. Solvent: methylene chloride/cyclohexane in a 1:99 volume ratio.

spectrophotometric Dewar flasks described in the emission study of the arylphosphines. For the room temperature and 77 K absorption spectra in EPA, the spectrophotometric Dewars were placed in the reference and sample holders of the Beckman ACTA V. The 4 mm inside width square quartz cells previously described were used to contain the sample and reference solutions. After the absorption spectrum was taken at room temperature, the spectrophotometric Dewars were filled with liquid nitrogen and the absorption spectrum was taken again.

Results

The dependence of the absorption spectra of $(Ph_3P)_3CuCl$ and $(MePh_2P)_3CuCl$ with concentration in a methylene chloride/cyclohexane (1:99 volume ratio) mixed solvent was recently reported.[8a,c] The absorption spectra of $(Ph_3P)_3CuX$ and $(MePh_2P)_3CuX$ (X = Cl, Br, I) showed no appreciable changes with halogen substitution. The absorption spectra of Ph_3P and various ratios of Ph_3P to CuCl are shown in Figure 1. The absorption spectra of (diphos)CuCl in comparison to diphos is shown in Figure 2. The absorption spectra of $(Ph_3P)_3CuCl$ and $(MePh_2P)_3CuCl$ were also taken in EPA (a 5:5:2 volume ratio) at room temperature and at 77 K. Figure 3 illustrates the results for the $(MePh_2P)_3CuCl$ complex. Similar to the $(MePh_2P)_3CuCl$ spectrum, the $(Ph_3P)_3CuCl$ spectrum shows an increase in intensity at 77 K in comparison to the 298 K spectrum. It also shows at 77 K a distinct absorption band centered at 295 nm as a shoulder on a slightly more intense absorption band centered at 260 nm, the 260-nm absorption region showing some fine structure.

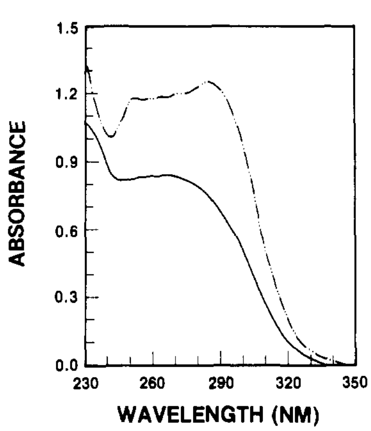

Figure 3. Absorption spectra of $(MePh_2P)_3CuCl$ of the same solution ($\sim 10^{-4}$ M) in EPA at room temperature (—) and at 77 K (— ·· —). A 4-mm² cell used.

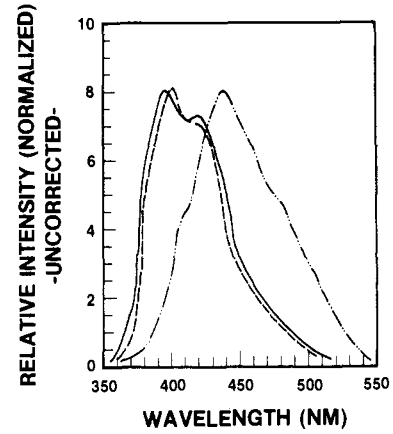

Figure 4. Phosphorescence spectra of $(MePh_2P)CuCl$ (—), $(MePh_2P)_3CuCl$ (- -), and $MePh_2P$ (— ·· —) in EPA at 77 K. Excitation at 305 nm. Emission spectra normalized to the same maximum intensity for comparison. The $(MePh_2P)CuCl$ formula indicates the ratio of $MePh_2P$ to CuCl in the EPA and not the actual structure that may be present in the EPA glass.

Table I. Phosphorescence Lifetimes, τ_{ph}, of (Arylphosphine)copper(I) Halide Complexes Measured in EPA at 77 K

compound	τ_{ph}, ms[d]	compound	τ_{ph}, ms[d]
Ph_3P	17	$MePh_2P$	40
$(Ph_3P)CuCl$[a]	3	$(MePh_2P)CuCl$[a]	4
$(Ph_3P)_2CuCl$[a]	5	$(MePh_2P)_2CuCl$[a]	5
$(Ph_3P)_3CuCl$	6	$(MePh_2P)_3CuCl$	5
		$(MePh_2P)_3CuBr$	4
$Ph_2P(CH_2)_2PPh_2$	38	$(MePh_2P)_3CuI$	2
$Ph_2P(CH_2)_2PPh_2CuCl$[c]	13	$(MePh_2P)_2ZnCl_2$[b]	55
		$(MePh_2P)HCl$[b]	49

[a] The formulas as written indicate the ratio of the ligand to CuCl and not the actual structure of the complexes that may exist in the EPA glass. [b] Included for comparison. [c] Empirical formula. [d] Lifetimes are given to a precision of 1 ms. Comparisons with known phosphorescence lifetimes were better than this.[8b]

The excitation and emission spectra of the phosphine complexes were also studied. The room temperature excitation and emission spectra of the L_3CuX complexes (L = Ph_3P, $MePh_2P$) in benzene or cyclohexane were identical with those of the free ligand. However, the emission efficiency was reduced greatly. The 2:1 ratio of L to CuCl solutions as well as (diphos)CuCl showed extremely weak emissions at very dilute concentration which also appeared identical with those

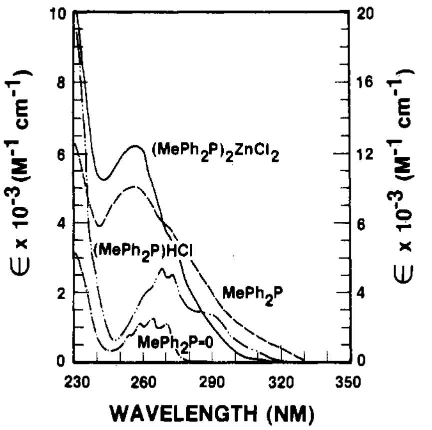

Figure 5. Absorption spectra of $(MePh_2P)_2ZnCl_2$ (—), $MePh_2P$ (- -), $(MePh_2P)HCl$ (– ·· –), and $MePh_2P{=}O$ (– · –). The right ordinate refers to $(MePh_2P)_2ZnCl_2$; the left ordinate refers to $MePh_2P$, $(MePh_2P)HCl$, and $MePh_2P{=}O$. Solvent: EPA (room temperature).

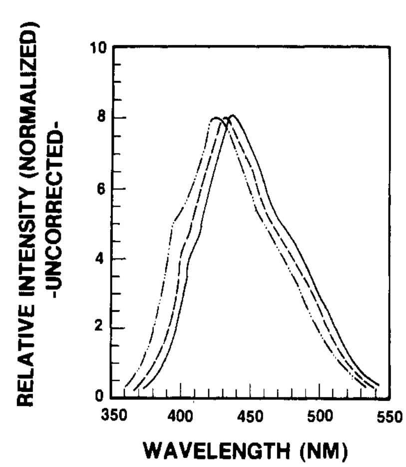

Figure 6. Phosphorescence spectra of $(MePh_2P)_2ZnCl_2$ (– ·· –), $(MePh_2P)HCl$ (- - -), and $MePh_2P$ (—) in EPA at 77 K. Excitation at 305 nm. Respective lifetime measurements are 55, 49, and 40 ms. Spectra are normalized to the same maximum intensity for comparison.

of the free phosphines. No emission was observed at room temperature for the 1:1 ratio of L to CuCl solutions. At 77 K (EPA glass) no fluorescence was detected for any of the (phosphine)copper complexes; however, rather strong phosphorescence was observed. The phosphorescence spectra of the complexes were all very similar, showing only very minor changes with the different phosphine to copper ratios. The phosphorescence spectrum of $(MePh_2P)_3CuCl$ in comparison to that of $MePh_2P$ is shown in Figure 4. Figure 4 also includes the phosphorescence spectrum of the 1:1 ratio of $MePh_2P$ to CuCl illustrating the minor change observed with different phosphine to copper ratios. Even though the emission spectra of the phosphine complexes showed very little variance with halogen substitution or with phosphine to copper ratio, the lifetime measurements showed some notable changes (Table I). The excitation spectra for phosphorescence of the (phosphine)copper(I) complexes were all the same, showing maximum emission with excitation at ~290 nm. The excitation characteristics were identical with those described for the free phosphines[8a,b] in that essentially no emission was observed for excitation at the shorter wavelengths of 200 to ~250 nm.

The absorption and emission spectra of $(MePh_2P)_2ZnCl_2$ and $(MePh_2P)HCl$ were also taken for comparison with the copper complexes. $(MePh_2P)HCl$ refers to solutions of $MePh_2P$ bubbled with dry HCl (see Experimental Procedures). The absorption spectra in EPA at room temperature of $(MePh_2P)_2ZnCl_2$, $(MePh_2P)HCl$, $MePh_2P{=}O$, and $MePh_2P$ are shown in Figure 5. The same spectra at 77 K all show more detail of the fine structure and an overall increase of intensity with the exception of $(MePh_2P)_2ZnCl_2$. At 77 K $(MePh_2P)_2ZnCl_2$ shows the typical increase in intensity at wavelengths <275 nm; however, a slight decrease in intensity is observed at the longer wavelengths (>275 nm) in comparison to the room temperature absorption. The excitation and emission spectra of $(MePh_2P)_2ZnCl_2$ and $(MePh_2P)HCl$ are similar to that of the free ligand with the exception of a small shift to shorter wavelengths. The phosphorescence spectra are shown in Figure 6. In contrast to the copper complexes of $MePh_2P$, the phosphorescence lifetimes of the zinc complex and the protonated phosphine increased in comparison to the free ligand rather than decreased (see Table I).

Discussion

The ligand dissociation of the L_3CuX complexes[8a,c] has obviously concealed the distinct changes that occur in the absorption spectra of the free ligand upon metal coordination. For example, the close correspondence of the shape and band maxima in the UV absorption spectra of $(Ph_3P)_3CuX$ to that of Ph_3P (Figure 1) has been stated as evidence that the electronic states of Ph_3P are not altered to any significant extent upon coordination of the ligand to copper(I).[3c] Solution dissociation studies have shown that the first ligand dissociation constant ($L_3CuX \rightleftharpoons L_2CuX + L$) of the Ph_3P complexes is relatively large[11] ($K_{eq} \simeq 10^{-2}$ in benzene at 37 °C),[8a,c] the large dissociation constant being attributed to intramolecular steric repulsion of Ph_3P in the tetrahedral structure. The absorption spectra of $(Ph_3P)_3CuX$ and Ph_3P must have the same general characteristics at 10^{-4} or 10^{-5} M because the solution made from $(Ph_3P)_3CuX$ will have an appreciable concentration of Ph_3P dissociated from the complex. The addition of the Ph_3P spectrum and $(Ph_3P)_2CuCl$ spectrum in Figure 1 gives almost the identical absorption spectrum measured for $(Ph_3P)_3CuCl$, indicating that very little or no tris complex, $(Ph_3P)_3CuCl$, exists in solution at 6.0×10^{-4} M CuCl. The room temperature emission of the complexes would also have to be associated with the free ligand dissociated from the complexes. The emission is very dependent on the concentration of the complex, the emission increasing with dilution. The room temperature emission of the complexes is identical with that of the fluorescence of the free ligands; however, at 77 K no fluorescence is observed, while the phosphorescence of the complexes is distinctly different from that of the uncoordinated ligand. The reduction of temperature to 77 K apparently eliminates the dissociation of the ligand from the complex, and the ligand fluorescence is not longer observed. The intersystem crossing of the $(MePh_2P)_3CuX$ complexes have been calculated as 1.0 from the photosensitized isomerization of NBD to Q in benzene at room temperature.[8a]

The absorption spectra of 2:1 and 1:1 ratios of Ph_3P or $MePh_2P$ to CuCl clearly show a distinction in comparison to the free ligand absorption spectra. By the use of higher concentrations and short path lengths, the true character of the $(MePh_2P)_3CuX$ complexes can be observed. The absorption spectra of $(MePh_2P)_3CuCl$ and $(Ph_3P)_3CuCl$ at 77 K also reveal the distinct absorption characteristics of the complexes in comparison to the ligand. At 77 K three distinct absorption regions become apparent in the complexes. The two regions associated with the benzene-like transitions are still present, the K region (200–240 nm) and the B band (with fine structure) at ~250–280 nm.[12] There is a third band at ~290–300 nm that is observed in the complexes (Figures 1–3)

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that is not apparent in the ligands at room temperature or at 77 K. The solutions were cooled such that the dissociation complex had time to reassociate. The equilibrium constant has a large temperature dependence.[8]

The absorption spectra of all the (arylphosphine)copper(I) halide complexes studied show a long-wavelength absorption band centered at 290–300 nm. The excitation spectra of the phosphorescent emission of the complexes must correspond to this absorption band since the maximum emission is observed with an excitation at 290 nm. The higher excited states which are most logically assigned to the $\pi \rightarrow \pi^*$ localized transitions of the phenyl π system apparently do not effectively decay to the lowest excited state associated with the 290–300-nm absorption. The intensity of the benzoid-like band in the 250–280-nm region of the complexes is decreased slightly from that of the free ligand (normalizing for the number of ligands in the complex) while the longer wavelength band at 290 nm which is not apparent in the free ligand is increased considerably. The slight change in intensity of the B band could be due to a combination of factors. With the bonding of the lone electron pair of the phosphorus to the metal, an inductive donation of electron density to a phenyl excited π system by the phosphorus would most likely be reduced. This effect would reduce the intensity of the localized phenyl transition in a similar manner to that observed in the phosphine oxide. However, the phenyl π structure of the ligand in the copper complex will also be affected by the electrostatic potential field caused by the central metal ion and the other ligands. Since the B band of benzene is a symmetry-forbidden band, any electrostatic perturbation of the six symmetrical π electrons in the $C_6H_6^{6+}$ core field would increase the intensity of the transition.[13] Other localized ligand electronic transitions have shown increased absorption intensity upon coordination with transition metals, with the increase attributed to an electrostatic potential field effect caused by the metal.[14] Thus, there seems to be two opposing factors in the determination of the change in the intensity of the B band of the phosphine with metal coordination. This could account for only a slight decrease in the intensity of the 250–270-nm absorption band of the phosphine with coordination to copper(I) as opposed to a much larger decrease with protonation or oxidation.

The lowest excited state of the (arylphosphine)copper(I) complexes appears to be an enhancement of the $l \rightarrow a_\pi$ ($n \rightarrow \pi^*$ character) transition[8a,b] assigned to the free arylphosphines in which one of the phosphorus lone pair electrons is excited into an antibonding phenyl π orbital. The phosphorescence spectra of the complexes as illustrated in Figure 4 show maxima with a separation of ~1400 cm^{-1}. Since this would correspond to a P–Ph stretching frequency, we have tentatively assigned it this way.[15] The first inflection of the phosphorescence spectra at 378 nm would correspond to a triplet energy of 76 kcal/mol. The millisecond phosphorescence lifetime is still reflective of an $n \rightarrow \pi^*$ state. The excitation spectra of the complexes are essentially identical with those of the free arylphosphines. However, the observation of an enhancement of an ($n \rightarrow \pi^*$)-like transition upon coordination of the nonbonding electrons with a metal would seem improbable. The nonbonding electrons upon coordination with a metal should require considerably higher energy for excitation. The disappearance or shift to shorter wavelengths of an absorption band upon protonation or metal coordination is one of the tests for an $n \rightarrow \pi^*$ transition in carbonyl compounds.[16] Protonation of $MePh_2P$ on coordination with zinc(II) gives the expected results of a shift in absorption spectra to shorter wavelengths, a longer lifetime, and a higher excited state energy (Figures 5 and 6). The increase in intensity of the benzoidlike band of the $(MePh_2P)_2ZnCl_2$ complex is most likely associated with the perturbation of the electronic structure of the phenyl ring by the metal. Apparently, with zinc(II) the perturbation of the phenyl electronic symmetry becomes more significant than in the case of copper(I).

Table II. Promotion Energy[a] and Electron Affinity of Ni(0), Cu(I), and Zn(II)[b]

	promotion energy, eV	electron affinity, eV
Ni(0)	1.72	1.2
Cu(I)	8.25	7.72
Zn(II)	17.1	17.96

[a] $nd^{10} \rightarrow nd^9 (n+1)p$. [b] Reproduced from ref 17.

The enhancement of intensity of the $l \rightarrow a_\pi$ transition of the arylphosphines (the 290–300-nm absorption band) upon corrdination to copper(I) can be rationalized by the involvement of d–d orbital bonding of the phosphine and copper. The electron density of the phosphorus would be transferred to copper by a σ bond as a result of lone-pair donation from the phosphorus to the copper(I). The d orbitals of the phosphorus could in turn be the recipient of electron density and a filled copper d orbital. The overall synergistic effect could result in a stabilization of a $\sigma \rightarrow a_\pi$ electronic transition. The $\sigma \rightarrow \alpha_\pi$ transition refers to an excitation of an electron from the phosphorus–metal σ bond to the phenyl antibonding π orbital system (a_π). A concerted response from the metal could be a large donation of electron density to the phosphorus through d–d bonding. The donation of electron density to the phosphorus during the excitation process could stabilize the excited state. The excited-state geometry of the free phosphines can be concluded to be considerably different from the ground state on the basis of the increased intensity of the higher vibronic structure in the fluorescence and phosphorescent emission. However, the excited-state geometry of the (arylphosphine)-copper complexes shows more similarity to the ground-state geometry. This is indicated by the stronger intensity or more allowed transitions observed in the lower vibronic states of the phosphorescent emission (Figure 4). The donation of electron density during the excitation process could stabilize the geometry of the excited state with respect to the ground state. This would greatly increase the probability of the electronic transition and thus enhance the intensity of absorption. The net effect of the excitation process described could be considered a charge transfer of metal to ligand (CTTL). There is no simple nomenclature to fully describe the excitation mechanism proposed. Using orbital nomenclature, the use of a $\sigma,d \rightarrow a_\pi$ transition would be appropriate. The σ,d indicates that synergistic bonding is involved in the transition, and thus the nature of the metal would have a great effect on the electronic transition.

The effect of the metal on the $\sigma,d \rightarrow a_\pi$ electronic transition described would depend on the metal's ability to accept electrons into the bonding orbitals and the metal's ability to donate electrons from its d orbitals. In describing concepts of metal–olefin binding, Bishop[17] suggested that the ability of the metal to accept electron density could be approximated by the electron affinity of the metal and the donating ability

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by its promotion energy. Table II presents the appropriate data for Ni(0), Cu(I), and Zn(II).

The high promotion energy and high electron affinity of Zn(II) indicate that Zn(II) would be a very poor electron donor but an excellent electron acceptor. Thus, the phosphine–zinc(II) bond would be considered to be primarily a σ bond with little or no orbital back-bonding. The σ,d → a_π transition of the (arylphosphine)zinc(II) complexes would be expected to have characteristics similar to a protonated arylphosphine, i.e., a shift to higher energies compared to the free ligand, longer phosphorescent lifetimes, and similar excited-state geometry to that of the free phosphine. All of these characteristics are observed for $(MePh_2P)_2ZnCl_2$ (Figures 5 and 6).

Copper(I) has a much lower promotion energy and electron affinity than zinc(II) and as described could stabilize the excited-state geometry and enhance the probability of the electronic transition of the ligand. The observed photophysical properties are consistent with this concept. The energies of the σ,d → a_π transitions of the (arylphosphine)copper complexes studied are all about the same as those of the free ligands. The phosphorescence lifetimes of these complexes are all shorter than those of the respective ligands (Table I), and their excited-state geometries are much more similar to the ground state than are those of the uncoordinated phosphines.

Nickel(0) with its very low promotion energy and electron affinity would be expected to result in even greater changes than copper(I) in the σ,d → a_π electronic transition. Tolman and co-workers[18] studied several nickel(0)–phosphine complexes and concluded that the longer wavelength absorptions of the complexes with P–Ph groups involved substantial excitation of the benzene ring. The longest wavelength absorption band of $(MePh_2P)_4Ni$ is centered at 380 nm with an extinction coefficient of 2×10^3 M^{-1} cm^{-1}. Apparently, the σ,d → a_π transition in the $(MePh_2P)_4Ni$ complexes is considerably lower in energy than the $(MePh_2P)_3CuCl$ transition, which has an absorption around 290–300 nm. Thus, the concept of a σ,d → a_π electronic transition as described is consistent with the d^{10} metal series Ni(0), Cu(I), and Zn(II). An area of future investigation involves the interesting observation that if the concept of the σ,d → a_π transition is correct, the energy of the transition in metals such as Ni(0) and Cu(I) might be regulated by controlling the electron density of the metal by the use of specific electron-donating or -withdrawing ligands mixed with the arylphosphine ligands coordinated to the metal. Of course the electron density controlling ligands could not have electronic transitions lower than the arylphosphines.

Conclusions

(1) The electronic transitions of the (arylphosphine)copper(I) halide complexes have never been adequately evaluated or defined. One of the principal reasons has probably been due to the absorption and room temperature fluorescence being dominated by the dissociated ligand in solution. Absorption and emission spectra are normally taken at very dilute concentrations where the monodentate (phosphine)copper(I) halide complexes show considerable dissociation. By the use of higher concentrations and short path lengths, the true character of the complexes can be observed. Also the absorption spectra taken at 77 K reveal the correct absorption spectra of the complexes without contamination by free ligand. The absorption spectra of the (arylphosphine)copper(I) halide complexes show some distinct differences when compared to those of the free phosphines.

(2) Coordination to copper(I) has a pronounced effect on the lowest excited electronic state of the ligand. The lowest electronic state of the (arylphosphine)copper halide complexes has been described as a perturbation or enhancement of the l → a_π (n → π^* character) electronic transition of the free arylphosphines. The orbital nomenclature assigned to the lowest energy electronic transition of the complexes is a σ,d → a_π transition, the σ,d indicating that both the σ bond of the phosphorus lone electron pair to the metal and the d–d orbital back-bonding of the metal to the phosphorus are involved in the transition. The excitation of an electron from the σ bond to the phenyl antibonding π orbital system (a_π) is countered by a concerted donation of electron density or electron transfer to the phosphorus through the d–d orbital bonding. The donation of electron density can be described as a stabilizing factor to the excited state. The σ,d → a_π transition mechanism could adequately explain the arylphosphine electronic transition differences upon coordination to Ni(0), Cu(I), and Zn(II).

(3) The lowest triplet energy of the (arylphosphine)copper(I) complexes studied shows very little variance from an average value of 76 kcal/mol.

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Registry No. Ph_3P, 603-35-0; $(Ph_3P)_3CuCl$, 15709-76-9; $MePh_2P$, 1486-28-8; $(MePh_2P)_3CuCl$, 36386-10-4; $(MePh_2P)_3CuBr$, 36386-11-5; $(MePh_2P)_3CuI$, 36386-12-6; $(MePh_2P)_2ZnCl_2$, 81314-25-2; $(MePh_2P)HCl$, 89486-27-1; $Ph_2P(CH_2)_2PPh_2$, 1663-45-2; $Ph_2P(CH_2)_2PPh_2CuCl$, 15380-26-4; $MePh_2P{=}O$, 2129-89-7.

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