yielding "theoretical" B and C values. The fact that such a fit was reasonably accurate is again related to the predominant d character of open-shell orbitals in the complex.

Clearly, the SCF calculations predict all interelectronic repulsion parameters to be smaller in the complex than in the free ion. The reasons are apparently related to the covalency of the complex, as originally invoked by Jørgensen.[31] The global reduction of the parameters may be described roughly by a factor 0.85, suggesting a significant "central-field covalency". The difference between the reduction of the $a(J_{tt})$ and the $e(J_{ee})$ parameters reflects the greater covalency of the dσ orbital ("symmetry-restricted covalency").

Qualitatively, the calculations thus reproduce the experimental finding that $\beta < 1$; but, quantitatively, the reduction factor of ~ 0.85 is not very satisfactory when compared to the semiempirical value of ~ 0.6. As stressed before, the agreement does not improve at the ΔSCF level, since the total energies hardly change upon relaxation.

Conceptually, the classical interpretation of the nephelauxetic effect can be maintained only at the frozen-orbital level of approximation: the open-shell repulsion is smaller in the more voluminous orbitals of the complex. But, at the ΔSCF level, the excitations within one given open shell do *not* correspond to an increase of the open-shell repulsion—neither in Cr^{3+} nor in the complex. In this sense, the nephelauxetic effect is only remotely connected to the open-shell repulsion.

Conclusions

Many features of classical crystal field theory are confirmed by detailed ab initio SCF calculations. Most notably the metal ion is found to behave more or less as an isolated entity within the complex; the open-shell orbitals are of predominant metal 3d character and are slightly antibonding with the ligands.

Conceptually, however, the crystal field picture is modified rather thoroughly at several points. More specifically, the intraconfigurational transitions from the $^4A_{2g}(t_{2g}^3)$ ground state to the excited t_{2g}^3 doublets are found to be accompanied by a *decrease* in interelectronic repulsion and an *increase* in the one-electron terms. The interconfigurational transition corresponding to the classical $10Dq$ excitation is found to correspond to a *decrease* in the potential energy and an *increase* in kinetic energy. Both conclusions are in conflict with the crystal field picture.

Numerically, the Hartree–Fock calculations are only qualitatively satisfactory; especially, the intraconfigurational transitions are calculated too high. Since the basis set used in this work is of rather high quality, the only method to improve the quantitative results would be to include extensive configuration interaction and/or the effect of the second coordination sphere.

Registry No. $Cr(CN)_6^{3-}$, 14897-04-2.

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Contribution from the Department of Chemistry and Biochemistry, Utah State University, UMC 03, Logan, Utah 84322

Solution Equilibria of Tertiary Phosphine Complexes of Copper(I) Halides

DENNIS J. FIFE, WILLIAM M. MOORE, and KAREN W. MORSE*

The solution equilibria in benzene of arylphosphine complexes of the type $L_mCu_nX_n$ (L = Ph$_3$P, MePh$_2$P; X = Cl, Br, I; m:n = 3:1, 4:2, 3:2, 2:2, 4:4) have been investigated by using UV spectrometry and vapor pressure osmometry. The halogen appears to have only a minor effect on the dissociation. A detailed analysis of the chloride complexes shows that ligand dissociation of the L$_3$CuCl complexes is also accompanied by dimerization of the coordinately unsaturated copper(I) complexes through halogen bridging. However, the dimeric and tetrameric species formed by halogen bridging are found to be significant species in solution only when the ratio of L to CuCl is less than 3:1. An equilibria system is proposed with equilibrium constants derived from the modeling of the experimental data. The constants for the single ligand dissociation from (Ph$_3$P)$_3$CuCl and (MePh$_2$P)$_3$CuCl are 2×10^{-2} and 2×10^{-4}, respectively. With the much greater dissociation of the Ph$_3$P complex, the (Ph$_3$P)$_2$CuCl species is the dominant form in a benzene solution made from the solid-state (Ph$_3$P)$_3$CuCl complex. Solution profiles of different ratios of L to CuCl are generated to show how various species present in solution vary with concentration. The stability of the $L_mCu_nCl_n$ complexes (Ph$_3$P $\ll$ MePh$_2$P) toward ligand dissociation is attributed to greater steric interactions of Ph$_3$P in comparison to MePh$_2$P.

Introduction

Detailed crystal structures have been determined for complexes of the general formula $L_mCu_nX_n$ (L = R$_3$P (R = alkyl or aryl); X = Cl, Br, I; m:n = 3:1, 4:2, 3:2, 2:2, 4:4).[1-6] Representations of the various structures are shown in Figure 1. The complete series of structures (a–f) have not been isolated for any one given ligand. The preferred crystal structure of a given complex of this type appears to be governed by the steric size of the ligand. For bulky ligands such as triphenylphosphine or tricyclohexylphosphine, substantial intramolecular steric repulsions (R--R and R--X) have been suggested to hinder the approach of the halogen to the metal atom prohibiting effective formation of halogen bridging.[6,7]

Structural integrity is not necessarily retained when these complexes are placed in solution.[7-9] Attempts to identify and determine the relative concentrations of the various species present in the solution phase have met with little success. The formation of polynuclear species through halogen bridging in conjunction with ligand dissociation causes many experimental

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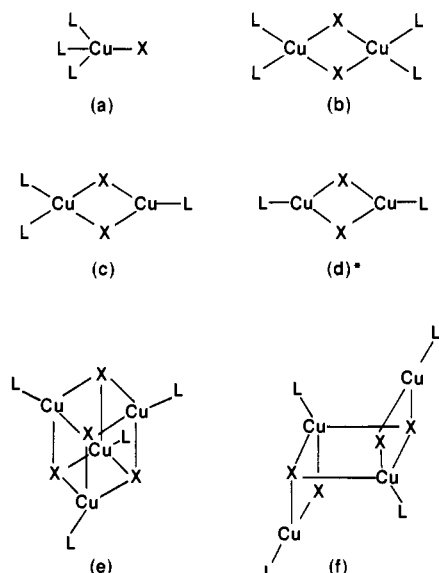
Figure 1. Solid-state structural types of monodentate tertiary phosphine copper(I) halide complexes (L = ligand; X = halide): (a) monomeric L_3CuX; (b) dimeric $L_4(CuX)_2$; (c) dimeric $L_3(CuX)_2$; (d) dimeric $L_2(CuX)_2$; (e, f) cube, chair of tetrameric $L_4Cu_4X_4$. The asterisk indicates the only known crystal structure of this form to date where L = tricyclohexylphosphine and X = chloride.[4]

and theoretical difficulties in the quantitative study of the equilibria. The equilibria are suggested to be dependent upon the nature of L, the solvent, and the temperature.[7] Due to rapid ligand exchange, NMR techniques are limited in providing meaningful data.[7,8] Ultraviolet spectrophotometric data appear sensitive for determining the ligand to metal ratio but insensitive to dimeric or tetrameric species formed by halogen bridging.[9,10] Colligative properties, being dependent on the number of dissolved particles, can be particularly useful for following complex equilibria; however, the inherent disadvantage and limitation of techniques based on colligative properties is that the solute concentration must necessarily be fairly high.[7] Despite these difficulties, our study of the photosensitization ability of L_3CuX complexes in benzene (L = Ph_3P, $MePh_2P$) required a more detailed investigation of the dissociation equilibria of the complexes in benzene near room temperature. Vapor pressure osmometry as well as UV spectrophotometry were the primary investigative techniques employed in the study.

Experimental Section

Materials. CuX (X = Cl, Br, I) was prepared by standard procedures.[11] All other chemicals were purchased commercially and used without further purification. Only spectral grade solvents were used.

$(Ph_3P)_3CuX$, $(MePh_2P)_3CuX$, $(Ph_3P)_2CuCl$, $(Ph_3P)_3Cu_2Cl_2$, $(MePh_2P)_3Cu_2Cl_2$, $[(Ph_3P)CuCl]_4$, and $[(MePh_2P)CuCl]_4$. These complexes were all prepared according to literature procedures[1-9,12-16] and also by a more simplified procedure. The simplified procedure gave the same results as the more time-consuming procedures in the literature and therefore was used exclusively. The simplified synthesis consisted of mixing stoichiometric amounts of the respective arylphosphine and CuX in a small volume of methylene chloride. For

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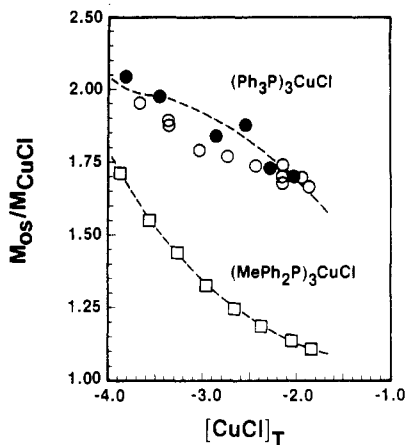(16) Blau, R. J. M.S. Thesis, Utah State University, Logan, UT, 1981.

5×10^{-3} mol of CuX, approximately 10-15 mL of methylene chloride mixed with the appropriate amount of phosphine was sufficient to bring the CuX into solution. The solutions containing a 1:1 ratio of CuX to phosphine were heated slightly while stirring until all the CuX was dissolved. Pentane, hexane, or cyclohexane was added to the clear solutions until a white precipitate began to form. The cloudy solutions were then cooled in an ice bath and allowed to stand for a few minutes before filtering. The product was usually used without further purification since recrystallization in many cases led to mixtures of CuX:phosphine ratios. Even though the synthesis of $[(MePh_2P)CuCl]_4$ has been reported[16] and the elemental analysis showed the proper 1:1 ratio of ligand to CuCl, the tetrameric form was apparently assumed by Blau[16] since no evidence was presented to distinguish between monomeric, dimeric, or tetrameric forms. The melting point reported was 126-130 °C.[16] When the simplified synthesis described was used, a 128-130 °C melting point was observed. The complex is extremely soluble in benzene and also shows rapid discoloration (2-3 days) if not stored under an inert atmosphere. These observations seemed to be more indicative of monomer crystal structure with incomplete coordination of the copper. However, a concentrated benzene solution gave a measured molecular weight of 1145 by vapor pressure osmometry. The calculated tetramer molecular weight would be 1197. Thus, the tetramer structure appears to be correct. The crystal lattice energy of $[(MePh_2P)CuCl]_4$ must be much weaker than that of $[(Ph_3P)CuCl]_4$, which is very insoluble in benzene and has a reported melting point of 236-240 °C.[12b,c]

$(MePh_2)_2CuCl$. The $(MePh_2P)_2CuCl$ formula as written is not meant to indicate a structure but a 2:1 ratio of $MePh_2P$ to CuCl. Even though the solid-state complex of the Ph_3P derivative has been suggested to exist as a monomer structure,[14] the 2:1 $MePh_2P$:CuCl complex has not been reported in the literature. The $(MePh_2P)_2CuCl$ complex was prepared according to the same procedures already described. Anal. Calcd for $C_{26}H_{26}P_2CuCl$: C, 62.53; H, 5.25; P, 12.40; Cl, 7.10. Found: C, 62.37; H, 5.16; P, 12.39; Cl, 7.13. The crystalline product gave a melting point of 159-161 °C. The calculated molecular weight for the empirical formula $(MePh_2P)_2CuCl$ would be 499. The measured molecular weight by vapor pressure osmometry in a benzene solution varied with concentration. With the more concentrated benzene solution (10^{-2} M) the molecular weight appeared to equilibrate at 660. As will be shown, the results of this study lead to the conclusion that an equilibrium is established between the following structures in a concentrated benzene solution: $(MePh_2P)_3CuCl$, $(MePh_2P)_2CuCl$, $(MePh_2P)_4(CuCl)_2$, and $(MePh_2P)_3(CuCl)_2$. Projection of the benzene equilibrium would indicate that crystallization from a solvent providing greater solubility would produce predominantly the saturated dimer, $(MePh_2P)_4Cu_2Cl_2$.

Osmometric Measurements. Measurements were done at 37 °C with two different vapor pressure osmometers: (1) Mechrolab Model No. 301A and (2) Wescan Instruments 233. The osmometers were calibrated with triphenylphosphine and triphenylphosphine oxide. The solvent was spectral grade benzene. The Mechrolab osmometer gave a reproducible value within 3-4% of the standard at 10^{-2} M. The Wescan osmometer gave a value within 10% of the standard at the most dilute concentrations ($\sim 2 \times 10^{-4}$ M) and within 2-3% of the standard at concentrations $\geq 10^{-3}$ M.

Mass Spectrometry. A Hewlett-Packard 5992 GC/MS and a LKB 2091 GC/MS system were used to obtain the mass spectra.

Absorption Spectra. UV absorption spectra and measurements were recorded on a Beckman ACTA V UV–visible spectrometer. Spectrophotometric cells with a path length varying from 1 to 20 mm were used.

Results

The electron impact mass spectra of $(Ph_3P)_3CuX$ and $(MePh_2P)_3CuX$ (X = Cl, Br, I) showed only the mass spectra identical with that of the respective free ligand. This was true for a column-injected benzene solution sample using the GC/MS or using a heated solid inlet probe.

Vapor pressure osmometry measurements of the L_3CuX (L = Ph_3P, $MePh_2P$; X = Cl, Br, I) complexes were originally done on the Mechrolab Model No. 301A osmometer. These osmometry measurements were limited to a very narrow concentration of 10^{-2} to 2.5×10^{-2} M due to the lower limit of the vapor pressure osmometer and the maximum solubility of the complexes in benzene. The ratios of the measured

Figure 2. Vapor pressure osmometry measurements: O, $(Ph_3P)_3CuCl$; □, $(MePh_2P)_3CuCl$. Measurements made by adding 1 equiv of Ph_3P to solutions made from $(Ph_3P)_2CuCl$ are indicated by ●. The ratio of the osmometric measured molarity of the benzene solutions at 37 °C to the calculated total molarity of CuCl (M_{OS}/M_{CuCl}) vs. log of the calculated total CuCl molarity ([CuCl]$_T$ where [CuCl]$_T$ = the sum of all CuCl forms). The dashed lines indicate the modeling values obtained by using the equilibria shown in Table I.
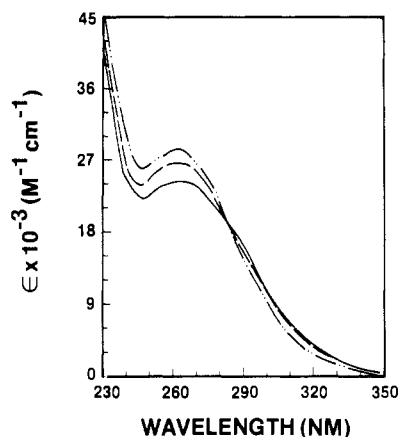
Figure 3. Absorption spectra of $(Ph_3P)_3CuCl$ showing a dependence on concentration: —, 6.0×10^{-4} M; --, 6.0×10^{-5} M; —·—, 3.0×10^{-6} M. Solvent: methylene chloride/cyclohexane in a 1:99 volume ratio.

Figure 4. Absorption spectra of $(MePh_2P)_3CuCl$ showing a strong dependence on concentration: —, 1.1×10^{-3} M; —·—, 1.1×10^{-4} M; --, 1.1×10^{-5} M; —·—, 3.3×10^{-6} M. Solvent: methylene chloride/cyclohexane in a 1:99 volume ratio.

Figure 5. Absorbance at 313 nm of $(MePh_2P)_3CuCl$ in benzene: □, 25 °C; △, 34 °C; O, 43 °C. The absorbance calculated from the extinction coefficient (1.1×10^4 M^{-1} cm^{-1}) of $(MePh_2P)_3CuCl$ determined with an excess of $MePh_2P$ is indicated by --. Predicted absorbance at 38 °C using osmometry modeling equilibria (Table I) and calculated extinction coefficients is indicated by —·—.

molarity of the benzene solution (M_{OS}) obtained from the osmometer to the calculated molarity of the cuprous halide (M_{CuX}) computed from the stoichiometric equation are reported. For $(Ph_3P)_3CuX$ (X = Cl, Br, I), the respective ratios, M_{OS}/M_{CuX}, equal 1.76, 1.82, and 1.86. For the $(MePh_2P)_3CuX$ complexes the analogous values are 1.09, 1.10, and 1.07. The values reported correspond to the average concentration of 1.8×10^{-2} M CuX. With the Wescan Model 233 vapor pressure osmometer, the concentration range that could be studied was greatly expanded. The Wescan Model 233 proved reliable down to approximately 2×10^{-4} M in benzene at 37 °C. The M_{OS}/M_{CuCl} ratios were measured for the chloride complexes over the expanded concentration range available with the Wescan osmometer (see Figure 2).

The UV absorption spectra could be obtained over a concentration range of approximately 10^{-3}–10^{-6} M. The absorption spectra were taken in a mixed solvent [methylene chloride/cyclohexane mixture (1:99 volume ratio)] and in benzene. The absorption spectra of $(Ph_3P)_3CuCl$ and $(MePh_2)_3CuCl$ in the mixed solvent are shown in Figures 3 and 4. 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 the complexes in benzene could only be taken at wavelengths greater than 285 nm because of the interference from the
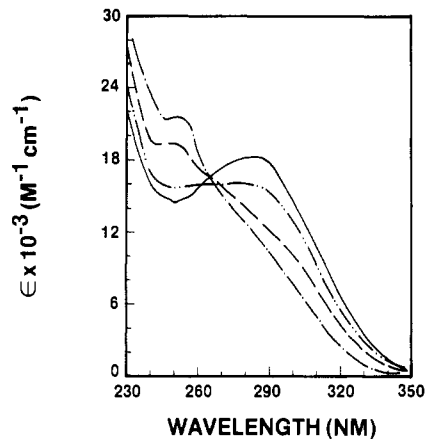
benzene absorption. The spectra show the initial increase in intensity from 350 to 285 nm analogous to that shown in Figures 3 and 4. Therefore, in benzene the UV absorption spectra of the complexes and the free ligands show no characteristic differences in the shape of the spectra. However, the extinction coefficient in benzene of $(MePh_2P)_3CuX$ changes considerably with concentration and temperature. A detailed analysis was accomplished for $(MePh_2P)_3CuCl$ by using absorbance at 313 nm and varying the temperature from 25 to 43 °C (see Figure 5). The extinction coefficient at 313 nm of $(MePh_2P)_3CuCl$ was determined by adding a constant excess of $MePh_2P$. With approximately a 10- to 50-fold excess of $MePh_2P$, the absorbance of the solutions followed the Beer–Lambert law, with the calculated extinction coefficient remaining constant at 1.1×10^4 M^{-1} cm^{-1}. The absorbance of the solution also remained constant with changes in temperature from 25 to 43 °C. The absorbance of $(MePh_2P)_3CuCl$ assuming no dissociation is shown in Figure 5 by the dashed line. The dashed line was calculated by using the extinction coefficient of 1.1×10^4 M^{-1} cm^{-1} determined with the excess free ligand. The free ligand ($MePh_2P$) adds little to the absorbance at 313 nm compared to the complex since the extinction coefficient of $MePh_2P$ equals only 65 M^{-1} cm^{-1} at 313 nm in benzene. The absorbance of $(Ph_3P)_3CuCl$ at 313 nm in benzene appeared to be linear over a concentration range of 5×10^{-5} to 5×10^{-4} M. The calculated
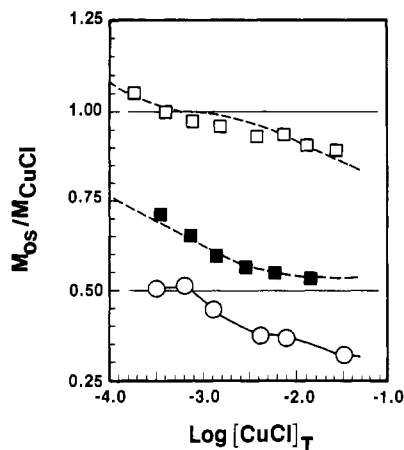
Figure 6. Osmometry measurements of different ratios of Ph_3P to CuCl: □, 2:1, ■, 1.5:1, O, 1:1. The ratio of the osmometry measured molarity of a benzene solution at 37 °C to the calculated total molarity of CuCl (M_{OS}/M_{CuCl}) vs. log of the calculated total CuCl concentration ($[CuCl]_T$ = sum of all CuCl forms) is given. M_{OS}/M_{CuCl} ratios of 0.25, 0.50, and 1.00 indicate the ratios expected for tetramers, dimers, and monomers, respectively. Dashed lines for the 2:1 and 1.5:1 Ph_3P:CuCl ratios indicate the modeling values obtained by using the equilibria shown in Table I.

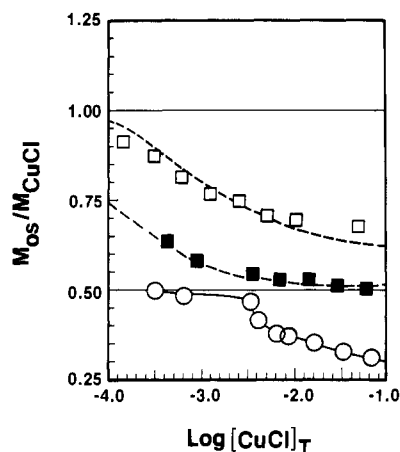**Figure 7.** Osmometry measurements of different ratios of $MePh_2P$ to CuCl: □, 2:1; ■, 1.5:1; O, 1:1. The ratio of the osmometry measured molarity of a benzene solution at 37 °C to the calculated total molarity of CuCl (M_{OS}/M_{CuCl}) vs. log of the calculated total CuCl concentration ($[CuCl]_T$ = sum of all CuCl forms) is given. M_{OS}/M_{CuCl} ratios of 0.25, 0.50, and 1.00 indicate the ratios expected for tetramers, dimers, and monomers, respectively. Dashed lines for the 2:1 and 1.5:1 $MePh_2P$:CuCl ratios indicate the modeling values obtained by using the equilibria shown in Table I.

extinction coefficient only showed a very slight increase to 5.8 × 10³ M^{-1} cm^{-1} with a 50-fold excess of Ph_3P to $(Ph_3P)_3CuCl$.

Since the monomer structures L_2CuCl and $LCuCl$ (L = Ph_3P, $MePh_2P$) along with dimeric or even tetrameric forms could be considered in the possible products of the dissociation of L_3CuCl, solutions containing 2:1, 1.5:1, and 1:1 ratios of L to CuCl were also studied. The vapor pressure osmometry results in benzene at 37 °C are reported by using the M_{OS}/M_{CuCl} ratio (Figures 6 and 7). There are two other osmometry measurements for the 1:1 ratio of $MePh_2P$ to CuCl not included in Figure 7. For M_{CuCl} = 0.13 and 0.38 M, the M_{OS}/M_{CuCl} ratio equals 0.29 and 0.26, respectively. Tetramer, dimer, and monomer structures would normally be indicated by M_{OS}/M_{CuCl} ratios of 0.25, 0.50, and 1.00, respectively. The absorption spectra of the solutions containing 2:1 and 1:1 ratios of $MePh_2P$ to CuCl are shown in Figure 8. The absorption spectra of the same Ph_3P to CuCl ratios are very similar, with the exception of an increase in intensity. A quantitative
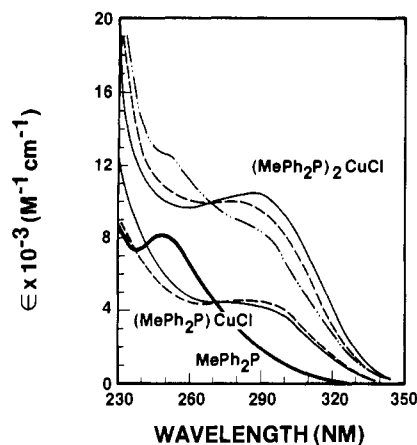

Figure 8. Absorption spectra of $(MePh_2P)_2CuCl$ (upper set of curves): —, 1.1 × 10⁻³ M; --, 1.1 × 10⁻⁴ M; -··-, 1.1 × 10⁻⁵ M. Absorption spectra of $(MePh_2P)CuCl$ (lower set of curves): --, 1.0 × 10⁻³ M; -, 5.0 × 10⁻⁴ M; —, 2.5 × 10⁻⁵ M. The $(MePh_2P)_2CuCl$ and $(MePh_2P)CuCl$ formulas indicate the ratio of $MePh_2P$ to CuCl present in the solution and not the actual structures of the complexes that may exist in solution. Solvent: methylene chloride/cyclohexane in a 1:99 volume ratio.
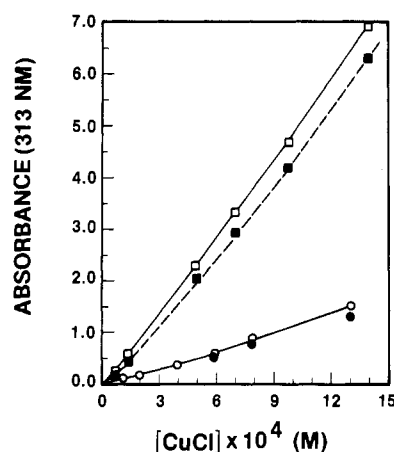

Figure 9. Absorbance at 313 nm of $(MePh_2P)_2CuCl$ (□, 25 °C; ■, 38 °C) and $(MePh_2P)CuCl$ (O, 25 °C; ●, 43 °C) in benzene. The $(MePh_2P)_2CuCl$ and $(MePh_2P)CuCl$ formulas indicate the ratio of $MePh_2P$ to CuCl present in the solution and not the actual structures of the complexes that may exist in the solution. The dashed line indicates the fit of absorbance data for the 2:1 ratio of $MePh_2P$:CuCl by using osmometry modeled equilibria (Table I).

analysis of absorbance at 313 nm in benzene is shown in Figure 9 for the solutions containing the 2:1 and 1:1 ratios of $MePh_2P$ to CuCl. At concentrations of 1 × 10⁻⁴ to 4 × 10⁻⁴ M, the 1:1 $MePh_2P$:CuCl solution showed no absorbance change when heated to 43 °C.

Discussion

Ligand dissociation appears to be the principal process of decomposition of the phosphine copper(I) halide complexes since no products other than the free ligands are observed in the mass spectra as the complexes are heated. The UV absorption spectra of the L_3CuX complexes (L = Ph_3P, $MePh_2P$; X = Cl, Br, I) also indicate a ligand dissociation process in the solution phase. The spectra of the complexes with dilution begin to resemble the spectra of the free ligand (Figures 3 and 4). In fact, the sum of the absorption spectra of the most dilute $LCuCl$ (1:1 ratio of L to CuCl) solutions plus twice the respective free ligand spectra is almost the same as the absorption spectra of the L_3CuCl solutions at the most dilute concentrations shown.

The results of this study clearly show that the dissociation of the L_3CuX complexes is very dependent on concentration

and temperature. The results also show that both $(Ph_3P)_3CuX$ and $(MePh_2P)_3CuX$ show extensive dissociation in solution; however, the equilibrium of dissociation for each is considerably different. A complicating factor in an analysis of the equilibrium of the dissociation of the L_3CuX complexes is the possibility of the dimeric or even tetrameric complexes formed by halogen bridging. Complexation of CuX and L without halogen bridging would be considered to occur in a stepwise manner forming $LCuX$, L_2CuX, and L_3CuX monomer structures. With the possibility of halogen bridging, Lippard and Mayerle[7] suggested that up to seven distinct types of complexes appear possible in solution (L_3CuX, L_2CuX, $LCuX$, $L_4Cu_2X_2$, $L_3Cu_2X_2$, $L_2Cu_2X_2$, $L_4Cu_4X_4$). Figure 1 shows the dimeric and tetrameric solid-state structures formed by halogen bridging. Lippard and Mayerle[7] made no attempt to quantify their osmometric data in terms of an equilibrium mechanism due to the complexity of the dissociation equilibria and the narrow concentration range studied (10^{-2} to 6×10^{-2} M CuCl). With the extended concentration range of the osmometry data available from this study in conjunction with the UV absorption and osmometry measurements of the various L to CuCl ratios, a more detailed analysis can be accomplished.

It is known that phosphine coordination is favored over halogen bridging since no halogen-bridging complexes are formed whenever there is sufficient phosphine to occupy the three available coordination sites of CuCl. Steric requirements of larger ligands could offer some exceptions to this rule. The main point is that bonding involving halogen bridging, being generally weaker than the phosphine to metal bond, would also be susceptible to coordination dissociation and would be favored in solutions having rather high concentrations of CuCl without sufficient phosphine for complete coordination. This conclusion is supported by the osmometry data of the 1:1 ratio of L to CuCl for both Ph_3P and $MePh_2P$ (Figures 6 and 7). The osmometry data indicate increased dissociation of the tetramer form upon dilution. The tetramer structure, $L_4Cu_4Cl_4$, is implied by a M_{OS}/M_{CuCl} ratio of 0.25. The UV absorption spectra of the 1:1 L to CuCl ratio indicate that ligand dissociation is negligible (Figure 8) since the absorption band at 300 nm, which is reflective of ligand coordination,[10] shows virtually no change with a change in concentration of complex from 10^{-3} to 10^{-5} M. Halogen bridging would have to be considered the primary source of dissociation of the $L_4Cu_4Cl_4$ tetramer indicated by the osmometry data (Figures 6 and 7). The M_{OS}/M_{CuCl} ratio at 5×10^{-4} M CuCl in both the Ph_3P and $MePh_2P$ complexes has a value of 0.50. Assuming only halogen-bridging dissociation from the tetramer structure, the M_{OS}/M_{CuCl} value of 0.50 would indicate an $L_2Cu_2Cl_2$ dimer structure in solution at 5×10^{-4} M CuCl. A slight inflection point is indicated at a M_{OS}/M_{CuCl} value of 0.35, which would be most reasonably associated with a trimer structure $L_3Cu_3Cl_3$. Comparison of the osmometry data for the 1:1 ratio of L to CuCl shows that the Ph_3P complex has a slightly greater tendency toward halogen bridging than the $MePh_2P$ complex. This observation would be anticipated when considering the relative basicities of the ligands ($MePh_2P$ > Ph_3P). The stronger base would be expected to create a greater electron density on the copper relative to the weaker base and thus reduce the relative tendency toward halogen bridging. Intramolecular repulsions should be insignificant with only one ligand coordinated to the copper.

Dissociation of the dimer, $L_2Cu_2Cl_2$, to the monomer, $LCuCl$, is difficult to project without data obtained at lower concentrations. The UV absorption data are available down to approximately 2×10^{-5} M; however, the UV absorption data are not very sensitive to halogen bridging in the region of the spectra (285 nm) where it can be measured in benzene. With use of only the osmometry data, a limit can be placed on the

dissociation equilibrium of the $L_2Cu_2Cl_2$ dimer to a $LCuCl$ monomer by using an estimated 10% error in the measurement of the solution molarity and the fact that the M_{OS}/M_{CuCl} ratio has not exceeded 0.50 at 5×10^{-4} M CuCl. In terms of

$$2LCuCl \rightleftharpoons L_2Cu_2Cl_2$$
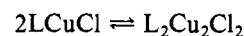
the formation constant, K_{D2}, is calculated to be greater than 9×10^4 or the dissociation constant, $1/K_{D2}$, is less than 1.1×10^{-5}.
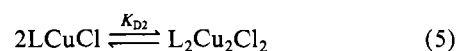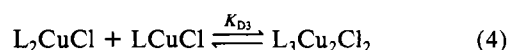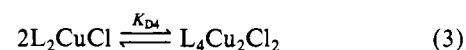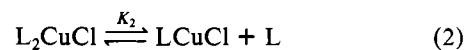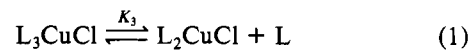
Other quantitative as well as qualitative conclusions can be made from the osmometry data. The 1.5:1 ratio of L to CuCl clearly indicates an $L_3Cu_2Cl_2$ dimer structure. The M_{OS}/M_{CuCl} ratio approaches 0.50 with increased CuCl concentration (Figures 6 and 7). Assuming halogen bridging is weaker than phosphine coordination, the first dissociation to be considered for the $L_3Cu_2Cl_2$ complex would be fragmentation via halogen bridging.

$$L_3Cu_2Cl_2 \rightleftharpoons L_2CuCl + LCuCl$$

Of course, the $LCuCl$ monomer could dimerize if there is sufficient concentration for association. In any case, the dissociation indicated in Figures 6 and 7 for the $L_3Cu_2Cl_2$ complexes could not conceivably include any appreciable concentration of the $L_4Cu_4Cl_4$ tetramer form since the concentration of $LCuCl$ monomer or $L_2Cu_2Cl_2$ dimer produced in the dissociation of $L_3Cu_2Cl_2$ would be far too low to form any significant halogen bridging beyond the dimer form. Thus, the tetramer form need not be considered in the dissociation of the phosphine complexes with L to CuCl ratios greater than or equal to 1.5:1.

A saturated dimer, $L_4Cu_2Cl_2$, is indicated by the M_{OS}/M_{CuCl} ratios of less than 1.0 for the 2:1 ratio of L to CuCl (Figures 6 and 7). The extent of dimerization is much greater for the $MePh_2P$ complex than the Ph_3P complex. This observation is in contrast to the 1:1 ratio of L to CuCl in which the Ph_3P complex showed the greater tendency toward halogen bridging. Intramolecular steric repulsions of the larger ligand Ph_3P must be invoked rather than the relative basicities of the ligands in order to rationalize the greater tendency of $MePh_2P$ to form the saturated $L_4Cu_2Cl_2$ dimer. The osmometry data does not indicate a simple dimerization equilibrium. At the higher concentrations of CuCl, the M_{OS}/M_{CuCl} ratio does not continue to decrease as rapidly as would be predicted by a simple dimerization equilibrium. In fact, the $MePh_2P$ data indicate that the M_{OS}/M_{CuCl} ratio has reached an equilibrium value of ~ 0.67 instead of 0.50. A disproportionation of the $L_4Cu_2Cl_2$ dimer structure to L_3CuCl and $L_3Cu_2Cl_2$ could account for the observed M_{OS}/M_{CuCl} value.

The osmometry data indicate six distinct types of complexes must be considered in the solution dissociation of the Ph_3P and $MePh_2P$ copper(I) chloride complexes: L_3CuCl, L_2CuCl, $LCuCl$, $L_4Cu_2Cl_2$, $L_3Cu_2Cl_2$, $L_2Cu_2Cl_2$. With six types of complexes, five independent equations are necessary to interrelate them. Equilibria 1–5 are sufficient to define the system completely. Other equilibria such as ligand dissociation from the dimer forms can be represented by suitable combinations of eq 1–5. Examples are shown in Table I. The

$$L_3CuCl \underset{}{\overset{K_3}{\rightleftharpoons}} L_2CuCl + L \tag{1}$$

$$L_2CuCl \underset{}{\overset{K_2}{\rightleftharpoons}} LCuCl + L \tag{2}$$

$$2L_2CuCl \underset{}{\overset{K_{D4}}{\rightleftharpoons}} L_4Cu_2Cl_2 \tag{3}$$

$$L_2CuCl + LCuCl \underset{}{\overset{K_{D3}}{\rightleftharpoons}} L_3Cu_2Cl_2 \tag{4}$$

$$2LCuCl \underset{}{\overset{K_{D2}}{\rightleftharpoons}} L_2Cu_2Cl_2 \tag{5}$$

Table I. Equilibria and Equilibrium Constants for $L_mCu_nCl_n$ Complexes in Benzene at 37 °C ($L = Ph_3P$, $MePh_2P$; $m:n = 3:1, 2:1, 4:2, 3:2, 2:2$)

	equilibrium constants^a			
	Ph₃P		MePh₂P	
	model value	sensitivity range	model value	sensitivity range
Modeling Equilibria^a				
$L_3CuCl \overset{K_3}{\rightleftharpoons} L_2CuCl + L$	2×10^{-2}	$1 \times 10^{-2} \leqslant K \leqslant 3 \times 10^{-2}$	2.0×10^{-4}	$1.5 \times 10^{-4} \leqslant K \leqslant 2.5 \times 10^{-4}$
$L_2CuCl \overset{K_2}{\rightleftharpoons} LCuCl + L$	2×10^{-6}	$6 \times 10^{-7} \leqslant K \leqslant 5 \times 10^{-6}$	1×10^{-6}	$6 \times 10^{-7} \leqslant K \leqslant 3 \times 10^{-6}$
$2(L_2CuCl) \overset{K_{D4}}{\rightleftharpoons} L_4Cu_2Cl_2$	20	$5 \leqslant K \leqslant 40$	6×10^2	$4 \times 10^2 \leqslant K \leqslant 9 \times 10^2$
$L_2CuCl + LCuCl \overset{K_{D3}}{\rightleftharpoons} L_3Cu_2Cl_2$	5×10^4	$3 \times 10^4 \leqslant K \leqslant 9 \times 10^4$	8×10^4	$4 \times 10^4 \leqslant K_{D3} \leqslant 2 \times 10^5$
$2(LCuCl) \overset{K_{D2}}{\rightleftharpoons} L_2Cu_2Cl_2$	2×10^5	$9 \times 10^4 \leqslant K \leqslant 6 \times 10^5$	1×10^5	$9 \times 10^4 \leqslant K_{D2} \leqslant 5 \times 10^5$
Other Equilibria^b				
$L_4Cu_2Cl_2 \overset{K_4}{\rightleftharpoons} L_3Cu_2Cl_2 + L$	5×10^{-3}	$1 \times 10^{-3} \leqslant K \leqslant 1 \times 10^{-2}$	1×10^{-4}	$7 \times 10^{-5} \leqslant K \leqslant 2 \times 10^{-4}$
$L_3Cu_2Cl_2 \overset{K_5}{\rightleftharpoons} L_2Cu_2Cl_2 + L$	8×10^{-6}	$7 \times 10^{-7} \leqslant K \leqslant 2 \times 10^{-5}$	1×10^{-6}	$5 \times 10^{-7} \leqslant K \leqslant 3 \times 10^{-6}$

^a Equilibria used to model the vapor pressure osmometry results; model equilibrium constants derived from reasonable fit of osmometry results. The sensitivity range indicates the range that the equilibrium constant can vary with the other equilibria constants fixed at the model value and still have the model fit within 5% of the observed osmometry measurements (Figures 2, 6, and 7). ^b Equilibria and constants calculated from appropriate combinations of modeling equilibria.

complete equilibrium (eq 1–5) can be modeled by expressing the free ligand concentration in terms of the equilibrium constants and the concentration of one of the complexes. A theoretical M_{OS}/M_{CuCl} ratio was calculated for a given set of equilibrium constants for comparison to the observed osmometric data for the Ph₃P and MePh₂P complexes with 3:1, 2:1, and 1.5:1 L to CuL ratios. The modeling was started with an initial set of equilibrium constants established by obvious limits on K_3, K_{D3}, and K_{D2}. For example, the osmometry data shown in Figure 2 for (MePh₂P)₃CuCl can be fit extremely well by using only eq 1 with $K_3 = 2.0 \times 10^{-4}$. If eq 1 is the only equilibrium, K_3 is easily calculated since $[L] = M_{OS} - M_{CuCl}$, $[L_2CuCl] = [L]$, and $[L_3CuCl] = M_{CuCl} - [L_2CuCl]$. The L₂CuCl monomer could possibly form the dimer, L₄Cu₂Cl₂, through chloride bridging. The formation of the dimer would reduce the M_{OS}/M_{CuCl} values, and thus the M_{OS}/M_{CuCl} ratio would not follow the simple one to two particle dissociation observed for (MePh₂P)₃CuCl. Thus, dimerization of the (MePh₂P)₂CuCl monomer formed in the dissociation of (MePh₂P)₃CuCl would be considered insignificant. With eq 1 and 3 with $K_3 = 2.0 \times 10^{-4}$, the dimerization would have no effect on the M_{OS}/M_{CuCl} ratio if $K_{D4} \leq 6 \times 10^2$. In principle, all that can be established with certainty from the above analysis is that $K_3 \geq 2.0 \times 10^{-4}$ since the L₄Cu₂Cl₂ dimer if formed could conceivably lose a ligand with a rate less than or perhaps comparable to L₃CuCl. Although the (Ph₃P)₃CuCl osmometry data has a considerable amount of scatter, a similar analysis shows $K_3 \geq 2 \times 10^{-2}$. Using only eq 4 for the dissociation of L₃Cu₂Cl₂ places $K_{D3} \geq 2 \times 10^4$ for Ph₃P and $K_{D3} \geq 5 \times 10^4$ for MePh₂P. The limit on K_{D2} of $\geq 9 \times 10^4$ for eq 5 has already been discussed.

The modeling of the observed osmometry data using eq 1–5 for the Ph₃P and MePh₂P complexes (3:1, 2:1, and 1.5:1 L to CuCl ratios) gives the results listed in Table I. Other equilibria that might be useful are also listed in Table I. The fit of the observed osmometry data using the equilibrium constants given in Table I is shown in Figures 2, 6, and 7 by the dashed lines. The M_{OS}/M_{CuCl} values for the 3:1 ratio of Ph₃P to CuCl (Figure 2, open circles vs. closed circles) suggest that the solid-state (Ph₃P)₃CuCl used to make the benzene solutions contained small amounts of the 2:1 ratio of ligand to CuCl. This is not surprising since the relatively large ligand dissociation constant ($K_3 = 2 \times 10^{-2}$) indicates that a considerable excess of Ph₃P should be used in preparing the solid-state

(Ph₃P)₃CuCl complex rather than the exact 3:1 ratio of ligand to metal.

Applying the model allows illustration of the differences in the equilibria of the Ph₃P and MePh₂P complexes (Figures 10 and 11). The composition of the benzene solutions with 3:1 and 2:1 ratios of L to CuCl were generated by using the modeling equilibria and model values shown in Table I. The solubility in benzene of the L₃CuCl complexes and the 2:1 ratio of L to CuCl is approximately 3×10^{-2} M; however, Figures 10 and 11 were extended by the modeling to 10^{-1} M. The first ligand dissociation equilibrium constant, K_3, is 100 times greater for the Ph₃P complex in comparison to the MePh₂P complex. Over the concentration range studied, the (Ph₃P)₃CuCl structure is only a minor component in a benzene solution made from the solid-state complex, (Ph₃P)₃CuCl. The (Ph₃P)₂CuCl monomer structure dominates from 10^{-2} to 10^{-5} M CuCl, with (Ph₃P)₃Cu₂Cl₂ being the other principal component (Figure 10). In contrast, a benzene solution made from the solid-state complex (MePh₂P)₃CuCl has (MePh₂P)₃CuCl as a principal solution structure from 10^{-2} to 3×10^{-4} M. Except for minor dimer components, the (MePh₂P)₃CuCl dissociation exhibits the expected stepwise ligand dissociation: L₃CuCl → L₂CuCl → LCuCl. Even though the dissociation of the L₃CuCl complexes has not been previously quantified, the much greater dissociation noted for the (Ph₃P)₃CuX complexes in comparison to the (MePh₂P)₃CuX complexes during Lippard and Mayerle's[7] study has received an adequate explanation based on the steric crowding of the Ph₃P ligand in the fully coordinated complexes. This steric crowding has been explained by the use of Tolman's cone angles.[17] With (Ph₃P)₂CuCl, the steric repulsion would be minimized and the K_2 dissociation constant would be considered to be more in the order of magnitude of the MePh₂P derivative. Indeed, the K_2 values in Table I reflect this concept; $K_2 = 2 \times 10^{-6}$ for (Ph₃P)₂CuCl and $K_2 = 1 \times 10^{-6}$ for (MePh₂P)₂CuCl. The slightly larger K_2 for (Ph₃P)₂CuCl would be of the order expected in terms of relative basicities, the MePh₂P ligand being more basic than Ph₃P.

The 2:1 ratio of L to CuCl solutions would be expected to be very similar for the MePh₂P and Ph₃P complexes since the

(17) (a) Tolman, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 2956. (b) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313. (c) Tolman, C. A.; Seidel, W. C.; Gosser, L. W. *J. Am. Chem. Soc.* **1974**, *96*, 53.
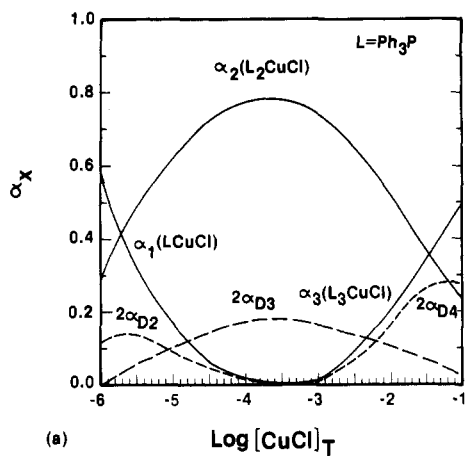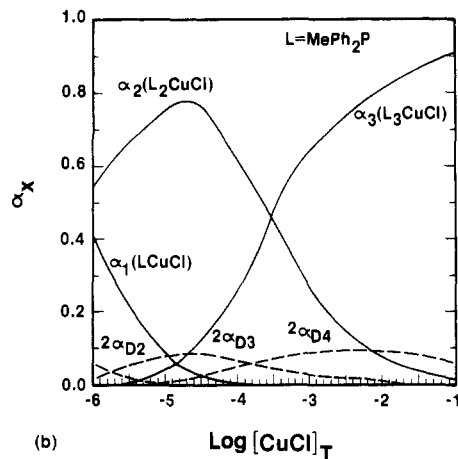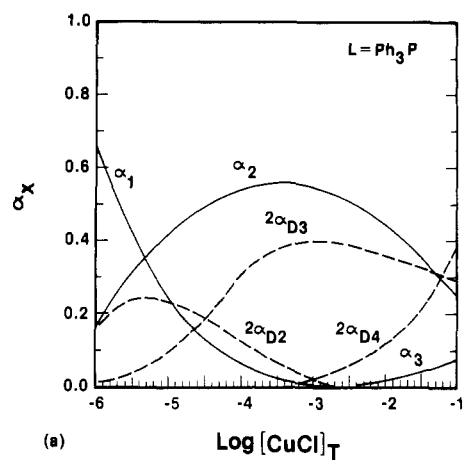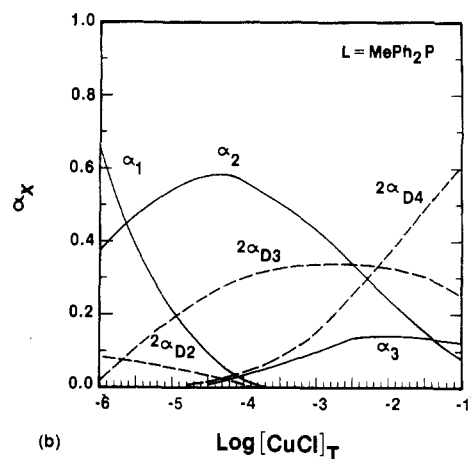
Figure 10. Model of $(Ph_3P)_3CuCl$ (a) and $(MePh_2P)_3CuCl$ (b) dissociation in benzene at 37 °C (α_x = the fraction of a given form (α_x = [x]/[CuCl]_T, [CuCl]_T = sum of all CuCl forms)). α_1, α_2, and α_3 represent the fraction of LCuCl, L_2CuCl, and L_3CuCl monomer structures, respectively. α_{D4}, α_{D3}, and α_{D2} represent the fraction of $L_4Cu_2Cl_2$, $L_3Cu_2Cl_2$, and $L_2Cu_2Cl_2$ dimer structures, respectively. $1 = \alpha_1 + \alpha_2 + \alpha_3 + 2\alpha_{D4} + 2\alpha_{D3} + 2\alpha_{D2}$.

Figure 11. Model of prominent species in a benzene solution at 37 °C containing a 2:1 ratio of L to CuCl (α_x = the fraction of a given form (α_x = [x]/[CuCl]_T, [CuCl]_T = sum of all CuCl forms)). α_1, α_2, and α_3 represent the fraction of the LCuCl, L_2CuCl, and L_3CuCl monomer structures, respectively. α_{D4}, α_{D3}, and α_{D2} represent the fraction of the $L_4Cu_2Cl_2$, $L_3Cu_2Cl_2$, and $L_2Cu_2Cl_2$ dimer structures, respectively. $1 = \alpha_1 + \alpha_2 + \alpha_3 + 2\alpha_{D4} + 2\alpha_{D3} + 2\alpha_{D2}$.

steric crowding of Ph_3P is greatly reduced in the $(Ph_3P)_2CuCl$ structure. However, there are still some striking differences in the relative concentrations of the various species present. Figure 11 shows that the principal difference between Ph_3P and $MePh_2P$ is that the saturated dimer $L_4Cu_2Cl_2$ is much more prevalent for $MePh_2P$. Also, the L_3CuCl and $L_3Cu_2Cl_2$ forms occur to a much greater extent in the case of $MePh_2P$. Figure 11 illustrates that the L_3CuCl form is produced in much greater concentrations in solutions containing the 2:1 ratio of L to CuCl for L = $MePh_2P$ than for L = Ph_3P. These differences can be explained by the greater steric repulsions of the Ph_3P ligand in the distorted tetrahedral copper(I) structure formed by dimerization. The large difference in the values of K_{D4}, K_4, and possibly K_5 between Ph_3P and $MePh_2P$ shows that steric repulsion is the controlling factor since the values are in contrast to that expected by electronic factors. Some steric crowding, though greatly reduced, may also be operative in the $(MePh_2P)_3CuCl$ complex. The equilibrium constant K_3 would be expected to be greater than K_2 with either phosphine not only because of decreased steric effects but also because of the decreasing electron density on the copper with the loss of each ligand, resulting in a concomitant increase in the electrophilic character of the copper. The magnitude of the difference between K_3 and K_2 would be difficult to predict. However, a comparison of K_4 to K_2 could be made. The halogen bridging of the $L_4Cu_2Cl_2$ structure would be expected to have only a minor change in electron density of the copper in comparison to L_2CuCl. Thus, K_4 based on electronic factors

would be anticipated to be approximately the same order of magnitude as K_2. In contrast to K_2 (1×10^{-6} for the $MePh_2P$ complex), K_4 (1×10^{-4}) is the same order of magnitude as K_3 (2×10^{-4}). Both K_4 and K_3 are dissociation constants for a distorted tetrahedral structure. This comparison suggests that even though the steric crowding of $MePh_2P$ in a tetrahedral structure is greatly reduced from that of Ph_3P, intramolecular steric repulsion may still have a considerable effect on the equilibrium associated with K_3 and K_4. A similar relationship holds for the Ph_3P complex.

The modeling of the equilibria of the (phosphine)copper(I) complexes by use of the osmometry data must also be consistent with the UV absorption data of the complexes. In order to compare the UV absorption data, extinction coefficients of the various complexes are needed. It is not possible to calculate an extinction coefficient for each of the six complexes with the available data. The absorbance calculation can be greatly simplified to show consistency with the osmometry model by assuming that the extinction coefficients of the dimer solution structures are the sum of the respective monomer structures; i.e., the extinction coefficient of $L_3Cu_2Cl_2$ equals the extinction coefficient of L_2CuCl plus that of LCuCl. This assumption should be reasonable since the UV absorbance at 313 nm shows significant changes in the extinction coefficient with changes in the ratio of L to CuCl but does not appear to show any significant changes with increasing amounts of halogen bridging in the region (>285 nm) where the benzene absorption measurements were taken. The extinction coefficient of $(MePh_2P)_3CuCl$ was calculated to be 1.1×10^4 M^{-1} cm^{-1}

when an excess of MePh$_2$P is used (Figure 5). The extinction coefficient of the monomer (MePh$_2$P)CuCl can be calculated from Figure 9 as 1.0×10^3 M^{-1} cm^{-1}. The small deviation from linearity of the 1:1 ratio of MePh$_2$P to CuCl shown in Figure 9 is most reasonably associated with halogen bridging. The extinction coefficient of (MePh$_2$P)$_2$CuCl cannot be obtained directly from the 2:1 ratio of MePh$_2$P to CuCl solution (Figure 9) since the solution contains an equilibrium mixture of L$_2$CuCl, L$_4$Cu$_2$Cl$_2$, L$_3$Cu$_2$Cl$_2$, and L$_3$CuCl in the concentration range studied. However, the extinction coefficient of the (MePh$_2$P)$_2$CuCl form can be calculated from the absorbance values of the 2:1 ratio of L to CuCl at 38 °C by using the known extinction coefficients and concentrations of the various solution structures calculated from the osmometry model at 37 °C. The extinction coefficient of (MePh$_2$P)$_2$CuCl becomes the only unknown, and when calculated in this manner, equals $3.9 \pm 0.2 \times 10^3$ M^{-1} cm^{-1}. The deviation reported is the absolute variance of the calculated value over the range of absorbance readings. The small deviation of the extinction coefficient over the entire range of absorption data suggests a consistent model. The absorbance curves of the 2:1 and 3:1 ratios of MePh$_2$P to CuCl calculated by using the osmometry model (Table I) and the calculated extinction coefficients are shown in Figures 5 and 9. An approximation of K_3 (eq 1) at the other temperatures shown in Figure 5 can be made by considering only eq 1 as the mechanism of dissociation of the (MePh$_2$P)$_3$CuCl complex. This approximation is within reason since the principal components in the concentration range of interest are (MePh$_2$P)$_2$CuCl and (MePh$_2$P)$_3$CuCl (Figure 10). K_3 calculated by using this approximation equals 9×10^{-5}, 2×10^{-4}, and 5×10^{-4}, respectively, at 25, 34, and 43 °C. A least-squares fit of log K_3 vs. $1/T$ yields $\Delta H = 74 \pm 4$ kJ/mol and $\Delta S = 172 \pm 10$ J/mol. An evaluation of K_2 with a temperature change using the 2:1 MePh$_2$P:CuCl ratio cannot be done because the dimerization equilibrium becomes a significant factor. The increase in absorption from 38 to 25 °C for the 2:1 MePh$_2$P to CuCl ratio suggests that the more strongly absorbing (MePh$_2$P)$_3$CuCl complex is produced in greater concentrations at 25 °C. The relatively small change could also be accounted for by a much greater concentration of the saturated dimer (MePh$_2$P)$_4$Cu$_2$Cl$_2$ at 25 °C, which could have a slightly higher extinction coefficient than twice that of the (MePh$_2$P)$_2$CuCl monomer. However, both theories complement one another. If more saturated dimer is produced, a greater concentration of (MePh$_2$P)$_3$CuCl will most likely be produced through disproportionation of the dimer.

A similar analysis of the UV absorption data of the Ph$_3$P complexes cannot be accomplished. With the much larger value of K_3 (2×10^{-2}), enough excess Ph$_3$P could not be added to obtain the extinction coefficient of the (Ph$_3$P)$_3$CuCl form and still obtain an absorbance reading. For example, when a 5×10^{-5} M calculated (Ph$_3$P)$_3$CuCl solution with $K_3 = 2 \times 10^{-2}$ is used, about 0.2 M Ph$_3$P would be needed to produce a 90% to 10% mixture of (Ph$_3$P)$_3$CuCl to (Ph$_3$P)$_2$CuCl. Since Ph$_3$P has an extinction coefficient of 450 M^{-1} cm^{-1} at 313 nm,[10] the absorbance of the solution would be ~80. The absorbance readings taken for a benzene solution made from the solid-state (Ph$_3$P)$_3$CuCl structure appeared to follow the Beer–Lambert law. The absorbance readings were taken over a concentration

range of 5×10^{-5} to 5×10^{-4} M CuCl. Inspection of Figure 10 shows that the composition of the species in the benzene solution remains virtually consant over the concentration range studied. Even though the absorbance data for the Ph$_3$P complexes are very limited, the dissociation model is still consistent.

The dissociation model (Table I) also shows consistency with the osmometry study done by Lippard and Mayerle.[7] Their limited osmometry data in chloroform at 37 °C can be used to estimate K_3. In chloroform $K_3 \geq 2.5 \times 10^{-1}$ for (Ph$_3$P)$_3$CuCl and $K_3 \geq 4 \times 10^{-4}$ for (MePh$_2$P)$_3$CuCl. The slightly larger values of K_3 in chloroform compared to benzene could easily be contributed to a greater solvent stabilization of the coordinatively unsaturated monomer L$_2$CuCl produced in the dissociation.

Summary and Conclusions

Complexes of the type L$_3$CuX (L = Ph$_3$P, MePh$_2$P; X = Cl, Br, I) show extensive ligand dissociation in solution. The dissociation is dependent on the temperature, concentration, and solvent. The halogen appeared to have only a minor effect on the dissociation. The detailed analysis of the chloride complexes by osmometry shows that ligand dissociation is also accompanied by dimerization of the coordinately unsaturated copper(I) complexes through halogen bridging. Complexes of the form L$_m$Cu$_n$Cl$_n$ ($m:n$ = 3:1, 2:1, 1:1, 4:2, 3:2, 2:2) must be considered in a complete analysis of the solution dissociation of the L$_3$CuCl complexes. The modeling of the dissociation of various ratios of L to CuCl in benzene at 37 °C was accomplished with the equilibrium constants derived from the modeling (Table I). Solution profiles of different ratios of L to CuCl can be generated to show the dependence of the various complexes with concentration (Figure 10 and 11). The much greater ligand dissociation values of the L$_3$CuCl, L$_4$Cu$_2$Cl$_2$, and L$_3$Cu$_2$Cl$_2$ complexes for Ph$_3$P in comparison to MePh$_2$P are explicable on the basis of the greater steric crowding of Ph$_3$P in the distorted tetrahedral form. The steric crowding has been adequately explained by the use of Tolman's cone angles.[17] The high cone angle (145°) for Ph$_3$P suggests that tetrahedral structures with more than one Ph$_3$P molecule in the tetrahedron will have considerable ligand–ligand repulsions. The formnation constants (eq 3 and 4) of the dimers L$_4$Cu$_2$Cl$_2$ and L$_3$Cu$_2$Cl$_2$ also reflect the greater steric requirements of Ph$_3$P in comparison to MePh$_2$P. Considering only the relative basicities of the ligands (MePh$_2$P > Ph$_3$P), the weaker base would be expected to create less electron density on the copper relative to the stronger base and thus favor the tendency toward halogen bridging. The halogen bridging is only stronger for the Ph$_3$P complexes in the case of the 1:1 ratio of L to CuCl where one ligand is coordinated to the copper.