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The Behavior of Tertiary Phosphine and Arsine Complexes of Copper(I) in Chloroform Solution

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The equilibria occurring in chloroform solutions containing phosphine and arsine complexes of the type $[(C_6H_5)_{3-n}(CH_3)_nY]_mCuX$ ($n = 0, 1, 2$; $m = 3, 2, 1.5$; Y = P, As; X = Cl, Br, I) have been investigated using vapor pressure osmometry. The effects of the substituents on the group V donor atom, the group V donor atom itself, and the choice of halide on the extent of ligand dissociation of the 3:1 compounds L_3CuX are presented and discussed. The most striking influence is shown to be a stereochemical one, exemplified by the relative stabilities of the L_3CuCl complexes, $L = (C_6H_5)_3P \ll (C_6H_5)_2(CH_3)P \simeq (C_6H_5)(CH_3)_2P$. The arsine compounds are in general more highly dissociated than their phosphine analogs, and the basicity of the ligand has a greater effect on the extent of dissociation. The system $(C_6H_5)_3P$–CuBr is discussed in detail, and the predominant complex in solutions having $(C_6H_5)_3P$:CuBr ratios of 3:2 is shown to be the ligand-deficient dimer $L_3Cu_2Br_2$. The synthesis of several new complexes in the $[(C_6H_5)_{3-n}(CH_3)_nY]_mCuX$ class is described.

Introduction

Monodentate tertiary phosphine and arsine complexes of the copper(I) halides (hereafter, L_mCuX) have been the subject of numerous investigations. Four types of compounds, having ligand:copper halide ratios of 3:1,[1-9] 2:1,[1,3,4,8,10-12] 3:2,[1,5,6,12-14] and 1:1,[1,2,4-6,8,11,12,14] have been isolated as stable solids. The 4:1 stoichiometry has only been observed for L_4CuX compounds in which X is a poorly coordinating anion such as nitrate or perchlorate,[4,15] although complexes of the type $(L\text{-}L)_2CuX$ (X = Cl, Br, I) are known, where L-L is a diarsine ligand.[16]

The solid-state structure has been determined for a representative member of each class of the L_mCuX halide complexes. Using X-ray crystallography, Mann, Purdie, and Wells[14] showed that the 1:1 complex $[(C_2H_5)_3As]CuI$ is tetrameric, the structure consisting of four copper atoms arranged at the apices of a tetrahedron, with a triply bridging iodine atom centered above each face. A triethylarsine ligand is bound to each copper atom along the threefold axes of the tetrahedron, raising the coordination number of each copper atom to 4. A recent crystal structure determination[13] revealed the 3:2 complex $[(C_6H_5)_3P]_3Cu_2Cl_2 \cdot C_6H_6$ to contain both three- and four-coordinate copper atoms linked by two bridging chlorine atoms. The 3:1 complex $[(C_6H_5)_2(CH_3)P]_3CuCl$ has been shown by X-ray diffraction[7] to be a monomer of pseudotetrahedral symmetry. Work now in progress[10] indicates that the 2:1 complex $[(C_6H_5)(CH_3)_2As]_2CuCl$ is a chloride-bridged dimer, each copper atom being tetracoordinate.

Although it has long been known that these complexes dissociate in solution, attempts to determine the relative concentrations of the various species have only recently met with notable success. Muetterties and Alegranti,[17] in a study of these complexes with the ligand tri-*p*-tolylphosphine, found that at temperatures of about −100°, the main species in a 50% v/v dichloromethane–toluene solution was the dimer $(L_2CuX)_2$. As the temperature was raised above −70°, the existence of L_3CuX, $L_3Cu_2X_2$, and a small amount of the L_2CuX monomer became evident. Because of rapid ligand exchange, the ^{31}P nmr spectrum collapsed to a single peak at higher temperatures. No evidence was cited for the existence of the $(LCuX)_4$ complex.

Investigating the complexes $[(C_6H_5)_2PH]_mCuX$ ($m = 3, 2, 1.5, 1$; X = Cl, Br, I) spectrophotometrically, Abel and coworkers[1] found that in methanol solution all complexes of $m \geqslant 1.5$ associated to the 1:1 complex. Solutions with ligand:copper ratios of 3:1 contained no appreciable quantities of complexes of stoichiometries intermediate between $m = 3$ and $m = 1$. Although these results are not consistent with those of Muetterties and Alegranti,[17] the comparison is not necessarily valid since the equilibria undergone by these complexes are probably very much dependent upon the nature of L, the solvent, and the temperature.

Previous work in this laboratory[18,19] on the reactions of L_mCuX complexes with hydroborate ligands led to our independent investigation of the equilibria undergone by the halide complexes near room temperature in chloroform solution. Of particular concern were the effects of variations of the stereochemical and electronic properties of the phosphine and arsine ligands and, to a lesser extent, of the choice of halide ion on the extent of ligand dissociation of L_3CuX compounds. Since ligand exchange is too rapid at ambient temperatures to allow magnetic resonance techniques to be use-

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fully employed[20] and since the high absorption energies of these complexes preclude chloroform as a suitable spectrophotometric solvent, a study of the L_mCuX compounds in solution over a range of concentrations and of ligand:copper ratios has been carried out using vapor pressure osmometry. The results are presented and discussed in this report.

Experimental Section

Diphenylmethylphosphine, dimethylphenylphosphine,[21] diphenylmethylarsine,[22] and dimethylphenylarsine[22] were all prepared by standard Grignard techniques and triply distilled prior to use. Methyldiiodoarsine,[23] used in the synthesis of diphenylmethylarsine, was prepared by the reduction of disodium methylarsonate, generously provided by the W. A. Cleary Corp., New Brunswick, N. J. Analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Melting points reported are uncorrected. All compounds were prepared and handled under an atmosphere of dry nitrogen.

Halotris(triphenylphosphine)copper(I).—Chlorotris(triphenylphosphine)copper(I) was prepared as described previously.[18] The bromide and iodide were prepared in a similar manner. *Anal.* Calcd for $C_{54}H_{45}P_3CuCl$: C, 73.22; H, 5.12; P, 10.49. Found: C, 72.80; H, 4.85; P, 10.11; mp 168–169° (lit.[6] mp 166°). Calcd for $C_{54}H_{45}P_3CuBr$: C, 69.72; H, 4.88; P, 9.99. Found: C, 69.79; H, 4.86; P, 10.16; mp 166–167° (lit.[6] mp 164–167°). Calcd for $C_{54}H_{45}P_3CuI$: C, 66.36; H, 4.64; P, 9.51. Found: C, 66.61; H, 4.82; P, 9.83; mp 150–151° (lit.[6] mp 150–151°).

Halotris(diphenylmethylphosphine)copper(I).—Cuprous chloride (1 g, 0.01 mol) and diphenylmethylphosphine (8.0 g, 0.04 mol) were refluxed in 150 ml of ethanol. The hot solution was filtered and, on cooling, yielded white crystals. These were filtered and dried *in vacuo* at room temperature. The bromide and iodide were similarly prepared. *Anal.* Calcd for $C_{39}H_{39}P_3CuCl$: C, 66.95; H, 5.62. Found: C, 66.37; H, 5.69; mp 181°. Calcd for $C_{39}H_{39}P_3CuBr$: C, 62.95; H, 5.28; P, 12.49. Found: C, 63.03; H, 5.20; P, 12.55; mp 189–190°. Calcd for $C_{39}H_{39}P_3CuI$: C, 59.21; H, 4.97. Found: C, 58.56; H, 4.93; mp 193–194°.

Chlorotris(dimethylphenylphosphine)copper(I).—Dimethylphenylphosphine (13.7 g, 100 mmol) and cuprous chloride (2.5 g, 25 mmol) were stirred for 2 hr in 200 ml of benzene. The volume of the resulting colorless solution was reduced at low pressure. Addition of cyclohexane yielded white needles which were filtered, washed several times with cyclohexane, and dried *in vacuo* at ambient temperature. The compound was found to be light sensitive. *Anal.* Calcd for $C_{24}H_{33}P_3CuCl$: C, 56.14; H, 6.48; P, 18.10. Found: C, 56.37; H, 6.73; P, 18.06; mp 90–91°.

Halotris(dimethylphenylphosphine)copper(I).—Dimethylphenylphosphine (5.5 g, 40 mmol) and cuprous bromide (1.4 g, 10 mmol) were refluxed in 60 ml of absolute ethanol. The solution was filtered hot and the solvent was reduced at low pressure. The addition of cyclohexane yielded 3.4 g (61%) of a white crystalline material which was filtered, washed several times with cyclohexane, and dried *in vacuo* at ambient temperature. The iodide was prepared in an analogous fashion. Both compounds were found to be light sensitive. *Anal.* Calcd for $C_{24}H_{33}P_3CuBr$: C, 51.67; H, 5.96; P, 16.65. Found: C, 51.87; H, 5.96; P, 16.82; mp 102°. Calcd for $C_{24}H_{33}P_3CuI$: C, 47.65; H, 5.50. Found: C, 48.40; H, 5.77; mp 91–92°.

Halotris(diphenylmethylarsine)copper(I).—These compounds were prepared as described by Nyholm.[8] *Anal.* Calcd for $C_{39}H_{39}As_3CuCl$: C, 56.33; H, 4.73. Found: C, 56.45; H, 4.91; mp 117° (lit.[8] mp 117°). Calcd for $C_{39}H_{39}As_3CuBr$: C, 53.47; H, 4.49; As, 25.66. Found: C, 53.26; H, 4.44; As, 25.69; mp 129° (lit.[8] mp 134°).

μ-Dichloro-tetrakis(dimethylphenylarsine)dicopper(I).—Dimethylphenylarsine (11.0 g, 0.060 mol) and cuprous chloride (1.5 g, 0.015 mol) were stirred in 150 ml of chloroform for 1 hr. The solution was filtered and half of the solvent was removed at reduced pressure. Addition of cyclohexane or petroleum ether (bp 30–60°) yielded 3.44 g (41%) of white crystalline material. This was washed with several small portions of cyclohexane and dried *in vacuo*. *Anal.* Calcd for $C_{32}H_{44}As_4Cu_2Cl_2$: C, 41.48; H, 4.79. Found: C, 41.40; H, 4.90; mp 125° dec.

μ-Dibromo-tris(triphenylphosphine)dicopper (I)–Chloroform.—This complex was prepared by a literature method.[6] Analysis indicated the presence of one chloroform molecule of crystallization. Heating *in vacuo* at 60° did not remove the chloroform. *Anal.* Calcd for $C_{55}H_{46}P_3Cu_2Br_2Cl_3$: C, 55.37; H, 3.87; P, 7.82. Found: C, 55.84; H, 4.09; P, 7.82; mp 231–232°.

Osmometric Measurements.—Measurements were carried out at 37° over a range of concentrations with a Mechrolab Model No. 301A vapor pressure osmometer calibrated with benzil. The solvent was Baker Analyzed Spectrophotometric grade chloroform deoxygenated prior to use. All solutions were made in a drybox and exposed to the atmosphere only for the short time necessary to make a measurement. The results were reproducible to ±2%.

Results and Discussion

General Considerations.—Since there can be as many as six distinct types of complexes—L_3CuX, $(L_2CuX)_2$, L_2CuX, $L_3Cu_2X_2$, $(LCuX)_4$, and $(LCuX)_2$[24]—present in solution, five independent equations are necessary to interrelate them. The following equilibria are sufficient to define the system completely

$$2L_3CuX \rightleftharpoons (L_2CuX)_2 + 2L \qquad (1)$$

$$(L_2CuX)_2 \rightleftharpoons 2L_2CuX \qquad (2)$$

$$(L_2CuX)_2 \rightleftharpoons L_3Cu_2X_2 + L \qquad (3)$$

$$L_3Cu_2X_2 \rightleftharpoons (LCuX)_2 + L \qquad (4)$$

$$2(LCuX)_2 \rightleftharpoons (LCuX)_4 \qquad (5)$$

Any other equilibria that might be useful in describing the solution behavior of these complexes could be represented by suitable combinations of eq 1–5. Since $[(C_6H_5)_3P]_3CuCl$ has been shown to be a nonconductor in acetonitrile,[19] dissociation of the halide ion was assumed to be unimportant in the less polar solvent chloroform. Complexes of the type L_4CuX have been ignored completely since they have never been isolated when L is a unidentate ligand and X = Cl, Br, or I. The data for all compounds investigated are summarized in Table I.

The Effect of the R Group Substituents on the Dissociation of $[(C_6H_5)_{3-n}(CH_3)_nP]_3CuX$ Complexes.—One can immediately draw some qualitative conclusions from the osmometric data. The values of N in Table I show that in going from the tris(triphenylphosphine)copper(I) halides to the tris(diphenylmethylphosphine)copper(I) halides the extent of ligand dissociation is reduced considerably, while the difference between the latter complexes and the tris(dimethylphenylphosphine)copper(I) halides is negligible. Figure 1 illustrates this result for the chlorotris(tertiary phosphine)copper(I) complexes. Evidently, substitution of a methyl group for a phenyl group on each triphenylphosphine ligand in the 3:1 complex $[(C_6H_5)_3P]_3CuCl$

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[20] For both the arsine and phosphine complexes, ligand exchange at −65° is too rapid to allow the ^1H resonances of the methyl-substituted ligands to be resolved into their component peaks. That this behavior is due to fast exchange, rather than a fortuitous degeneracy of overlapping resonances, was established by concentration- and temperature-dependent studies: J. J. Mayerle, unpublished results.

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[24] Although compounds of the type $(LCuX)_4$ are generally too insoluble for molecular weight measurements in chloroform, certain of these complexes are known to undergo extensive dissociation in solution.[2,6] The fact that all evidence points to a dimeric structure for the compounds $[(C_6H_{11})_3PCuCl]_x$ in the solid state[11] offers some indication that the predominant equilibrium undergone by $(LCuX)_x$ complexes is that described by eq 5. The existence of monomers, trimers, or ligand-deficient tetramers cannot be ruled out, however. Since most of the work reported here was performed on solutions with L:CuX ratios of 3:1, this ambiguity does not pose a serious problem.

TABLE I
RESULTS OF OSMOMETRIC STUDIES

Compound	10^2[Cu], *M*	$10^2[M_{os}]$,^a *M*	N^b	10^2[Cu], *M*	$10^2[M_{os}]$, *M*	*N*
$[(C_6H_5)_3P]_3CuCl$	1.02^c	2.09	2.05	3.97	7.28	1.83
	1.99	3.84	1.93	4.51	8.41	1.86
	2.51	4.80	1.91	5.00	9.25	1.85
	3.02	5.82	1.94	5.99	10.89	1.81
	3.53	6.81	1.93			
$[(C_6H_5)_3P]_3CuBr$	0.99^c	1.95	1.97	4.00	7.06	1.77
	2.00	3.73	1.87	4.99	8.80	1.76
	3.00	5.48	1.83	6.00	10.28	1.71
$[(C_6H_5)_3P]_3CuI$	1.01^c	1.79	1.77	5.00	8.30	1.66
	1.99	3.51	1.76	6.01	9.90	1.65
	3.00	5.20	1.73	7.00	11.48	1.64
	4.00	6.70	1.68			
$[(C_6H_5)_2(CH_3)P]_3CuCl$	0.99^c	1.19	1.20	6.04	6.51	1.08
	1.99	2.27	1.14	7.11	7.68	1.08
	3.00	3.34	1.11	8.10	8.81	1.09
	3.99	4.47	1.12	8.91	9.54	1.07
	5.05	5.65	1.12	10.01	10.66	1.06
$[(C_6H_5)_2(CH_3)P]_3CuBr$	1.01^c	1.19	1.18	5.98	6.26	1.05
	2.01	2.40	1.19	7.01	7.44	1.06
	3.03	3.18	1.05	8.06	8.48	1.05
	3.98	4.21	1.06	9.06	9.92	1.09
	5.04	5.34	1.06	10.01	10.47	1.05
$[(C_6H_5)_2(CH_3)P]_3CuI$	1.00^c	1.07	1.07	5.99	6.20	1.04
	2.00	2.13	1.07	7.01	7.20	1.03
	3.01	3.14	1.04	8.01	8.27	1.03
	3.99	4.21	1.06	8.99	9.20	1.02
	5.00	5.22	1.04	10.01	10.33	1.03
$[(C_6H_5)(CH_3)_2P]_3CuCl$	2.02^c	2.31	1.14	6.00	6.51	1.04
	2.99	3.40	1.14	7.98	8.42	1.06
	4.00	4.40	1.10	10.00	10.57	1.06
	5.98	6.49	1.09	10.02	10.62	1.06
$[(C_6H_5)(CH_3)_2P]_3CuBr$	1.98^c	2.20	1.11	7.03	7.44	1.06
	3.07	3.33	1.08	7.98	8.12	1.02
	4.07	4.32	1.06	9.05	9.36	1.03
	5.03	5.35	1.06	10.03	10.34	1.03
	5.97	6.22	1.04			
$[(C_6H_5)(CH_3)_2P]_3CuI$	1.07^c	1.17	1.09	5.02	5.10	1.02
	1.94	2.01	1.04	6.06	6.11	1.01
	3.09	3.14	1.02	7.99	8.06	1.01
	4.17	4.27	1.02	9.95	10.12	1.02
$[(C_6H_5)_2(CH_3)As]_3CuCl$	1.98^c	3.35	1.69	6.01	8.56	1.42
	3.01	4.64	1.54	8.00	11.18	1.40
	4.01	6.11	1.52			
$[(C_6H_5)_2(CH_3)As]_3CuBr$	1.02^c	1.75	1.72	3.98	5.74	1.44
	1.97	3.13	1.59	5.01	7.14	1.43
	3.00	4.37	1.46	6.01	8.33	1.39
$[(C_6H_5)_3P]_3Cu_2Br_2\cdot CHCl_3$	3.01^d	3.92	1.30	5.98	7.30	1.20
	4.04	5.06	1.25	7.08	8.59	1.21
	5.03	6.23	1.24			
$\{[(C_6H_6)(CH_3)_2As]_2CuCl\}_2$	1.01^e	1.78	1.76	3.00	4.71	1.57
	1.50	2.57	1.71	4.00	6.20	1.55
	1.99	3.30	1.66	5.00	7.60	1.52

[a] Apparent molarity of the solution obtained from the osmometer. [b] $[M_{os}]/[Cu]$. [c] Copper concentration computed as L_3CuX. [d] Copper concentration computed as $L_3Cu_2Br_2\cdot CHCl_3$. [e] Copper concentration computed as $(L_2CuX)_2$.

causes a marked change in the extent of ligand dissociation, whereas further substitution of this type to give $[(C_6H_5)(CH_3)_2P]_3CuCl$ is of little or no significance. If the solution behavior of these complexes were governed predominantly by the basicity of the ligands, then the extent of ligand dissociation should decrease by increments following inversely the order of basicity: triphenylphosphine < diphenylmethylphosphine < dimethylphenylphosphine.[25] That this is not the case seems to exclude basicity as being useful in explaining the extent of ligand dissociation of these phosphine complexes.

Recent work has shown that stereochemical factors are largely responsible for the relative solution stabilities of tertiary phosphine complexes of d^{10} metals. Tolman[26] has drawn a correlation between the stability of Ni(0) complexes of the type NiL_4 (L = tertiary phosphine or phosphite ligand) and the size, not the electronic nature, of the ligand. Defining the cone

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(25) W. A. Henderson and C. A. Streuli, *J. Amer. Chem. Soc.*, **82**, 5791 (1960).

(26) C. A. Tolman, *ibid.*, **92**, 2956 (1970).

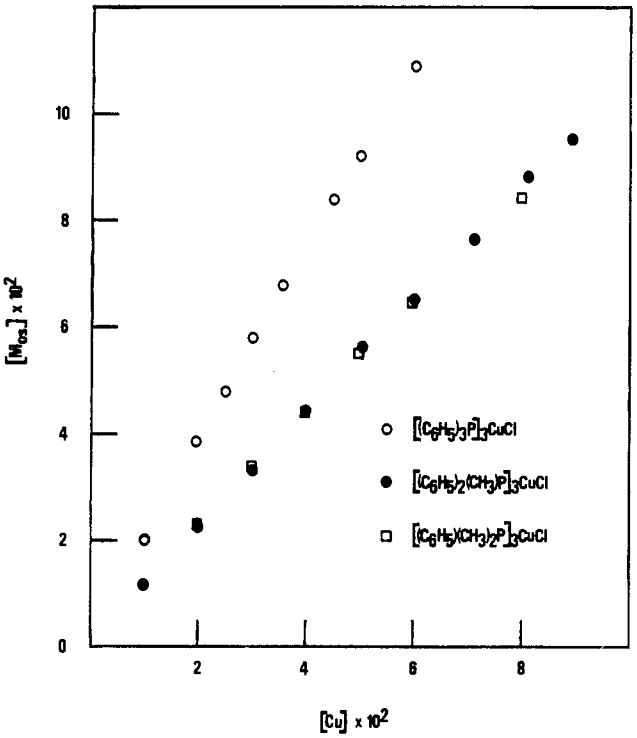

Figure 1.—Plots of the osmometric molarity $[M_{os}]$ as a function of total copper concentration for $[(C_6H_5)_{3-n}(CH_3)_nP]_3CuCl$ complexes.

angle of a ligand as being the angle needed to encompass complete rotation of the ligand, the angle apex being the nickel atom, a semiquantitative correlation was found between minimum cone angle and stability of the complex in ligand competition experiments of the type

$$NiL_4 + nL' \rightleftharpoons NiL_{4-n}L'_n + nL \qquad (6)$$

In general, ligands having small cone angles yielded the most stable complexes regardless of their basicity.

From the osmometric results it seems that the degree of ligand dissociation of tris(phosphine)copper(I) halide complexes is also controlled by steric factors. The crystal structure determination of $[(C_6H_5)_2(CH_3)P]_3CuCl$[7] revealed the phosphine ligands to be oriented in such a manner that each methyl group is directed toward, rather than away from, the chlorine atom. Replacing these methyl by phenyl groups would increase both the L–L and L–Cl nonbonded interactions (the cone angle for nickel of trimethylphosphine is 118 ± 4° compared to 145 ± 2° for triphenylphosphine).[26] If this feature of the structure persists in solution, substitution of phenyl for methyl should produce greater ligand dissociation, as observed. Substitution in the other direction, that is, of $(C_6H_5)_2(CH_3)P$ by $(C_6H_5)(CH_3)_2P$, does not lead to a further large reduction of stereochemical strain, as evidenced by the fact that the extents of ligand dissociation of the $[(C_6H_5)_2(CH_3)P]_3CuX$ and $[(C_6H_5)(CH_3)_2P]_3CuX$ complexes are nearly identical (Table I and Figure 1).

An extreme example of the influence of ligand size on the stability of L_mCuX compounds is manifest by the complexes of tricyclohexylphosphine, a ligand having a cone angle of 179°.[26] This ligand is so large that it forms no 3:1 complexes even though it is much more basic than any of the ligands used in this study.[25] Furthermore, the complexes $[(C_6H_{11})_3P]_2CuX$ (X = Cl, Br), which might be expected to be dimeric, appear to be monomeric in solution.[11] Presumably the compounds dissociate according to eq 2, although this process and that of eq 3, or any combination of the two, will give the same molecular weight by vapor pressure osmometry.

The Effect of the R Group Substituents on the Dissociation of $[(C_6H_5)_{3-n}(CH_3)_nAs]_3CuX$ Complexes and Comparison of Arsine and Phosphine Compounds.—Comparison of the N values of the tris-arsine with the corresponding tris-phosphine complexes (Table I) reveals the arsine compounds to be much less stable than their phosphine analogs. Also, in contrast to the phosphine series, there is a somewhat greater difference in the extent of ligand dissociation between the complexes of $(C_6H_5)_2(CH_3)As$ and $(C_6H_5)(CH_3)_2As$ for X = Cl (Figure 2). Assuming, therefore, that the difference in the degree of ligand dissociation between complexes of $(C_6H_5)_2(CH_3)As$ and $(C_6H_5)_3As$ will be as large as or larger than that between $(C_6H_5)_2(CH_3)P$ and $(C_6H_5)_3P$, the quantity of $[(C_6H_5)_3As]_3CuX$ that would exist in solutions of ligand:copper ratio 3:1 should be extremely small. In fact, this type of complex has never been synthesized by the usual (see Experimental Section) methods.[26a] Although $[(C_6H_5)_3As]_3CuCl$ has reportedly been prepared by mixing the

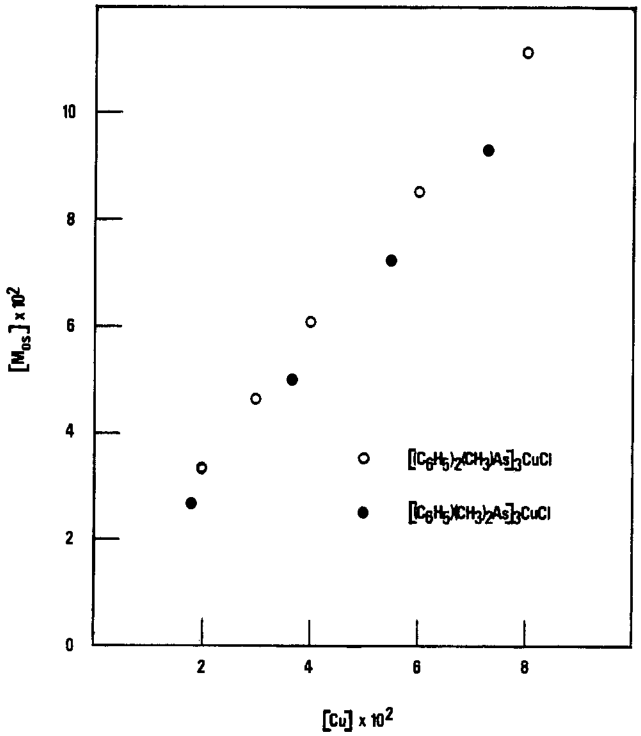

Figure 2.—Plots of the osmometric molarity $[M_{os}]$ as a function of total copper concentration for $[(C_6H_5)_{3-n}(CH_3)_nAs]_3CuCl$ complexes. Solutions for n = 2 were prepared by dissolving a mixture of L_2CuCl and L in 1:2.1 mole ratios. The values for $[M_{os}]$ were corrected for the very slight excess of added ligand.

(26a) NOTE ADDED IN PROOF.—The synthesis of $[(C_6H_5)_3As]_3CuBr$ has recently been reported [F. H. Jardine and F. J. Young, *J. Chem. Soc. A.*, 2444 (1971)] but its decomposition in chloroform precluded a molecular weight determination. Of greater interest is the fact that the reported molecular weight of $[(C_6H_5)_3As]_3Cu_2Br_2$ in chloroform indicates that this complex dissociates to a much greater extent in that solvent than does the analogous phosphine complex.

copper halide with the melted ligand,[9] we have not been able to duplicate this reaction.

It is possible that the differences in the covalent radii of phosphorus and arsenic would permit stereochemical factors to be operative between $(C_6H_5)_2(CH_3)As$ and $(C_6H_5)(CH_3)_2As$ complexes but not between the corresponding phosphine compounds. A more likely rationale is that with arsine ligands, being weaker donors than phosphines,[27] slight differences in basicity exert a greater effect on the extent of ligand dissociation. A similar argument was put forth by Cass and coworkers[3] to explain the relative stabilities of complexes of ligands $(p\text{-}XC_6H_5)(CH_3)_2Y$ where X = NH_2 or CF_3 and Y = P or As. It was found that the stability of the complexes was sensitive to the nature of X only when Y was arsenic.

The Effect of Halide on Ligand Dissociation.—The extent of ligand dissociation of the 3:1 type complexes with any given ligand (Table I) decreases in the order Cl > Br > I. This effect appears to be the most pronounced in the $[(C_6H_5)_3P]_3CuX$ complexes, being of smaller magnitude as methyl-substituted phosphines replace $(C_6H_5)_3P$ (Figure 3).

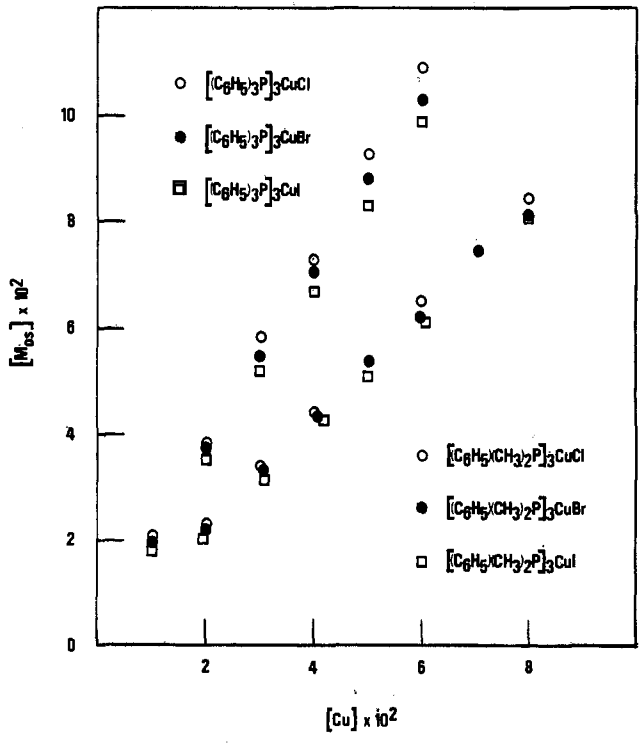

Figure 3.—Osmometric plots for $[(C_6H_5)_3P]_3CuX$ and $[(C_6H_5)(CH_3)_2P]_3CuX$ (X = Cl, Br, I).

Semiquantitative Interpretation and the Identification of the Major Species in Solution.—The equations specifying the quantity of each complex present in solution cannot be solved exactly from the osmometric data. Nevertheless, statements concerning the predominant species can be made with some confidence. The system $(C_6H_5)_3P$–CuBr will be examined in detail.

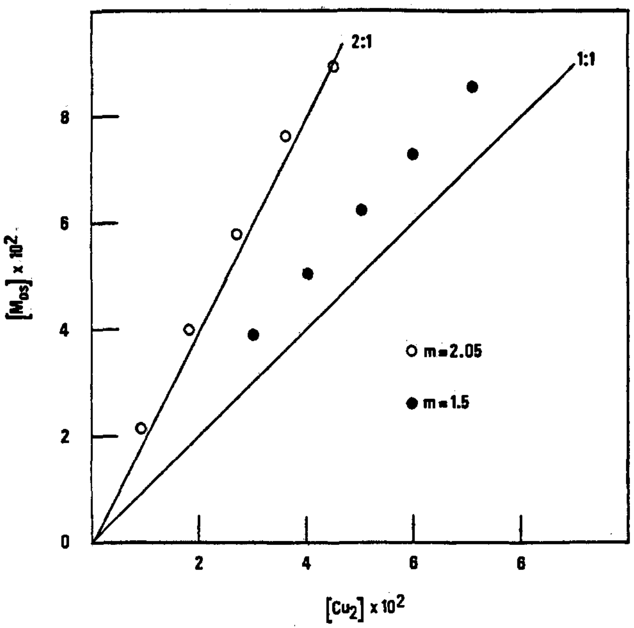

Figure 4.—Osmometric plots for $(L_mCuBr)_2$ complexes (L = $(C_6H_5)_3P$). The copper concentration was computed as $L_3Cu_2Br_2$ (m = 1.5). Data for m = 2.05 were obtained on solutions containing the appropriate mole ratios of $L_3Cu_2Br_2$ and L. The solid lines are theoretical plots for various possible solution equilibria, defined in the text.

The osmometric data for the complex $[(C_6H_5)_3P]_3Cu_2Br_2$ are plotted in Figure 4. The values of $[M_{os}]$ lie between the 1:1 line, expected if this complex underwent no ligand dissociation, and the 2:1 line, expected if it dissociated completely to $(LCuBr)_2$ by loss of a phosphine ligand, eq 4. In order for the system to be completely defined, eq 7–9 would have to be solved

$$[L]_T = 3[L_3CuX] + 4[(L_2CuX)_2] + 2[L_2CuX] + 3[L_3Cu_2X_2] + 4[(LCuX)_4] + 2[(LCuX)_2] + [L] \quad (7)$$

$$[Cu] = [L_3CuX] + 2[(L_2CuX)_2] + [L_2CuX] + 2[L_3Cu_2X_2] + 4[(LCuX)_4] + 2[(LCuX)_2] \quad (8)$$

$$[M_{os}] = [L_3CuX] + [(L_2CuX)_2] + [L_2CuX] + [L_3Cu_2X_2] + [(LCuX)_4] + [(LCuX)_2] + [L] \quad (9)$$

exactly, where $[L]_T$ is the total ligand concentration, bound and unbound, [Cu] is the total copper concentration, and $[M_{os}]$ is as defined in Table I. Since $(LCuX)_4$ is extensively dissociated in solution,[6] one can assume that all complexes having ligand:copper ratios of 1:1 exist as $(LCuBr)_2$.[24] Two further assumptions can be made. First, the quantity of L_3CuBr formed by disproportionation of $L_3Cu_2Br_2$ is assumed to be small. As shown in Figure 3, $[(C_6H_5)_3P]_3CuBr$ undergoes extensive ligand dissociation even under conditions in which the ligand:copper ratio (3:1) is twice that under discussion, suggesting that its concentration in solutions of $[(C_6H_5)_3P]_3Cu_2Br_2$ would be low. The second assumption is that the concentration of $(L_2CuBr)_2$ is also very small. Figure 4 shows that at ligand:copper ratios of 2.05:1, $[M_{os}]$ is approximately twice the value computed for the $(L_2CuBr)_2$ dimer (1:1 line). The second assumption therefore also appears to be a valid one. The problem can then be approached in either of two ways. The first is to assume that $L_3Cu_2Br_2$ disproportionates according to eq 10,

$$2L_3Cu_2Br_2 \rightleftharpoons 2L_2CuBr + (LCuBr)_2 \quad (10)$$

$K_{10} = K_2K_4/K_3$, and that the only additional species of importance in solution are L_2CuBr and $(LCuBr)_2$. The second approach is to assume that the predominant equilibrium is that of eq 4, the only additional species

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[27] S. Ahrland, J. Chatt, and N. R. Davies, *Quart. Rev., Chem. Soc.*, **12**, 265 (1958).

of importance being $(LCuBr)_2$ and L. Equations 7–9 can be solved exactly for each of the two cases and equilibrium constants calculated for eq 4 and 10 over a range of copper concentrations. The results of these calculations are listed in Table II. The absence of systematic errors in the values of K_4, compared to those for K_{10}, implies that eq 4 more aptly describes the system. The possibility that both equilibria occur simultaneously cannot be rigorously excluded, however. In any case, the mole fraction of copper existing as $L_3Cu_2Br_2$ can be calculated for the extremes in which either eq 4 or eq 10 exclusively describes the equilibrium undergone by $L_3Cu_2Br_2$. The results of these computations are also shown in Table II. In the midrange of copper concentrations studied, the $L_3Cu_2Br_2$ complex accounts for 50–75% of the total copper, indicating the stability of this complex relative to both L_2CuBr and $(LCuBr)_2$.

TABLE II

CALCULATIONS FOR THE SYSTEM $(C_6H_5)_3P$–CuBr[a]

10^2[Cu],[b] *M*	$10^2[M_{os}]$, *M*	10^3K_4, mol/l.	10^3K_{10}, mol/l.	χ_4 $(L_3Cu_2Br_2)$[c]	χ_{10} $(L_3Cu_2Br_2)$[d]
3.01	3.92	3.94	21.0	0.698	0.396
4.04	5.06	3.45	10.6	0.748	0.495
5.03	6.23	3.76	10.0	0.761	0.523
5.98	7.30	3.73	8.2	0.779	0.558
7.08	8.59	4.04	8.3	0.787	0.573
	Av	3.78 ± 0.23			

[a] Ligand:copper ratio = 3:2. [b] Total copper concentration computed as $(L_3Cu_2Br_2)$. [c] Mole fraction of copper as $L_3Cu_2Br_2$ from eq 4. [d] Mole fraction of copper as $L_3Cu_2Br_2$ from eq 10.

Figure 4 also shows that solutions with $(C_6H_5)_3P$:CuBr ratios of 2.05:1 have apparent molarities approximately twice the concentration of copper, computed as $(L_2CuBr)_2$. This result immediately eliminates $\{[(C_6H_5)_3P]_2CuBr\}_2$ as being an important species, since the molarity would approach the computed copper concentration if it were, and the points would fall on or near the 1:1 line. Approximate solutions to eq 7–9 are more difficult to obtain here, because of the inability to determine the importance of the monomeric L_2CuBr complex. To include the equilibrium between monomer and dimer, eq 2, in the calculation would introduce more variable than known parameters. The relative amounts of L_2CuBr, $L_3Cu_2Br_2$, and L, although believed to be the major compounds in solution, can therefore not be determined. The concentration of L_3CuBr, probably more important than in solutions of ligand:copper ratio 3:2, must still be fairly small. Again the ligand size is seen to be a major influence on the equilibria undergone in these systems, the extent of dissociation in chloroform solutions with L:CuBr ratios of 2:1 being markedly reduced for L = $(C_6H_5)_2PH$[1] compared to the present results for the triphenylphosphine analog.

As the values of *N* in Table I show, the quantity of $[(C_6H_5)_3P]_3CuBr$ in solutions of ligand:copper ratio 3:1 is rather small. The most abundant species are presumed to be $[(C_6H_5)_3P]_2CuBr$ and $[(C_6H_5)_3P]_3Cu_2Br_2$, the formation of $[(C_6H_5)_3PCuBr]_2$ being greatly suppressed by the large quantity of free ligand that arises from the dissociation of the 3:1 complex.

The 3:1 complexes L_3CuX [L = $(C_6H_5)_2(CH_3)P$, $(C_6H_5)(CH_3)_2P$; X = Cl, Br, I] are the only species of importance in solutions having ligand:copper ratios of 3:1 regardless of the products of ligand dissociation. For, as Figures 1 and 3 and the data of Table I indicate, the extent of this dissociation is rather small. Of interest in this respect is the fact that mixtures of these complexes with the borohydride ion, BH_4^-, in chloroform–ethanol solution are stable for several days, with no apparent reaction taking place, whereas solutions of halotris(triphenylphosphine)copper(I) react rapidly with BH_4^- giving $[(C_6H_5)_3P]_2CuBH_4$.[2,18,28] The borohydride ion probably reacts with the $[(C_6H_5)_3P]_2CuX$ monomer whereas in solutions of $[(C_6H_5)_{3-n}(CH_3)_nP]_3CuX$ (*n* = 1, 2) it would have to displace both the halide and one of the phosphine ligands.

Summary and Conclusions

The most striking result of the present study is the effect that substitution of diphenylmethylphosphine for the triphenylphosphine has in reducing the dissociation of L_3CuX complexes in chloroform solution. This behavior serves to illustrate further the influence of steric factors on the properties of d^{10} phosphine complexes.[26,29] The results for the arsine compounds generally parallel those for the phosphine analogs, the major difference being their greater tendency to dissociate in solution. In addition, the relative basicities of the $(C_6H_5)_n(CH_3)_{3-n}As$ ligands (*n* = 1, 2) are more important in determining the relative stabilities of L_3CuX complexes than for the corresponding phosphine compounds. For all L_3CuX compounds investigated dissociation of L was observed to increase in the series I < Br < Cl.

Positive identification of the various species present in solution is of course not possible by vapor pressure osmometry, and indirect methods involving concentration-dependent studies and addition of free ligand had to be employed. These experiments strongly suggest, if not prove, the preponderance of the ligand-deficient dimer $L_3Cu_2X_2$ in solutions of a L:CuX ratio of 1.5:1 for L = $(C_6H_5)_3Y$ and its importance in solutions with L:CuX ratios of 3:1 and 2:1. The discovery that a solid complex of composition L_2CuX has an observed molecular weight approximately half that calculated for the $(L_2CuX)_2$ dimer should not therefore necessarily be interpreted solely in terms of dissociation to monomers (eq 2), as has frequently been done. As pointed out earlier,[13] serious consideration must be given to the possible occurrence of the ligand-deficient dimer (eq 3).

In conclusion it should be emphasized that the results of the present study, carried out in chloroform solution at 37°, do not imply parallel behavior in other solvent systems or at other temperatures. Thus, for example, the addition of 4% of ethanol to a benzene solution of $[(C_6H_5)_3P]_3RhCl$ completely inhibits the dissociation of this complex,[30] and a similar dependence upon solvent composition could also be of great importance in the L_mCuX compounds. Perhaps the most valuable discovery of the present investigation is the dependence of solution behavior upon the steric properties of the R group substituents. The conclusion that ligand size largely determines the extent of dissociation is in

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general agreement with Tolman's work on nickel(0)–phosphine complexes[26] and may facilitate the design of d^{10} complexes containing tertiary group V donor ligands as specific catalysts.

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N-Aralkylpolyamine Complexes. II.[1] Five- and Six-Coordinate Complexes of Copper(II) with *N*,*N*′-Dibenzylethylenediamine

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The preparation and characterization of $[Cu(DBen)_2Br]ClO_4$, $[Cu(DBen)_2(NCS)(NO_3)]$, $[Cu(DBen)_2(SeCN)(NO_3)]$, $[Cu(DBen)_2(SeCN)(ClO_4)]$, $[Cu(DBen)_2(SCN)]Br$, and $[Cu_2(DBen)_4(SCN)(ClO_4)_2]ClO_4$ are reported. $[Cu(DBen)_2Br]Br$ was also characterized. Reflectance spectra at room temperature and at liquid nitrogen temperature, magnetic susceptibilities from room temperature to liquid nitrogen temperature, infrared and far-infrared spectra, and visible spectra and molar conductivities in DMF and methanol were used to deduce the structures. Preliminary electron spin resonance spectra of some of the complexes are also reported. Most noteworthy is the existence of the $[Cu(DBen)_2Br]^+$ cation in both trigonal-bipyramidal and square-pyramidal forms.

Introduction

Ethylenediamine and *N*-alkylethylenediamines are well known for their high coordinating abilities, but little is known of *N*-aralkylethylenediamines. There is one description of the electronic and magnetic properties of some copper(II) dibenzylethylenediamine (DBen) complexes.[1] According to the method of preparation, the $Cu(DBen)_2Br_2$ complex can be isolated in two geometric forms—a five-coordinate form and a tetragonal form.[1] There are two reports on stability constants of DBen complexes,[2,3] and further stability constant work, in dilute solution, has recently been completed.[4] $Ni(DBen)_2Br_2$ exists as a five-coordinate complex.[5]

There has recently been great interest in the bonding of the thiocyanate ligand to metal ions.[6] Jørgensen[7] has suggested that a given metal ion in either high or low oxidation state may exhibit M–SCN bonding, whereas in an intermediate oxidation state, the bond type may be M–NCS. Until Brown and Lingafelter[8] showed from X-ray analysis that the thiocyanate ligand is S bonded to copper in the $Cu(en)_2(SCN)_2$ complex, it was commonly believed that all of the thiocyanate complexes of first transition series metals are N bonded. Basolo, *et al.*,[9] have shown that Pd–NCS bonding occurs in $[Pd(Et_4dien)(NCS)]^+$, while Pd–SCN bonding occurs in $[Pd(dien)(SCN)]^+$, a difference which was considered to result from the steric factors and the differing basicities of the amines. At present, the thiocyanate ligand is known to bond in five different ways:[10] MSCN, MNCS, MSCNM, M_2SCN, and M_2SCNM. The selenocyanate ligand is also known to bond through either its nitrogen atom, its selenium atom, or both.

Experimental Section

Copper(II) salts (reagent grade), potassium selenocyanate (K & K Laboratories), and dibenzylethylenediamine (Aldrich Chemical Co.) were used without further purification. Spectro Grade solvents were used for solution spectra and for conductance measurements. Analytical data are presented in Table I.

Diffuse reflectance spectra at room temperature and at liquid nitrogen temperature were recorded on a Cary Model 14 spectrophotometer equipped with a diffuse reflectance accessory using magnesium oxide as reference. Solution spectra were recorded on the same instrument, using 1-cm silica cells and 10^{-3} *M* solutions.

Molar conductances of the 10^{-3} *M* solutions were determined at 25° using a Wayne Kerr Universal conductivity bridge, Model B221. Infrared spectra of Nujol or hexachlorobutadiene mulls were recorded between KBr plates over the range 5000–650 cm^{-1} with a Perkin-Elmer Model 21 spectrophotometer. The far-infrared spectra were measured between polyethylene plates over the range 600–250 cm^{-1} on a Perkin-Elmer Model 457 spectrophotometer. They and the magnetic susceptibility measurements were done on a Gouy balance at the University of Surrey, Guildford, Surrey, England. The esr spectra were recorded at Hunter College of the City University of New York on a Varian V4502 spectrometer.

(I) **Bromobis(*N*,*N*′-dibenzylethylenediamine)copper(II) Perchlorate.**—$[Cu(DBen)_2Br]Br$ was prepared from aqueous solution.[1] To a suspension of this compound (0.01 mol) in absolute ethanol was added solid $LiClO_4$ (0.012 mol). The solids were dissolved by heating at 95°. The resulting filtrate yielded navy blue crystals, which were washed with absolute ethanol.

(II) **Isothiocyanatonitratobis(*N*,*N*′-dibenzylethylenediamine)copper(II).**—A suspension of $Cu(DBen)_2(NO_3)_2$ (0.01 mol), prepared as described previously,[1] in absolute ethanol was treated with solid NH_4SCN (0.01 mol). The pink solid turned blue on shaking the mixture. The product was filtered and washed with ethanol. Recrystallization from DMF is not possible because of its very high solubility, but ethanol or a mixture of DMF and ethanol yields solid $Cu(DBen)_2(NO_3)_2$.

(III) **Selenocyanatonitratobis(*N*,*N*′-dibenzylethylenediamine)-**

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