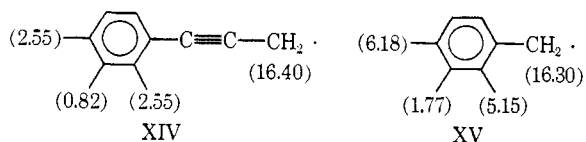


sizable splittings by the aromatic hydrogens in relationship to the benzyl radical XV.⁹ Using McConnell's



relationship we estimate that the interposition of two more carbon atoms of an acetylenic group into XV only reduces the spin density in the aromatic nucleus to a value 47% of that in the parent radical.²³

(23) This conclusion is a variance with an earlier chemical study.^{3b}

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Solution Structure of Coinage Metal-Phosphine Complexes

Sir:

We report preliminary nmr data that establish solution-state structures of copper-, silver-, and gold(I)-phosphine complexes. Solution behavior has proved to be unexpectedly complex. Many discrete crystalline complexes were found to dissolve in non-polar media to give *several* solution species even at low temperatures. The character and the number of solution species, in some cases, was markedly affected by temperature and by the nature of the solvent. The following structural information pertains to dichloromethane and dichloromethane-toluene solutions at temperatures in the range of ~ -100 to -50° ¹ and to a standard reference phosphine, L, tri-*p*-tolylphosphine.²

Solution structures for the phosphine-silver complexes are tetrahedral, trigonal coplanar, or linear with a relatively strong structural dependence on the character of the anion. The tetrahedral L_4Ag^+ ion was the only complex detected by ³¹P nmr³ for a wide range of silver salts⁴ in the presence of four or more equivalents of L.⁵ The $J_{107Ag-31P}$ and $J_{109Ag-31P}$ values were 227 ± 3 and 258 ± 3 Hz, respectively (hereafter only the ¹⁰⁷Ag value will be cited),⁶ and the chemical shifts fell in the

(1) Lability of phosphine ligands was kinetically evident from the ³¹P nmr spectra. Onset of rapid ligand exchange ranged from -70 to 0° depending on the specific complex.

(2) Structural assignments are based primarily on ³¹P coupling constants (silver) and ³¹P chemical shift data. Integrity of postulated species was further shown in mixtures of L_2MX and $L_{2-1}MX$, where the characteristic resonances for both species were found. Conductivity data in dichloromethane were also obtained as a function of temperature from 25 to -78° in dichloromethane. Conductivity data are reported for $0.01 M$ solutions at 25° . Sample reference values are 35, 40, and 35 mhos for the tetraphenylarsonium salts of Cl^- , $B_3H_8^-$, and $B_3H_2S^-$, respectively. Conductivity decreases from $+25$ to -78° in the ionic phosphine complexes were proportionate to those found in reference tetraphenylarsonium salts.

(3) Triethylphosphine internal capillary reference and proton noise decoupling.

(4) $B_3H_8^-$, $S_2PF_2^-$, $OCOCF_3^-$, NO_3^- , PF_6^- , ClO_4^- , $B_9H_{12}S^-$, $B_9H_{14}^-$, $B_{10}H_{13}^-$, $B_{11}H_{11}^-$, and BF_4^- .

(5) At low temperatures, there is no fast exchange of L between L_4Ag^+ and free L; the ³¹P spectrum consisted of the characteristic L_4Ag^+ and L resonances.

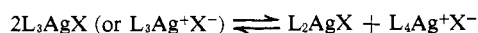
narrow range of -25.7 to -25.3 ppm.⁷ Ligand exchange was rapid above $\sim -50^\circ$ where the lines broadened and then a single resonance emerged. A few strong-field anions effectively competed with L for the silver coordination sphere; these included Cl^- , Br^- , I^- , and CN^- . The equilibrium constant at -80° for



was $\sim 10^{-1}$ for Br^- and Cl^- and at least 10^4 mol/l. for I^- and CN^- . No L_4Ag^+ was detected with the latter two counterions nor could $L_4Ag^+X^-$ solid phases be isolated with these four anions.

In solution, the L_3AgX species were of two types: pseudotetrahedral molecules and trigonal coplanar cations. The ionic set was based on anions such as PF_6^- , BF_4^- , and ClO_4^- . The chemical shift for these fell at lowest fields and in a narrow region, -30.6 ± 0.1 ppm, and the conductivities were high, 45–46 mhos. The observed J_{Ag-P} values were 316–321 Hz, comparing favorably with the calculated⁸ value for sp^2 silver of 303 Hz based on the observed 227-Hz value for sp^3 L_4Ag^+ . The halide, cyanate, and cyanide complexes were pseudotetrahedral L_3AgX aggregates. The J_{Ag-P} values for this set ranged from 230 to 280 Hz, and essentially no conductivity could be detected in dichloromethane solutions of these complexes. A large group⁹ of the L_3AgX complexes had J_{Ag-P} values ranging from 300 to 316 Hz and conductivities at 25° as high as 33 mhos. With but one exception, it is impossible at this stage to state whether there is *any binding* of the anion. The exception is the salt based on $S_2PF_2^-$. The ¹⁹F and the ³¹P data (J_{PF} and δ) at -80° for the anion in this salt were comparable to those for bound, unidentate $S_2PF_2^-$ in transition metal complexes.¹⁰ The conductivity was low, 3.5 mhos at 25° .

In solution, some L_3AgX complexes disproportionate extensively



This phenomenon was detected for the complexes with the counterions NO_3^- , $B_3H_8^-$, and $OCOCF_3^-$. The equilibrium constant for the nitrate was $\sim 10^{-2}$ at -84° . There was also evidence of significant phosphine dissociation at 25° in some of these complexes. For example, ³¹P chemical shift data and molecular weight information indicated that L_3AgCl , a discrete entity at low temperatures, was essentially completely dissociated at room temperature into L_2AgCl and L.

Linear L_2Ag^+ complexes were observed for the group with the PF_6^- , BF_4^- , and ClO_4^- counteranions. The coupling constants were about 500 Hz, compared with a calculated value of 452 Hz for sp linear L_2Ag^+ . Conductivities were high, ~ 39 mhos, and ¹⁹F data in the case of PF_6^- showed that even at low temperatures

(6) Observed $J(109)/J(107) = 1.15 \pm 0.1$; theory, 1.15.

(7) The conductivities of $L_4Ag^+X^-$ salts in dichloromethane were high, ranging from 26 to 50 mhos depending on the anion.

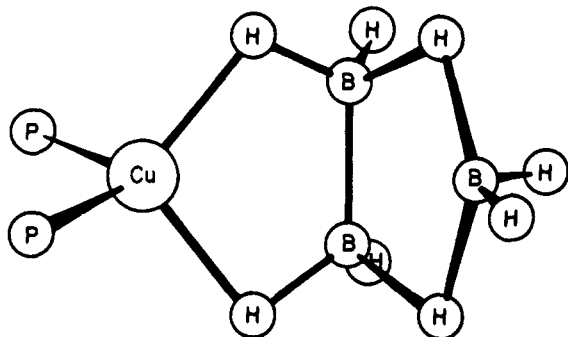
(8) This is based on estimation of the amount of s character in the Ag-P bond without any adjustment for changes in the effective nuclear charge on the metal. In those instances where the anion is bound, an electronegativity effect (or strength of the AgX bond) is operating and the coupling constants are not amenable to a simplistic analysis, at least in a quantitative sense. For reference to similar analyses in organic compounds, cf. N. Muller and D. E. Pritchard, *J. Chem. Phys.*, 31, 768 (1959).

(9) E.g., X = SCN^- , $B_3H_8^-$, NO_3^- , $B_9H_{12}S^-$, $S_2PF_2^-$, $OCOCF_3^-$.

(10) F. N. Tebbe and E. L. Muettterties, *Inorg. Chem.*, 9, 629 (1970).

the ion was not bound. All other salts¹¹ of the L_2AgX class investigated to date showed binding of the anion. The strength of the anion binding apparently varies significantly within this group. This was reflected in variations of the coupling constants and the chemical shifts. The cyanide, halide, thiocyanate, and isocyanate groups had very low coupling constants (278–383 Hz), and at room temperature these complexes showed essentially no conductance in dichloromethane. The other anions within this group, most of which are conjugate bases of strong acids, had substantially larger coupling constants, 390–470 Hz, and exhibited a detectable although very low conductance in dichloromethane at 25° (1–2 mhos). The ^{19}F nmr data for the anion in the $S_2PF_2^-$ derivative clearly showed binding of this anion.¹⁰ For all complexes in the L_2AgX group with bound anion there was no evidence of dimerization by bridging through the anion functionality, although this possibility cannot be rigorously excluded.

Copper(I) salts interact with tri-*p*-tolylphosphine to give primarily tetrahedral species, but in contrast to silver, most anions compete far more effectively than L for the coordination sphere. For example, $L_2CuB_3H_3$, even in the presence of a large excess of phosphine, exists solely as the pseudotetrahedral complex with $B_3H_3^-$ functioning as a bidentate ligand. The ^{31}P spectrum at -110° is an AB pattern fully consistent with the solid-state structure¹² established for $[(C_2H_5)_3P]_2CuB_3H_3$.



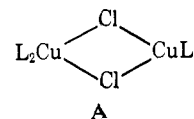
A similar AB pattern was found for $L_2CuB_{10}H_{13}$. The $S_2PF_2^-$ ion, although not effective as a bidentate ligand in the copper system, proved to be sufficiently well bound to prevent the formation of an L_4Cu^+ ion. Discrete $L_3CuS_2PF_2$ and $L_2CuS_2PF_2$ molecules were detected, and the ^{19}F nmr showed that the anion was bound at low temperatures in both of these complexes. The trisphosphino complex, however, underwent dissociation at room temperature to give solely $L_2CuS_2PF_2$ and L.¹³

One of the most complex systems encountered was phosphinocopper(I) chloride. Here the phosphine cannot displace chloride ion; there was no evidence for the formation of $L_4Cu^+Cl^-$. L_3CuCl was a pseudotetrahedral species. The dimeric complex (A) showed two lines of relative intensity 2:1 in the ^{31}P spectrum, consistent with the established solid-state structure.¹⁴

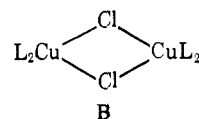
(11) CN^- , I^- , Br^- , Cl^- , SCN^- , OCN^- , $S_2PF_2^-$, $B_3H_3^-$, NO_3^- , and $OCOCF_3^-$.

(12) S. J. Lippard and K. M. Melmed, *Inorg. Chem.*, **8**, 2755 (1969).

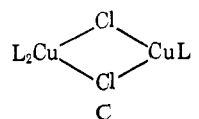
(13) This was definitively established from the temperature dependence of the ^{31}P and ^{19}F nmr spectrum as well as the change in the anion J_{PF} values as a function of temperature.



The saturated dimer (B) was the major species present in



solution at $\sim -100^\circ$. Above this, two kinds of dissociation occurred so that at about -70 to -80° there was present in addition to the saturated dimer (C),



L_3CuCl and a small amount of monomeric L_2CuCl . The bromide and iodide underwent a similar dissociation; however, monomeric L_2CuBr was present in higher concentrations and little monomeric or dimeric L_2CuI were discernible. Tetrakisphosphinocopper cations were detected in PF_6^- and NO_3^- systems; corroboration of this formulation was gained from an ^{19}F nmr study of the PF_6^- salt and from conductivity studies at low temperatures. The only tricoordinate species, $L_3Cu^+X^-$, detected was the PF_6^- derivative, where again ^{19}F and conductivity data substantiated this formulation. In contrast, the nitrate ion in L_3CuNO_3 was bound.

For gold, complexes of the form L_2Au^+ , L_3Au^+ , and possibly L_4Au^+ were identified from ^{31}P chemical shifts¹⁵ and conductivity data. Unlike the copper and silver systems, there was no evidence of anion binding except for $LAuX$ complexes. In solution, L_2AuCl partially disproportionates



The K_{eq} value at -80° was $\sim 10^{-1}$.

The effect of solvent change on the character of the solution complexes is now under intensive study and the dynamics of L and X exchange is being explored.

Acknowledgments. We are indebted to Mrs. Jean Read and Mr. Lou Walther for assistance in obtaining the 40.5-MHz ^{31}P spectra.

(14) D. F. Lewis, S. J. Lippard, and P. S. Welcker, *J. Amer. Chem. Soc.*, **92**, 3805 (1970), report the crystal structure of this unusual dimer based on the triphenylphosphine ligand.

(15) The ^{31}P resonance of a mixture of L_2Au^+ and L_3Au^+ salts consisted of the two resonances characteristic of these two cationic species.

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Electron Paramagnetic Resonance Study of Alkylimino Radicals Obtained by Photoinduced Decomposition of Aminoalkyl Radicals in Adamantane

Sir:

The observation of isotropic epr spectra of X-ray-induced free radicals trapped in an adamantane matrix