# Solution Structure and Kinetic Study of Metal–Phosphine and –Phosphite Complexes. I. The Silver(I) System

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**Abstract:** The character of the solution interaction of silver(I) salts with the phosphorus ligands (L), tri-*p*-tolylphosphine and triethyl phosphite, has been elucidated primarily through analysis of $^{31}$P nmr data. The $L_4Ag^+$ cationic complex prevails in solution at low temperatures for all salts except cyanide, iodide, bromide, and chloride, provided that at least 4 equiv of phosphorus ligand per silver salt are present. The ligands are labile in $L_4Ag^+$ as shown by the loss of the Ag–P coupling at temperatures above ∼−70°. The exchange is independent of free ligand concentration but dependent upon the nature of the counteranion. Ligand lability is higher in the phosphine than in the phosphite system. In the bromide and chloride systems the equilibrium, $L_4Ag^+X^- \rightleftharpoons L_3AgX + L$, was detected by adding excess ligand to the solution. In 3L–AgX solutions at ∼−90°, either $L_3Ag^+X^-$ or $L_3AgX$ forms; the determinant factor is the complexation character of the anion. $L_3Ag^+X^-$ was the predominant form for the $PF_6^-$, $BF_4^-$, and $ClO_4^-$ salts and tetrahedral $L_3AgX$ for the $Cl^-$, $Br^-$, $I^-$, $NCO^-$, $CN^-$, and $S_2PF_2^-$ derivatives. Surprisingly, some $L_3AgX$ compounds underwent disproportionation in solution at −90°: $2L_3AgX$ (or $L_3Ag^+X^-$) $\rightleftharpoons L_4Ag^+X^- + L_2AgX$. This behavior was found for the nitrate, triborohydride, and trifluoroacetate derivatives in the phosphine system and for the perchlorate and nitrate in the phosphite system. There was some evidence at 25° for dissociation of $L_3AgX$ to $L_2AgX$ and L. For the 2:1 solutions, $L_2Ag^+$ cationic complexes dominated in the $PF_6^-$, $BF_4^-$, and $ClO_4^-$ group and neutral $L_2AgX$ complexes for most other derivatives. Ligand lability in $L_3Ag^+$ was greater than that in $L_2Ag^+$, and the same ordering obtained for the neutral $L_3AgX$ and $L_2AgX$ complexes. In the neutral $L_3AgX$ and $L_2AgX$ series, phosphorus ligand lability was sensitive to the binding power of the anion, with the cyanide complex most labile.

Trivalent phosphorus compounds as exemplified by phosphines and phosphites serve as a very important class of ligands in metal complex chemistry.[1a] Especially distinctive are the catalytically active phosphine complexes which are a common feature of modern developments in homogeneous catalysis.[1b] Explication of mechanistic details in these catalytic systems requires an understanding of the solution structure of the complexes, stereochemistry, and a knowledge of the kinetic and thermodynamic parameters of the phosphorus ligands. We are making a systematic study of such solution-state, metal complex chemistry with primary reliance on nuclear magnetic resonance data. A preliminary report on coinage metal–phosphine complexes[2] has appeared as well as a study of phosphinometalloboranes.[3] We report here extensive data and general qualitative conclusions about structural and kinetic features of phosphine and phosphite complexes of silver(I) salts.[4]

Reference ligands (L) are tri-*p*-tolylphosphine and triethyl phosphite. These two ligands were selected primarily for the good, low-temperature solubility characteristics of the silver complex derivatives.

## $[(C_7H_7)_3P]_4Ag^+$ and $[(C_2H_5O)_3P]_4Ag^+$ Complexes

Isolable crystalline $L_4AgX$ compounds were obtained in the reaction of most silver salts with four or more equivalents of tri-*p*-tolylphosphine.[8] These tetrakis complexes dissolve in nonpolar solvents to give essentially the same $^{31}$P spectrum (Figures 1 and 2 and Table I) which below −60° consists of two doublets arising

**Table I.** $^{31}$P Nmr Parameters for $[(C_7H_7)_3P]_4AgX$ and $[(C_2H_5O)_3P]_4AgX$ Complexes

| X | $[(C_7H_7)_3P]_4AgX^a$ |  | $[(C_2H_5O)_3P]_4AgX^b$ |  |
|---|---|---|---|---|
|  | $J_{^{107}Ag-P}$ | $\delta^c$ | $J_{^{107}Ag-P}$ | $\delta^c$ |
| F | 224 | 25.3 |  |  |
| Cl | 225 | 25.3 | 341 | 153 |
| Br | 230 | 25.5 | 340 | 153.1 |
| I |  |  | 340 | 153 |
| SCN |  |  | 342 | 153.1 |
| $B_3H_8$ | 230 | 25.6 |  |  |
| $S_2PF_2$ | 225 | 25.6 |  |  |
| $OOCCF_3$ | 230 | 25.7 |  |  |
| $NO_3$ | 224 | 25.5 | 342 | 153.2 |
| $PF_6$ | 224 | 25.6 |  |  |
| $ClO_4$ | 225 | 25.6 | 341 | 153 |

[a] Parameters were obtained at −80°. The solvent was dichloromethane. [b] Parameters were obtained at −100°. The solvent was 80/20 dichloromethane–toluene mixture. [c] Chemical shifts are reported in parts per million with reference to an internal capillary of $(C_2H_5)_3P$; tri-*p*-tolylphosphine is at 11.1 ppm and triethyl phosphite at 159.9 ppm.

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(1) (a) G. Booth, *Advan. Inorg. Chem. Radiochem.*, **6**, 1 (1964); (b) E. L. Muetterties, Ed., "Transition Metal Hydrides," Marcel Dekker, New York, N. Y., 1971.

(2) E. L. Muetterties and C. W. Alegranti, *J. Amer. Chem. Soc.*, **92**, 4114 (1970).

(3) E. L. Muetterties, W. G. Peet, P. A. Wegner, and C. W. Alegranti, *Inorg. Chem.*, **9**, 2447 (1970).

(4) For background literature and for leading references to work on silver(I) complexes of this type, see ref 5–8. Most of the solution studies were on dilute solutions of the complexes at room temperature. Colligative properties, electronic spectra, and conductivities were the primary data collected.

(5) C. Kowala and J. M. Swan, *Aust. J. Chem.*, **19**, 555 (1966).

(6) H. C. Brinkhoff, A. G. Matthijssen, and C. G. Oomes, *Inorg. Nucl. Chem. Lett.*, **7**, 87 (1971).

(7) K. J. Coskran, R. D. Bertrand, and J. G. Verkade, *J. Amer. Chem. Soc.*, **89**, 4535 (1967), report $^{31}$P data at 25° for solutions of $L_4AgClO_4$ and $L_4AgNO_3$ with phosphite ligands.

(8) F. A. Cotton and D. M. L. Goodgame, *J. Chem. Soc.*, 5267 (1960), isolated tetrakis(phosphine)silver(I) salts with $ClO_4^-$, $BrO_3^-$, and $NO_3^-$ as counterions.

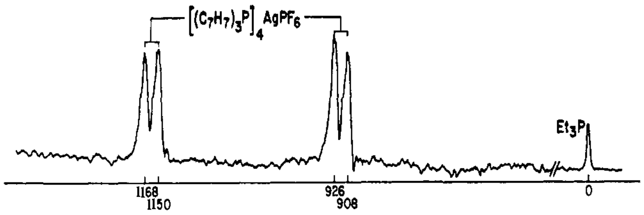

Figure 1. The $^{31}P$ 40.5-Mc spectrum of tetrakis(tri-*p*-tolylphosphine)silver hexafluorophosphate at −86° in dichloromethane.

from $^{107}Ag$–$^{31}P$ and $^{109}Ag$–$^{31}P$ spin–spin coupling.[9] The analogous phosphite complexes yielded similar spectra. All chemical shifts for the phosphine set fell in a narrow range, and those for the phosphites fell in another narrow range (Table I). Nmr intensity relations between free and bound ligand for mixtures of known amounts of $L_4Ag^+X^-$ and L were determined to definitely establish that four phosphorus ligands are bound to the metal nucleus. The counterion in not bound. This state was inferred from the invariability of the nmr parameters for the phosphine (and phosphite) complexes with change in counterion and was confirmed by conductivity studies which showed the complexes to have conductivities comparable to several tetraphenylarsonium salts (Table II).

Table II. Conductivity Data

| Compound[a] | Equivalent conductance ($\Omega^{-1}$ cm$^2$ equiv$^{-1}$) in dichloromethane $10^{-2}$ equiv/l. | $10^{-3}$ equiv/l. |
|---|---|---|
| $(n\text{-}C_3H_7)_4NCl$ | 9.2 | 19.0 |
| $(n\text{-}C_3H_7)_4NS_2PF_2$ | 14.6 | 28.0 |
| $(C_6H_5)_4AsCl$ | 35.0 | 52.0 |
| $(C_6H_5)_4AsB_3H_8$ | 40.0 | 60.0 |
| $(C_6H_5)_4AsNO_3$ | 34.9 | 55.0 |
| $(C_6H_5)_4AsNO_3$ (−78°) | 10.5 | 16.0 |
| $(C_6H_5)_4AsOOCCF_3$ | 36.0 | 56.0 |
| $(C_6H_5)_4AsOOCCF_3$ (−78°) | 13.9 | 17.0 |
| $L'_2AgCl$ | 0.1 | |
| $L'_2AgCl$ (−78°) | 0.1 | |
| $L'_3AgCl$ | 0.2 | |
| $L'_3AgCl$ (−78°) | 0.07 | |
| $L'_2AgNO_3$ | 0.7 | 0.9 |
| $L'_2AgNO_3$ (−78°) | 0.08 | |
| $L'_4AgNO_3$ | 20.0 | |
| $L'_4AgNO_3$ (−78°) | 10.8 | |
| $L_2AgCl$ | 0.2 | |
| $L_3AgCl$ | 0.4 | |
| $L_3AgI$ | 0.2 | |
| $L_2AgS_2PF_2$ | 0.7 | 1.0 |
| $L_3AgS_2PF_2$ | 3.5 | |
| $L_2AgO_2CCF_3$ | 2.4 | 4.0 |
| $L_3AgO_2CCF_3$ | 15.0 | 17.0 |
| $L_3AgO_2CCF_3$ (−78°) | 6.9 | 9.7 |
| $L_2AgNO_3$ | 1.8 | 3.9 |
| $L_3AgNO_3$ | 26.0 | 28.0 |
| $L_3AgNO_3$ (−30°) | 21.0 | |
| $L_4AgNO_3$ | | 37.0 |
| $L_4AgNO_3$ (−30°) | 28.0 | |
| $L_2AgPF_6$ | | 60.0 |
| $L_2AgPF_6$ (−78°) | 10.0 | 14.0 |
| $L_3AgPF_6$ | 46.0 | 58.0 |
| $L_3AgPF_6$ (−30°) | 32.0 | |
| $L_4AgPF_6$ | 50.1 | 66.0 |
| $L_3AgClO_4$ | 45.1 | 55.0 |
| $L_2AgB_9H_{12}S$ | 5.2 | 10.0 |
| $L_3AgB_9H_{12}S$ | 33.0 | 39.2 |

[a] $L = (C_7H_7)_3P$; $L' = (C_2H_5O)_3P$.

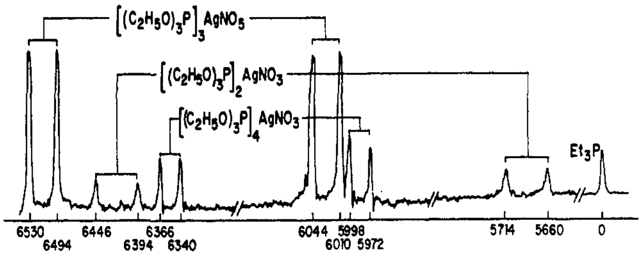

Figure 2. The $^{31}P$ 40.5-Mc spectrum of the tris(triethyl phosphite)-silver nitrate at −90° in 80/20 dichloromethane–toluene. This tris complex partially disproportionates to give the bis and tetrakis complexes.

Silver(I) chloride, bromide, and cyanide did not form isolable $L_4AgX$ complexes, but the tetrakis complexes were detected for some salts in the nmr experiment by addition of phosphine to the $L_3AgX$ solutions. Equilibrium constants calculated for (1) at low temperatures

$$L_4Ag^+X^- \rightleftharpoons L_3AgX + L \qquad (1)$$

from nmr intensities, are shown in Table III. The value given for the fluoride is only an estimate. A competing fluorination reaction (2) made quantitative measurements difficult. The marked tendency of cyanide and halide ions to bind, to the exclusion or near exclusion of a fourth phosphorus ligand, to $L_3Ag^+$ more strongly than other counterions employed (Table I) in this study is not unexpected.

Table III. Equilibrium Data for $L_4AgX \rightleftharpoons L_3AgX + L$ in Dichloromethane

| Anion | Ligand | *K*, mol/l. | Temp, °C |
|---|---|---|---|
| F | $(C_7H_7)_3P$ | 0.7 (est) | −100 |
| Cl | $(C_2H_5O)_3P$ | 0.03 | −100 |
| Cl | $(C_7H_7)_3P$ | 0.3 | −86 |
| Br | $(C_2H_5O)_3P$ | 0.04 | −100 |
| Br | $(C_7H_7)_3P$ | 0.7 | −86 |
| I | $(C_2H_5O)_3P$ | 0.7 | −100 |
| I | $(C_7H_7)_3P$ | $>10^4$ (est) | −100 |
| CN | $(C_2H_5O)_3P$ | $>10^4$ (est) | −100 |
| CN | $(C_7H_7)_3P$ | $>10^4$ (est) | −100 |

$$2AgF + R_3P \longrightarrow 2Ag + R_3PF_2 \qquad (2)$$

Lability of the phosphorus ligands in $L_4Ag^+$ was evident in the temperature dependence of the $^{31}P$ nmr spectra. Broadening of the $^{31}P$ multiplets commenced at temperatures above ∼−70° and was followed by coalescence at −40 and −15° for phosphine and phosphite complexes, respectively. Exchange rates (Table IV) were essentially identical for the relatively nonpolarizable anions, *e.g.*, $NO_3^-$, $ClO_4^-$, and $PF_6^-$ in the phosphine series and in the phosphite series. Added phosphorus compound did not detectably alter the ligand exchange rate. Absence of a marked anion effect suggests the ligand exchange mechanism in these tetrahedral, closed shell (18 electron) complexes[1b] closely approximates a simple dissociative S$_N$1 mechanism (3) where $k_1 \ll k_2$. Similar mechanistic con-

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(9) The multiplets were identified from the relative peak intensities and the magnitude of the coupling constant. Ratios of $J(^{109}Ag-^{31}P)/J(^{107}Ag-^{31}P)$ were consistently close to the $\mu(^{109}Ag)/\mu(^{107}Ag)$ ratio of 1.149.

Table IV. Rate Data for Ag–P Bond Rupture in Silver(I) Complexes

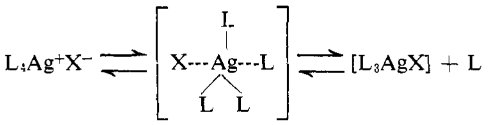
| Compound[a] | Approximate rate,[b,c] sec$^{-1}$ |
|---|---|
| $L_2AgCl$[d] | 3612 (−45) |
| $L_2AgNO_3$[d] | 4478 (+10) |
| $L_2AgPF_6$[d] | 4731 (+25) |
| $L_2AgPF_6$[d] | 4400 (+20) |
| $L'_2AgCl$[e] | 5245 (−45) |
| $L'_2AgNO_3$[e] | 6490 (−10) |
| $L_3AgCl$[d] | 2675 (−50) |
| $L_3AgPF_6$[d] | 3037 (−10) |
| $L'_3AgCl$[e] | 3894 (−45) |
| $L'_3AgClO_4$[e] | 4509 (−15) |
| $L_4AgNO_3$[d,f] | 75 (−70) |
| | 175 (−60) |
| | 2000 (−40) |
| | 13,000 (−20) |
| $L_4AgPF_6$[d] | 2094 (−40) |
| $L_4AgClO_4$[d] | 2094 (−40) |
| $L'_4AgNO_3$[e] | 3265 (−30) |
| $L'_4AgClO_4$[e,f] | 7 (−70) |
| | 17 (−60) |
| | 150 (−40) |
| | 4500 (−10) |
| $L'_4AgNO_3$[d] | 3265 (−30) |
| $L'_4AgNO_3$[g] | 3265 (−60) |
| $L'_4AgNO_3$[h] | 3265 (−40) |
| $L_4AgNO_3$[e] | 2095 (−40) |
| $L_4AgNO_3$[i] | 2095 (−50) |

[a] L = $(C_7H_7)_3P$; L′ = $(C_2H_5O)_3P$. [b] Temperatures in parentheses, accuracy ±5°. [c] Based on coalescence temperature. [d] Dichloromethane. [e] 80/20 dichloromethane–toluene. [f] Based on line-shape analysis of nmr data. The $E_a$ for dissociation of phosphine is 9 ± 1 kcal/mol and for phosphite is 11 ± 1 kcal/mol in the tetrakis complexes. [g] Toluene. [h] Acetonitrile. [i] 50/50 dichloromethane–toluene.

$$L_4Ag^+ \underset{k_2}{\overset{k_1}{\rightleftharpoons}} L_3Ag^+ + L^- \qquad (3)$$

clusions[10,11] have been reached for the isoelectronic $ML_4$ complexes in the nickel triad. The studies of Meier, *et al.*,[10] showed conclusively that in $ML_4$ substitution reactions the ligand dissociation step (3) is rate determining.

In $[(C_2H_5O)_3P]_4Ag^+SCN^-$, the exchange rate is substantially higher than in the analogous perchlorate and hexafluorophosphate salts. Since the thiocyanate is a much more effective nucleophile than these other anions, it is possible that the ligand exchange mechanism for the thiocyanate more closely approximates an SN2 (4) than an SN1 (3) mechanism.[12,13]



$$L_4Ag^+X^- \rightleftharpoons \left[ X\text{---}Ag(L)(L)(L)\text{---}L \right] \rightleftharpoons [L_3AgX] + L \qquad (4)$$

Ligand exchange rates for the $L_4Ag^+$ series were slightly higher in the phosphine than in the phosphite complexes (Table IV). However, the dissociation constants $K$ ($k_1/k_2$ in eq 1) must be just slightly higher for phosphite than phosphine in $L_4Ag^+$. Triethyl phosphite addition[14] to tetrakis(tri-*p*-tolylphosphine)silver salts led to the appearance of the $^{31}P$ resonance line characteristic of free phosphine and of multiplets due to various Ag(I)–phosphine–phosphite mixed complexes. In the converse experiment, addition of phosphine[14] gave a similar result; slightly more free phosphite appeared than free phosphine in the former experiment. This relative stability does not parallel the trend in the equilibrium data for eq 1 (Table III). In the isoelectronic nickel series, dissociation constants are much higher in a triarylphosphine than in triethyl phosphite complex.[11] We suggest that the small difference, if any, between the two ligands in the silver case reflects the formal positive charge of these complexes; phosphine should be far more effective than phosphite in reducing the charge on the metal atom. This effect nearly outweighs the steric factor that dominates ligand dissociation in the nickel complexes.[11,15,16]

The rates of ligand exchange in $L_4Ag^+$ are solvent dependent (Table IV); *e.g.*, the rate increases for $[(C_2H_5O)_3P]_4Ag^+$ in going from dichloromethane to acetonitrile to toluene. These rates do not correlate with the dielectric constant of the medium; specific solvation effects must be operative.

## Tetrahedral and Planar Tris(phosphine)- and Tris(phosphite)-Silver(I) Complexes

The $L_3AgX$ complexes are of two limiting types: neutral, tetrahedral $L_3AgX$ and ionic $L_3Ag^+X^-$. Included in the ionic phosphine set are the $PF_6^-$ and $ClO_4^-$ salts. Conductivities in dichloromethane were high (Table II). The nmr chemical shifts were at the lowest field in the tris series and coupling constants (Table V)

Table V. $^{31}P$ Nmr Parameters for $[(C_7H_7)_3P]_3AgX$ and $[(C_2H_5O)_3P]_3AgX$ Complexes

| | $[(C_7H_7)_3P]_3AgX$[a] | | $[(C_2H_5O)_3P]_3AgX$[b] | |
|---|---|---|---|---|
| X | $J_{^{107}Ag-P}$ | $\delta$[c] | $J_{^{107}Ag-P}$ | $\delta$[c] |
| F | 273 | 22.5 | | |
| Cl | 280 | 22.7 | 408 | 155.5 |
| Br | 278 | 21.7 | 398 | 153.2 |
| I | 266 | 18.8 | 390 | 150.1 |
| CN | 230 | 24.2 | 324 | 158.7 |
| SCN | ∼270 | ∼25 | 397 | 155.4 |
| $B_3H_8$ | 300 | 26.8 | | |
| $S_2PF_2$ | 308 | 26.5 | | |
| $OOCCF_3$ | 310 | 27.3 | | |
| $NO_3$ | 312 | 27.3 | 450 | 154.8 |
| $PF_6$ | 321 | 30.6 | | |
| $ClO_4$ | | | 472 | 149.1 |
| $B_9H_{12}S$ | 316 | 28.9 | | |

[a] Parameters were obtained at −80°. The solvent was dichloromethane. [b] Parameters were obtained at −100°. The solvent was 80/20 dichloromethane–toluene mixture. [c] Chemical shifts are reported in parts per million with reference to an internal capillary of $(C_2H_5)_3P$; tri-*p*-tolylphosphine is at 11.1 ppm and triethyl phosphite at 159.9 ppm.

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(10) M. Meier, F. Basolo, and R. G. Pearson, *Inorg. Chem.*, **8**, 795 (1969).

(11) C. A. Tolman, *J. Amer. Chem. Soc.*, **92**, 2956 (1970).

(12) It was noted above that added phosphorus compound did not affect the ligand exchange rates. In such reaction systems, a reaction intermediate or transition state analogous to $L_4AgX$ in (4) with L substituted for X is much less likely than in the anion case because of steric factors and charge considerations.

(13) Addition of a tenfold molar excess of $(C_2H_5)_4N^+SCN$ to the $L_4Ag^+SCN^-$ solution did not affect the temperature dependence of the nmr line shapes. However, this addition of thiocyanate ion probably did not substantially raise the activity of the ion in solution because of ion pairing and because of the necessarily high concentrations employed in the nmr studies.

(14) 0.5 mol of free ligand per $L_4Ag^+$.

(15) C. A. Tolman, *J. Amer. Chem. Soc.*, **92**, 2953 (1970).

(16) Furthermore, $Ag^+$ is larger than $Ni^0$.

were close to the estimated 303 Hz for sp$^2$ silver.[17] Ionic tris(triethyl phosphite)silver derivatives included the nitrate and perchlorate which had coupling constants ($^{107}$Ag) comparable to the calculated value of 449 Hz.[17]

A tetrahedral, neutral form was unequivocally established as the predominant solution species for the cyanide, cyanate, and halide complexes in the phosphine series. Conductivity was near zero (Table II), the $^{107}$Ag coupling constants approached the calculated sp$^3$ value of 227 Hz (Table V), and the established equilibria (3) require ion binding. Similar arguments apply to the cyanide, halide, and thiocyanate complexes in the phosphite series.

Intermediate in character were the trifluoroacetate, octahydridotriborate, and nitrate derivatives. The relatively large conductivities and coupling constants (Tables I and V) for these complexes suggest at least partial dissociation to $L_3Ag^+X^-$. However, the conductivities are not relevant because of the disproportionation these derivatives undergo (*vide infra*). In the case of the $S_2PF_2^-$ derivative, the conductivity was quite low and the $^{19}$F and $^{31}$P nmr data for the anion were comparable to those for bound, unidentate $S_2PF_2^-$ in transition metal complexes.[19]

Unexpectedly, some $L_3AgX$ species show extensive disproportionation, even at very low temperatures.

$$2L_3Ag^+X^- \rightleftharpoons L_4Ag^+X^- + L_2AgX \text{ (or } L_2Ag^+X^-) \quad (5)$$

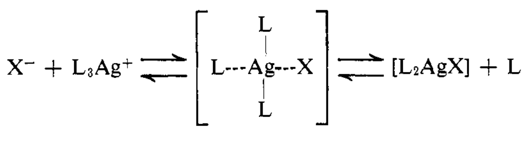
Estimates for the equilibrium constants were obtained by intensity measurements from the low-temperature $^{31}$P nmr spectra and are given in Table VI. There was no nmr evidence of disproportionation for any $L_3AgX$ complexes in which the counterion is tightly bound, *e.g.*, cyanide and halide.[20]

**Table VI.** Equilibrium Constants for the Reaction $2L_3AgX \rightleftharpoons L_4AgX + L_2AgX$

| | Phosphite (−90°)[a] | Phosphine (−86°)[b] |
|---|---|---|
| $NO_3^-$ | 0.1 | 0.15 |
| $ClO_4^-$ | 0.06 | $<10^{-4}$ (not detected) |
| $OOCCF_3^-$ | | 0.40 |
| $B_3H_8$ | | 0.64 |

[a] Dichloromethane–toluene in 8:2 volume ratio. [b] Dichloromethane.

All $L_3AgX$ complexes are kinetically labile. Phosphorus ligand exchange was fast on the nmr time scale above −70 to −50°. In the phosphine series, the ligand exchange rates for the neutral, tetrahedral complexes are just slightly higher than that for the $L_4Ag^+$ complexes with $NO_3^-$, $PF_6^-$, and $ClO_4^-$ counteranions (Table IV). Lower rates were found for the cationic trigonal $[(C_7H_7)_3P]_3Ag^+PF_6^-$ complex. These rates for the coordinately unsaturated $L_3Ag^+X^-$ complex are also lower than those for the coordinately saturated $L_4Ag^+X^-$ complexes. However, this expected rate reduction is small in contrast to the relatively large difference between $L_4Pt$ and $L_3Pt$.[18] A dissociative process is the only plausible mechanism for ligand exchange in the coordinately saturated $L_3AgX$ complexes. Ligand exchange in the ionic set may be more complex since there is the possibility of an SN2 contribution (6).[21]



$$X^- + L_3Ag^+ \rightleftharpoons \left[\begin{matrix} & L & \\ & | & \\ L\text{---} & Ag & \text{---}X \\ & | & \\ & L & \end{matrix}\right] \rightleftharpoons [L_2AgX] + L \quad (6)$$

Variation in ligand lability for the phosphite system paralleled that for the phosphines. Rate of ligand exchange decreased in the series CN > Cl ~ Br > SCN > $NO_3$ > $ClO_4$.

## Trigonal and Linear Bis(phosphine)- and Bis(phosphite)-Silver(I) Complexes

Nmr parameters for the $L_2AgX$ complexes are listed in Table VII. The estimated[17] coupling constants for sp linear $L_2Ag^+$ complexes are 452 and 676 Hz for phosphine and phosphite ligands, respectively; and the nmr data suggest that the $PF_6^-$, $BF_4^-$, and $ClO_4^-$ derivatives are ionic $L_2Ag^+X^-$ complexes. This is consistent with the high conductivities of these derivatives in dichloromethane (Table II).

In the phosphine series, the halide and pseudohalide complexes are neutral $L_2AgX$ complexes in solution at

**Table VII.** $^{31}$P Nmr Parameters for $[(C_7H_7)_3P]_2AgX$ and $[(C_2H_5O)_3P]_2AgX$ Complexes

| X | $[(C_7H_7)_3P]_2AgX$[a] $J_{^{107}Ag-P}$ | $[(C_7H_7)_3P]_2AgX$[a] $\delta$[c] | $[(C_2H_5O)_3P]_2AgX$[b] $J_{^{107}Ag-P}$ | $[(C_2H_5O)_3P]_2AgX$[b] $\delta$[c] |
|---|---|---|---|---|
| F | 450 | 28.1 | | |
| Cl | 378 | 21.4 | 550 | 154.3 |
| Br | | | 536 | 151.5 |
| CN | 278 | 23.8 | | |
| $B_3H_8$ | 390 | 29.3 | | |
| $S_2PF_2$ | 410 | 27.4 | | |
| $OOCCF_3$ | 451 | 29.5 | | |
| $NO_3$ | 470 | 29.8 | 680 | 149.5 |
| $PF_6$ | 496 | 33.4 | | |
| $ClO_4$ | 503 | 33.1 | 756 | 143.6 |
| $B_9H_{12}S$ | 420 | 33.9 | | |

[a] Parameters were obtained at −80°. The solvent was dichloromethane. [b] Parameters were obtained at −100°. The solvent was an 80/20 dichloromethane–toluene mixture. [c] Chemical shifts are reported in parts per million with reference to an internal capillary of $(C_2H_5)_3P$; tri-*p*-tolylphosphine is at 11.1 ppm and triethyl phosphite at 159.9 ppm.

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(17) The calculated value, simply an estimate of s character in the Ag–P bond, was not adjusted for changes in the effective nuclear charge on the metal. The model is crude but seems applicable to these cases. A similar relationship is not found for the zerovalent platinum–phosphine complexes.[18] In the platinum complexes, there is a significant change in color with change in coordination number, indicating large changes in $\Delta E$, the mean excitation energy (average energy of all triplet excited states interacting with the ground state). $\Delta E$ is an explicit term in the expression for the coupling constant. If $\Delta E$ changes substantially, then linear correlation of $J$ and s character may not follow. There was no evidence of color change with coordination number change in the silver series.

(18) D. H. Gerlach, A. R. Kane, G. W. Parshall, J. P. Jesson, and E. L. Muetterties, *J. Amer. Chem. Soc.*, **93**, 3543 (1971).

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

(20) A trigonal $L_3Ag^+$ complex is coordinately unsaturated. Some energy reduction in solution may be achieved by formation of the coordinately saturated $L_4Ag^+X^-$ especially if in the coformed $L_2AgX$ species the counteranion is bound. In fact, the counteranion appears to be bound in $L_2AgX$ where X is nitrate, trifluoroacetate, and octahydridotriborate. These anions are potentially bidentate; thus $L_2AgX$ could also be coordinately saturated in these derivatives.

(21) The high exchange rates observed for ionic $L_3Ag^+X^-$ complexes are probably not due to very small concentrations of free ligand. We found nmr line-shape changes with temperature to be virtually identical for solutions of $L_{3.0}Ag^+X^-$ and $L_{2.8}Ag^+X^-$ (synthetically prepared from $L_2AgX$ + 0.8L).

low temperature. The coupling constants were low compared to the linear sp estimate;[17] and conductivities were very low (Tables II and VII). Molecular weight data taken at 25° indicated that these complexes are monomeric with *possibly* some ligand dissociation. A number of derivatives had coupling constants that fell in the range of 380–470 Hz. Conductivities of these derivatives were measurable but low (Table II). Thus, it would appear that some derivatives in this intermediate group dissociate slightly in solution (7).

$$L_2AgX \rightleftharpoons L_2Ag^+ + X^- \tag{7}$$

Some neutral $L_2AgX$ complexes may be tetrahedral complexes with a bidentate anion, *e.g.*, $CF_3COO^-$, $NO_3^-$, $B_3H_8^-$, and $S_2PF_2^-$.[20,22] Nmr evidence supports this hypothesis for $S_2PF_2^-$. The $\delta_{^{19}F}$ and $J_{PF}$ values for $[(C_7H_7)_3P]_2AgS_2PF_2$ are close to the characteristic values[19] for the ion bound through both sulfur atoms, to give a tetrahedral, neutral complex.

The bisphosphite complexes of silver(I) were not extensively examined, but their behavior generally parallels that of the phosphine analogs. The perchlorate derivative is best characterized as $L_2Ag^+ClO_4^-$ and the halide and cyanide derivatives as neutral complexes based on the observed coupling constants and conductivities (Tables II and VII).

The ligands are labile in the trigonal $L_2AgX$ and linear $L_2Ag^+$ complexes. In the phosphine and phosphite series, the neutral $L_2AgX$ complexes undergo ligand exchange at a rate (Table IV) comparable to those of the tetrahedral $L_3AgX$ complexes. It is rather surprising that the rates for the bromide and chloride derivatives are so similar to those for the $L_3AgX$ and $L_2AgX$ species in both the phosphine and phosphite series. The linear $L_2Ag^+$ complexes are kinetically the most stable species, yet the rate differences between these coordinately deficient molecules and $L_4Ag^+$ are small (Table IV) compared to differences found in the platinum series.[18]

## Solution Structure at 25°

Because of the kinetic lability of the silver–phosphorus bond in the phosphine and phosphite systems, the nmr spectra provide no information concerning solution structure or composition of the silver complexes at 25°. All silver phosphite and phosphine complexes show an averaged chemical shift that is temperature dependent, whereas the free phosphorus ligands have essentially temperature-independent chemical shifts. The temperature dependence of chemical shift for the complexes could be taken as evidence for significant dissociation of ligand. This may be the case for $L_4Ag^+X^-$ species and perhaps other specific $L_3Ag^+$ or $L_3AgX$ complexes. However, $L_3AgNO_3$ cannot be significantly dissociated to $L_2AgNO_3$ because the conductivity of the former at 25° is substantially higher than that of $L_2AgNO_3$. Molecular-weight studies of the complexes suggested that dissociation was a common phenomenon. However, we are reluctant to interpret these data since the concentrations employed for the nmr and the molecular-weight studies are so different as to make comparative conclusions virtually meaningless. Also, where there is the possibility of ion dissociation as well as neutral ligand dissociation interpretation of "molecular weight" data is somewhat speculative.

## Experimental Section

**Nmr Studies.** The $^{31}P$ spectra were obtained on a Varian Associates HA-100 with a variable temperature controller at 40.5 MHz. The mode of operation employed a homonuclear lock on triethylphosphine with random noise decoupling of the protons and use of the CAT. The $^{19}F$ spectra were obtained on the HA-100 at 94.1 MHz with a trichlorofluoromethane lock and on the HR-60 at 56.4 MHz with trichlorofluoromethane internal reference. The temperature readings were accurate to ±6°. The results are tabulated in Tables I, V, and VII.

**Conductivity Studies.** The conductivities were measured on dichloromethane solutions at concentrations of $10^{-2}$ and $10^{-3}$ *M*. An Industrial Instruments conductivity bridge Model RC16B2 and a cell of constant 1.0 were used. The measurements were done at 25, −30, and −78°. Low-temperature determinations were carried out in a dry nitrogen atmosphere (Vacuum Atmospheres Dribox Model Dri-Lab He-43).

**Molecular Weight Studies.** Molecular weight studies were done in a dry nitrogen atmosphere. Ethanol was removed from chloroform for the vapor pressure osmometry measurements. The dichloromethane was Fisher Scientific and used as received. The freezing point determinations were carried out in benzene in a nitrogen atmosphere.

**Preparations of Solutions of the Triethyl Phosphite–Silver Complexes.** Since the triethyl phosphite–silver complexes generally melted below room temperature, they were not isolated. The commercial samples of the silver salts were analyzed prior to use. The triethyl phosphite was distilled in a nitrogen atmosphere prior to use. The solutions were prepared by adding the appropriately weighted amounts of the reactants to the solvent. All operations were effected in a dry nitrogen atmosphere (Vacuum Atmospheres Dribox).

**Synthesis of Tri-*p*-tolylphosphine–Silver Complexes.** The tri-*p*-tolylphosphine–silver complexes were isolatable, colorless, crystalline solids except for the tetrakis(tri-*p*-tolylphosphino)silver halides and the tris- and tetrakis(tri-*p*-tolylphosphino)silver difluorodithiophosphates which existed only in solution. These were prepared in solution by adding the appropriate amount of the phosphine to the $[(C_7H_7)_3P]_3AgX$ and $[(C_7H_7)_3P]_2AgS_2PF_2$ complexes.

**$[(C_7H_7)_3P]_2AgF$.** Silver fluoride (1 g, 7.9 × $10^{-2}$ mol) was dissolved in 25 ml of water and a solution of 4.7 g (1.5 × $10^{-2}$ mol) of tri-*p*-tolylphosphine in 75 ml of acetone was added. During this time the solution became brown. The reaction mixture was stirred 30 min, filtered, and evaporated to dryness. The glass-like solid was dissolved in acetonitrile and filtered to remove metallic silver and the filtrate evaporated to dryness to give a brown gum. Diethyl ether was slurried with the gum. The gum dissolved and a colorless solid separated, mp 162–166° dec.

*Anal.* Calcd for $C_{42}H_{42}P_2FAg$: C, 68.6; H, 5.8; F, 2.6; P, 8.4. Found: C, 66.0; H, 6.1; F, 2.6; P, 7.8.

Obtaining a pure compound proved difficult since in a competing reaction tri-*p*-tolylphosphine reduced Ag(I) to Ag(0) in solution. A pure $[(C_7H_7)_3P]_3AgF$ was not obtained. The nmr parameters were obtained from nmr solutions of mixtures of the bis and tris complexes.

**$[(C_7H_7)_3P]_2AgCl$ and $[(C_7H_7)_3P]_3AgCl$.** These complexes were prepared from silver chloride and tri-*p*-tolylphosphine in acetonitrile or chloroform using 1:2 and 1:3.5 molar ratios of reactants. The reaction solutions were evaporated to dryness. Recrystallization of crude $L_2AgCl$ and $L_3AgCl$ from acetone gave pure colorless crystals.

*Anal.* Calcd for $C_{42}H_{42}P_2ClAg$: C, 67.1; H, 5.6; mol wt, 752.5. Found: C, 67.6; H, 5.7; mol wt VPO ($CHCl_3$), 662; VPO ($CH_2Cl_2$), 413; cryoscopic ($C_6H_6$), 792; mp 188–190°. Calcd for $C_{63}H_{63}P_3ClAg$: C, 71.6; H, 6.0; Cl, 3.4; Ag, 10.2; mol wt. 1056. Found: C, 71.4; H, 6.1; Cl, 3.3; Ag. 10.3; mol wt VPO ($CHCl_3$), 540; VPO ($CH_2Cl_2$) 522; cryoscopic ($C_6H_6$), 498; mp 154–156°.

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[22] If this is the case for the triborohydride ion, then the phosphorus atom environments would be inequivalent and this should be evident in the $^{31}P$ nmr. An AB $^{31}P$ pattern was observed below −70° for the copper analog;[2,8] and the phosphorus environments equilibrated through a fast intramolecular rearrangement of the $CuB_3$ framework above −70°. There was no evidence of phosphorus atom inequivalence in $[(C_7H_7)_3F]_2AgB_3H_8$ at temperatures down to −100°. However, we find it difficult to visualize the $B_3H_8^-$ ligand being anything but a bifunctional moiety in this case and suggest that the absence of $^{31}P$ inequivalence under the conditions of our experiments simply reflects a very rapid rearrangement process.

**$[(C_7H_7)_3P]_2AgBr$.** Silver bromide (1.88 g, 1 × $10^{-2}$ mol) was added to a slurry of 6.08 g of tri-*p*-tolylphosphine (2 × $10^{-2}$ mol) in 100 ml of acetonitrile. The reaction mixture was heated at reflux ~6 hr until almost all the AgBr dissolved and then filtered. On cooling, colorless crystals appeared, which were recrystallized from acetone, mp 188–189°.

*Anal.* Calcd for $C_{42}H_{42}P_2BrAg$: C, 63.3; H, 5.3; P, 7.8; Br, 10.0. Found: C, 62.9; H, 5.5; P, 7.3; Br, 9.8.

**$[(C_7H_7)_3P]_3AgBr$.** The reaction was run as above but with 3 equiv of $(C_7H_7)_3P$ per equivalent of silver bromide. The colorless solid was recrystallized from acetone, mp 176–177°.

*Anal.* Calcd for $C_{63}H_{63}P_3BrAg$: C, 68.7; H, 5.8; Br, 7.3; Ag, 9.8. Found: C, 68.1; H, 5.8; Br, 8.4; Ag, 9.9.

**$(C_7H_7)_3PAgI$ and $[(C_7H_7)_3P]_3AgI$.** Silver iodide (2.34 g, 1 × $10^{-2}$ mol) was added to a solution of 6.08 g (2 × $10^{-2}$ mol) of tri-*p*-tolylphosphine in 40 ml of toluene. The reaction mixture was stirred at room temperature about 3 hr. During this time the silver iodide dissolved and a colorless solid formed. The reaction was filtered and the colorless solid was recrystallized from dichloromethane to give LAgI, mp 263–265°.

The filtrate from the above reaction was evaporated to dryness and the colorless solid recrystallized from acetone to give $L_3AgI$, mp 156–158°.

*Anal.* Calcd for $C_{21}H_{21}PIAg$: C, 46.8; H, 3.9. Found: C, 45.9; H, 4.1. Calcd for $C_{63}H_{63}P_3IAg$: C, 65.9; H, 5.5; Ag, 9.4. Found: C, 65.7; H, 5.4; Ag, 10.0.

No $L_2AgI$ was isolated from the reaction.

**$[(C_7H_7)_3P]_2AgCN$ and $[(C_7H_7)_3P]_3AgCN$.** Silver cyanide (2.68 g, 2 × $10^{-2}$ mol) was added to a solution of 12.2 g (4 × $10^{-2}$ mol) of tri-*p*-tolylphosphine in 100 ml of toluene. The silver cyanide immediately dissolved. The solution was evaporated to dryness, and the colorless solid was recrystallized from acetone, mp 154–156°. The infrared CN stretching frequency was ~2110 $cm^{-1}$.

*Anal.* Calcd for $C_{43}H_{42}NP_2Ag$: C, 69.5; H, 5.7; N, 1.9; P, 8.3; Ag, 14.5; mol wt, 742.6. Found: C, 69.5; H, 5.7; N, 2.0; P, 8.2; Ag, 14.6; mol wt VPO ($CH_2Cl_2$), 447.

The $L_3AgCN$ complex was synthesized similarly using 3 equiv of $(C_7H_7)_3P$ per AgCN. The colorless solid was recrystallized from diethyl ether, mp 128–133°. The CN stretch in the ir (Nujol spectrum) was at ~2110 $cm^{-1}$.

*Anal.* Calcd for $C_{64}H_{63}NP_3Ag$: C, 73.4; H, 6.1; N, 1.3; P, 8.9. Found: C, 71.3; H, 6.0; N, 1.8; P, 8.8.

**$[(C_7H_7)_3P]_2AgB_3H_8$.** Synthesis procedure was that of Muetterties, *et al.*[3] The product is light sensitive.

**$[(C_7H_7)_3P]_2AgS_2PF_2$.** The reaction was run in a dry nitrogen atmosphere. Tri-*p*-tolylphosphine (6 g, 2 × $10^{-2}$ mol) was dissolved in 130 ml of acetonitrile and a solution of 2.4 g (1 × $10^{-2}$ mol) of $AgS_2PF_2$ dissolved in 25 ml of acetonitrile was added. A colorless solid precipitated which was isolated by filtration. The solid was recrystallized from toluene, mp 198–205°.

*Anal.* Calcd for $C_{42}H_{42}F_2S_2P_3Ag$: C, 59.3; H, 5.0; F, 4.5; P, 10.9; Ag, 12.7. Found: C, 59.7; H, 5.1; F, 4.8; P, 11.2; Ag, 12.3.

**$[(C_7H_7)_3P]_3AgS_2PF_2$.** Attempts to isolate $[(C_7H_7)_3P]_3AgS_2PF_2$ by the procedure above but using 3 equiv of tri-*p*-tolylphosphine per equivalent of $AgS_2PF_2$ gave only $[(C_7H_7)_3P]_2AgS_2PF_2$. A solution of $[(C_7H_7)_3P]_3AgS_2PF_2$ was prepared by dissolving equivalent amounts of $(C_7H_7)_3P$ and $[(C_7H_7)_3P]_2AgS_2PF_2$ in dichloromethane.

**$[(C_7H_7)_3P]_2AgOOCCF_3$ and $[(C_7H_7)_3P]_3AgOOCCF_3$.** To a solution of tri-*p*-tolylphosphine (6 g, 2 × $10^{-2}$ mol) dissolved in 40 ml of toluene was added silver trifluoroacetate (2.2 g, 1 × $10^{-2}$ mol). The silver trifluoroacetate quickly dissolved. After stirring for 1 hr, the reaction mixture was filtered and the filtrate was evaporated to dryness to give a colorless solid which was recrystallized from acetone, mp 197–199°.

*Anal.* Calcd for $C_{44}H_{42}O_2F_3P_2Ag$: C, 63.7; H, 5.1; P, 7.5; F, 6.9; Ag, 13.0. Found: C, 63.4; H, 5.1; P, 7.6; F, 6.9; Ag, 13.0.

The synthesis of $[(C_7H_7)_3P]_3AgOOCCF_3$ was carried out by the same procedure as above using 6 g (2 × $10^{-2}$ mol) of tri-*p*-tolylphosphine and 1.47 g (6.7 × $10^{-3}$ mol) of silver trifluoroacetate, mp 174–176°.

*Anal.* Calcd for $C_{65}H_{63}O_2F_3P_3Ag$: C, 68.9; H, 5.6; F, 5.0. Found: C, 67.7; H, 5.6; F, 5.4.

**$[(C_7H_7)_3P]_2AgNO_3$, $[(C_7H_7)_3P]_3AgNO_3$, and $[(C_7H_7)_3P]_4AgNO_3$.** The silver nitrate–tri-*p*-tolylphosphine complexes were prepared by dissolving 1 equiv of silver nitrate in acetonitrile and adding it to a slurry of 2, 3, or 4 equiv of $(C_7H_7)_3P$ in acetonitrile. The tri-*p*-tolylphosphine dissolved immediately on addition of the silver nitrate solution. All the complexes were recrystallized from acetone.

*Anal.* Calcd for $C_{42}H_{42}NO_3P_2Ag$: C, 64.8; H, 5.4; N, 1.8; P, 8.0; Ag, 13.9; mol wt, 778.6. Found: C, 64.7; H, 5.7; N, 1.8; P, 7.5; Ag, 13.9; mol wt VPO ($CHCl_3$), 805; VPO ($CH_2Cl_2$), 783; cryoscropic ($C_6H_6$), 439; mp 185° coalesces, 199–202° melts. Calcd for $C_{63}H_{63}NO_3P_3Ag$: C, 69.9; H, 5.9; N, 1.3; P, 8.6; Ag, 10.0; mol wt, 1082.9. Found: C, 69.3; H, 5.9; N, 1.2; P, 8.6; Ag, 9.5; mol wt VPO ($CHCl_3$), 595; cryoscopic ($C_6H_6$) 609; mp 193–196°. Calcd for $C_{84}H_{84}NO_3P_4Ag$: C, 72.7; H, 6.1; N, 1.0; mol wt, 1387.3. Found: C, 72.6; H, 6.2; N, 1.1; mol wt VPO ($CHCl_3$), 554; cryoscopic ($C_6H_6$), 415; mp 147° coalesces, 177–190° melts.

**$[(C_7H_7)_3P]_2AgPF_6$, $[(C_7H_7)_2P]_3AgPF_6$, and $[(C_7H_7)_3P]_4AgPF_6$.** The hexafluorophosphate complexes were obtained by metathesis of $NH_4PF_6$ with the appropriate tri-*p*-tolylphosphine–silver nitrate complex in an acetonitrile–water solution or ethanol–water solution. The recrystallization solvent was a diethyl ether–tetrahydrofuran mixture for $L_2AgPF_6$, and acetone for $L_3AgPF_6$ and $L_4AgPF_6$.

*Anal.* Calcd for $C_{42}H_{42}P_3F_6Ag$: C, 58.6; H, 4.9. Found: C, 60.2; H, 5.9; mp 229–234°. Calcd for $C_{63}H_{63}P_4F_6Ag$: C, 64.9; H, 5.4. Found: C, 64.0; H, 5.4; mp 190° coalesces, 225–226° melts. Calcd for $C_{84}H_{84}P_5F_6Ag$: C, 68.6; H, 5.8; P, 10.5. Found: C, 68.4; H, 5.8; P, 10.2; mp 256–258° cloudy, 262° clear.

**$[(C_7H_7)_3P]_2AgClO_4$, $[(C_7H_7)_3P]_3AgClO_4$, and $[(C_7H_7)_3P]_4AgClO_4$.** No attempt was made to isolate the perchlorate complexes because of possible instability. Solutions were prepared by adding the appropriate ratios of tri-*p*-tolylphosphine and silver perchlorate to dichloromethane.

**$[(C_7H_7)_3P]_2AgB_9H_{12}S$[3] and $[(C_7H_7)_3P]_3AgB_9H_{12}S$.** The $L_2AgB_9H_{12}S$ was synthesized according to Muetterties, *et al.*[3] The $L_3AgB_9H_{12}S$ was not isolated but studied in solution by adding 1 equiv of tri-*p*-tolylphosphine to $L_2AgB_9H_{12}S$.

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