

Structural, Far-IR, and ^{31}P NMR Studies of Two-Coordinate Complexes of Tris(2,4,6-trimethoxyphenyl)phosphine with Silver(I) Halides

Lisa-Jane Baker,^{1a} Graham A. Bowmaker,^{*1a} David Camp,^{1b} Effendy,^{1c} Peter C. Healy,^{1b} Hubert Schmidbaur,^{1d} Oliver Steigelmann,^{1d} and Allan H. White^{1c}

Department of Chemistry, University of Auckland, Private Bag, Auckland, New Zealand, Division of Science and Technology, Griffith University, Brisbane 4111, Australia, Department of Physical and Inorganic Chemistry, University of Western Australia, Perth 6009, Australia, and Anorganisch-Chemisches Institut der Technischen Universität München, D-8046 Garching, Germany

Received September 20, 1991

Reaction of the highly basic, sterically hindered tertiary phosphine ligand tris(2,4,6-trimethoxyphenyl)phosphine [$\equiv\text{TMPP}$] with silver(I) halides, AgX ($\text{X} = \text{Cl}, \text{Br}$), yields the 1:1 adducts $[(\text{TMPP})\text{AgX}]$. The structures of these complexes have been determined by X-ray crystallography. The two compounds are isomorphous, crystallizing in the tetragonal space group $P4_1$. For the chloride ($\text{C}_{27}\text{H}_{33}\text{AgClO}_9\text{P}$), $a = 15.310$ (1) Å, $c = 12.366$ (1) Å, $Z = 4$, and $R = 0.031$ for 5771 "observed" ($I/\sigma(I) \geq 3.0$) reflections, while for the bromide ($\text{C}_{27}\text{H}_{33}\text{AgBrO}_9\text{P}$), $a = 15.319$ (4) Å, $c = 12.441$ (6) Å, $Z = 4$, and $R = 0.029$ for 2114 "observed" reflections. Both complexes contain mononuclear $[(\text{TMPP})\text{AgX}]$ molecules with approximately linear two-coordination about the silver atom. For the chloro complex, $\text{Ag}-\text{P}$ is 2.379 (1) Å and $\text{Ag}-\text{Cl}$ is 2.342 (1) Å, while for the bromo complex, $\text{Ag}-\text{P}$ is 2.374 (2) Å and $\text{Ag}-\text{Br}$ is 2.448 (1) Å. In both complexes, the silver atom is slightly displaced toward one of the *o*-methoxy oxygens with $\text{Ag}-\text{O} = 2.818$ (3) Å (Cl) and 2.826 (5) Å (Br), giving rise to slightly nonlinear $\text{P}-\text{Ag}-\text{X}$ angles of 175.0 (1)° (Cl) and 174.40 (6)° (Br). This represents the first complete structural characterization of compounds with a two-coordinate $\text{P}-\text{Ag}-\text{X}$ grouping. The far-infrared spectra of these complexes show strong $\nu(\text{Ag}-\text{Cl})$ and $\nu(\text{Ag}-\text{Br})$ bands at 282 and 215 cm^{-1} , respectively. Reaction of TMPP with AgI in a 1:1 mole ratio yields a solid which shows no band that is assignable to $\nu(\text{Ag}-\text{I})$. The ^{31}P NMR spectra of these complexes in chloroform solution show a superposition of two doublets due to coupling of the phosphorus nucleus with the two magnetic isotopes of silver (^{107}Ag , ^{109}Ag). The ^{31}P NMR parameters are $\delta = -67.2, -66.4$, and -64.6 ppm and $^1J(^{107}\text{Ag}^{31}\text{P}) = 821, 796$, and 745 Hz for $\text{X} = \text{Cl}, \text{Br}$, and I , respectively. Reaction of $[(\text{TMPP})\text{AgX}]$ with TMPP in a 1:1 mole ratio yields $[(\text{TMPP})_2\text{Ag}]^+\text{X}^-$ in solution, as evidenced by the halogen-independence of the ^{31}P NMR parameters and the closeness of these parameters to those for $[(\text{TMPP})_2\text{Ag}]^+[\text{ClO}_4]^-$ ($\delta = -70.9$ ppm; $^1J(^{107}\text{Ag}^{31}\text{P}) = 665.4$ Hz). The $^1J(\text{Ag}-\text{P})$ coupling constants for the species observed in the present study are larger in magnitude than those previously observed for corresponding complexes with other phosphine ligands, providing further evidence for the high base strength of TMPP. The ^{31}P CP/MAS solid-state NMR spectra of the $\text{X} = \text{Cl}$ and Br complexes are similar to the solution spectra and provide the first examples of $^{107}\text{Ag}/^{109}\text{Ag}$ isotopic splitting in the solid state. Attempts to characterize the 1:1 $[(\text{TMPP})\text{AgI}]$ complex by X-ray crystallography have thus far been unsuccessful. The ^{31}P CP/MAS NMR and far-IR spectra of the solid complex obtained from the 1:1 reaction of TMPP with AgI suggest that this is an ionic complex (or a mixture of such complexes), containing $[(\text{TMPP})_2\text{Ag}]^+$ as the cation; the solution ^{31}P NMR results indicate that this forms the molecular species $[(\text{TMPP})\text{AgI}]$ upon dissolution.

Introduction

The group 11 or coinage metals show a considerable variation in their properties from the lighter to the heavier members. This is reflected, for example, in the preferred oxidation states for these metals, the +I and +II states being the most common for copper under normal conditions, while the +I state is almost exclusively observed for silver and both the +I and +III states are found for gold. The +I oxidation state is thus the frequently encountered one which all of these metals have in common and corresponds to the d^{10} electron configuration. This configuration gives rise to some unusual features in the bonding properties of these metals, and one of these is the occurrence of the unusually low coordination numbers of 2 or 3 in some of their compounds. However, in this respect the variation in behavior between the different members of the group is also considerable. Thus, for Au^{I} , linear two-coordination is by far the most common situation, whereas for Cu^{I} and Ag^{I} , tetrahedral four-coordination is more frequently encountered. The early identification of species such as $[\text{Ag}(\text{NH}_3)_2]^+$ and $[\text{MX}_2]^-$ ($\text{M} = \text{Cu}, \text{Ag}; \text{X} = \text{Cl}, \text{Br}, \text{I}$) suggested that two-coordination would be common for Cu^{I} and Ag^{I} , but

subsequent studies have shown that this is not the case and that this type of coordination is rather rare.²⁻⁴ Two-coordination has been found, for example, in complexes with anionic ligands such as halides,⁴⁻⁸ cyanide,⁹ glycinate,¹⁰ and phosphorus ylides^{11,12} and with neutral ligands such as NH_3 ,¹³ amines,^{14,15} and imidazoles.^{16,17}

- (2) Lancashire, R. J. *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon: Oxford, England, 1987; Vol. 5, p 775.
- (3) Hathaway, B. J. *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon: Oxford, England, 1987; Vol. 5, p 533.
- (4) Bowmaker, G. A. *Adv. Spectrosc.* **1987**, *14*, 1.
- (5) Waters, D. N.; Basak, B. *J. Chem. Soc. A* **1971**, 2733.
- (6) Bowmaker, G. A.; Brockliss, L. D.; Whiting, R. *Aust. J. Chem.* **1973**, *26*, 29.
- (7) Asplund, M.; Jagner, S.; Nilsson, M. *Acta Chem. Scand.* **1983**, *37A*, 57.
- (8) Helgesson, G.; Jagner, S. *Inorg. Chem.* **1991**, *30*, 2574.
- (9) Gans, P.; Gill, J. B.; Griffin, M.; Cahill, P. C. *J. Chem. Soc., Dalton Trans.* **1981**, 968.
- (10) Acland, C. B.; Freeman, H. C. *J. Chem. Soc., Chem. Commun.* **1971**, 1016.
- (11) Schmidbaur, H.; Adlkofer, J.; Buchner, W. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 415.
- (12) Nardin, G.; Randaccio, L.; Zangrando, E. *J. Organomet. Chem.* **1974**, *74*, C23.
- (13) Maurer, H. M.; Weiss, A. Z. *Kristallogr.* **1977**, *146*, 227.
- (14) Engelhardt, L. M.; Pakawatchai, C.; White, A. H.; Healy, P. C. *J. Chem. Soc., Dalton Trans.* **1985**, 117.
- (15) Healy, P. C.; Kildea, J. D.; White, A. H. *Aust. J. Chem.* **1989**, *42*, 137.

(1) (a) University of Auckland. (b) Griffith University. (c) University of Western Australia. (d) Technische Universität München.

In these cases the factors which determine the low coordination number appear to be electronic, although in some cases steric factors may also be important.¹⁴ In contrast to this, complexes of Cu^I and Ag^I with tertiary phosphine ligands generally display coordination numbers of 4,^{2,3,18–22} although in the case of Cu^I several examples of three-coordination have been observed for complexes involving triphenylphosphine, PPh₃.²³ Two-coordination has been achieved in several cases, however, by using more sterically demanding ligands.^{24–29} Thus, complexes of the type [L₂Ag]Y (L = tricyclohexylphosphine,²⁴ tri-*tert*-butylphosphine,²⁵ trimesitylphosphine,^{26,27} tris(dimethylamino)phosphine,²⁸ tri-*tert*-butyl phosphite,²⁹ cyclopentylidiphenylphosphine and -arsine;³⁰ Y = ClO₄⁻, BF₄⁻, and other noncoordinating or weakly coordinating anions) have been reported. However, in several of these compounds the coordination at Cu^I or Ag^I deviates significantly from linearity as a result of interaction of the metal with the anion,^{24,28,30} and only in the case of the very bulky trimesitylphosphine ligand has a P–Ag–P bond angle greater than 170° been observed.²⁷

The highly basic, sterically hindered tertiary phosphine ligand tris(2,4,6-trimethoxyphenyl)phosphine [≡TMPP] forms complexes [(TMPP)₂M][ClO₄] (M = Cu, Ag),³¹ but the structures of these complexes have not yet been determined. We have recently shown that the 1:1 adducts of this ligand with the copper(I) halides CuX (X = Cl, Br) yield mononuclear [(TMPP)–CuX], which contain almost linear two-coordinate copper, a slight deviation from linearity (P–Cu–X angles about 173°) being caused by a weak interaction with one of the *o*-methoxy oxygens in the ligand.³² As part of a study of potentially two-coordinate complexes formed by silver(I) with this ligand, we have attempted the preparation of the series of its 1:1 adducts with the silver(I) halides, AgX (X = Cl, Br, I). The structures of the chloro and bromo complexes have been determined by X-ray crystallography. The complexes have been studied in the solid state by infrared and ³¹P CP/MAS NMR spectroscopy, and in solution by ³¹P NMR spectroscopy. The existence of mononuclear two-coordinate phosphine or phosphite complexes of silver(I) halides in solution has been postulated previously,^{25,29} but structural details for such complexes have not yet been reported. The characterization of such complexes is important because they allow the comparison of structures, spectroscopic parameters, and bonding in an isostructural series of complexes [LMX] of the group 11 metals in one of the simplest possible coordination environments, something which is not normally possible because of the tendency which these metals have to prefer different coordination numbers.

- (16) Antti, C. J.; Lundberg, B. K. S. *Acta. Chem. Scand.* **1971**, *25*, 1758.
 (17) Sorrell, T. N.; Jameson, D. L. *J. Am. Chem. Soc.* **1983**, *105*, 6013.
 (18) Jardine, F. H. *Adv. Inorg. Chem. Radiochem.* **1975**, *17*, 115.
 (19) McAuliffe, C. A. *Phosphine, Arsine and Stibine Complexes of the Transition Elements*; Elsevier: Amsterdam, 1979.
 (20) Gill, J. T.; Mayerle, J. J.; Welcher, P. S.; Lewis, D. F.; Ucko, D. A.; Barton, D. J.; Stowens, D.; Lippard, S. J. *Inorg. Chem.* **1976**, *15*, 1155.
 (21) Healy, P. C.; Pakawatchai, C.; Raston, C. L.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1983**, 1905.
 (22) Dyason, J. C.; Healy, P. C.; Engelhardt, L. M.; Pakawatchai, C.; Patrick, V. A.; Raston, C. L.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1985**, 831.
 (23) Bowmaker, G. A.; Skelton, B. W.; White, A. H.; Healy, P. C. *J. Chem. Soc., Dalton Trans.* **1988**, 2825.
 (24) Restivo, R. J.; Costin, A.; Ferguson, G.; Carty, A. J. *Can. J. Chem.* **1975**, *53*, 1949.
 (25) Goel, R. G.; Pilon, P. *Inorg. Chem.* **1978**, *17*, 2876.
 (26) Alyea, E. C.; Dias, S. A.; Stevens, S. *Inorg. Chim. Acta* **1980**, *44*, L203.
 (27) Alyea, E. C.; Ferguson, G.; Somogyvari, A. *Inorg. Chem.* **1982**, *21*, 1369.
 (28) Socol, S. M.; Jacobson, R. A.; Verkade, J. G. *Inorg. Chem.* **1984**, *23*, 88.
 (29) Socol, S. M.; Verkade, J. G. *Inorg. Chem.* **1984**, *23*, 3487.
 (30) Baiada, A.; Jardine, F. H.; Willett, R. D. *Inorg. Chem.* **1990**, *29*, 3042.
 (31) (a) Wada, M.; Higashizaki, S. *J. Chem. Soc., Chem. Commun.* **1984**, 482. (b) Wada, M.; Higashizaki, S.; Tsuboi, A. *J. Chem. Res., Synop.* **1985**, 38; *J. Chem. Res. Miniprint* **1985**, 467.
 (32) Bowmaker, G. A.; Cotton, J. D.; Healy, P. C.; Kildea, J. D.; Silong, S. B.; Skelton, B. W.; White, A. H. *Inorg. Chem.* **1989**, *28*, 1462.

Table I. Summary of Crystal Data

	[(TMPP)AgCl]	[(TMPP)AgBr]
formula	C ₂₇ H ₃₃ AgClO ₉ P	C ₂₇ H ₃₃ AgBrO ₉ P
fw	675.9	720.3
cryst syst	tetragonal	tetragonal
space group	P4 ₁ (C ₄ ² , No. 76)	P4 ₁ (C ₄ ² , No. 76)
T/K	295	295
λ/Å	0.7106 ₉	0.7106 ₉
a/Å	15.310 (1)	15.319 (4)
c/Å	12.366 (1)	12.441 (6)
V/Å ³	2899	2921
Z	4	4
D _c /g cm ⁻³	1.55	1.64
μ _{Mo} /cm ⁻¹	8.3	20.5
A* _{min,max}	1.00, 1.09	1.46, 1.68
2θ _{max}	54	50
N, N ₀	6308, 5771 ^a	2417, 2114
R ^b	0.031	0.029
R _w ^b	0.030	0.030

^a The data include (h, k, ±l). ^b R = (ΣΔ|F|)/(Σ|F₀|); R_w = ((ΣwΔ|F|²)/(Σw|F₀|²))^{1/2}.

Experimental Section

Preparation of Compounds. The ligand tris(2,4,6-trimethoxyphenyl)phosphine was prepared according to the procedure outlined in the literature³¹ by the reaction of P(OPh)₃ and (2,4,6-trimethoxyphenyl)lithium in diethyl ether, followed by recrystallization of the solid product from ethanol. Chloro- and bromo(tris(2,4,6-trimethoxyphenyl)phosphine)silver(I), [(TMPP)AgX] (X = Cl, Br) complexes were prepared by dissolution of equimolar quantities of TMPP and AgX in acetonitrile under nitrogen, followed by slow cooling and filtration of the resultant colorless crystals. Anal. Calcd for [(TMPP)AgCl] (C₂₇H₃₃AgClO₉P): C, 48.0; H, 4.9. Found: C, 47.9; H, 4.9. Calcd for [(TMPP)AgBr] (C₂₇H₃₃AgBrO₉P): C, 45.0; H, 4.6. Found: C, 45.3; H, 4.9. The colorless microcrystalline product obtained from the attempted synthesis of the corresponding AgI complex gave an analysis which is approximately correct for the 1:1 adduct (Calcd for [(TMPP)AgI] (C₂₇H₃₃AgIO₉P): C, 42.3; H, 4.3. Found: C, 41.8; H, 4.4), but, on the basis of ensuing studies (see below), its composition is believed to be more complex. Bis-(tris(2,4,6-trimethoxyphenyl)phosphine)silver(I) perchlorate, [(TMPP)₂Ag][ClO₄], was prepared by a literature method.³¹ Given the danger inherent in filling the solid-state NMR rotor with a ground sample of the perchlorate complex, we prepared bis(tris(2,4,6-trimethoxyphenyl)phosphine)silver(I) hexafluorophosphate, [(TMPP)₂Ag][PF₆], for solid-state NMR studies by dissolution of equimolar quantities of TMPP and AgPF₆ in acetonitrile under nitrogen, followed by slow cooling and filtration of the resultant colorless microcrystalline solid. Anal. Calcd for [(TMPP)₂Ag][PF₆] (C₅₄H₆₆AgF₆O₁₈P₃): C, 49.2; H, 5.1. Found: C, 49.0; H, 5.2.

Spectroscopy. Far-infrared spectra were recorded at ambient temperature as polyethylene pellets on a Digilab FTS-60 Fourier transform infrared spectrometer employing a FTS-60V vacuum optical bench with a 6.25-μm Mylar film beam splitter, a mercury-lamp source, and a TGS detector. Solution ³¹P{¹H} NMR spectra were obtained at room temperature on a Bruker AM400 spectrometer at 162.0 MHz. Solid-state cross-polarization magic angle spinning (CP/MAS) ³¹P{¹H} NMR spectra were obtained at ambient temperature on a Bruker CXP-300 spectrometer at 121.47 MHz by using ¹H–³¹P cross-polarization with radio-frequency fields of 8 and 10 G for ¹H and ³¹P respectively. The chemical shifts were referenced to 85% H₃PO₄ via an external sample of solid PPh₃ (δ = –9.9 ppm).

X-ray Crystal Structure Determinations. Substantial colorless crystals of chloro- and bromo(tris(2,4,6-trimethoxyphenyl)phosphine)silver(I) were grown directly from the reaction mixtures; it was not possible to obtain crystals of the iodo complex suitable for an accurate structure determination. Crystal data and additional details/abnormalities/variations of data collection and refinement are given in Table I. Unique data sets were measured at ≈295 K using specimens mounted in capillaries, within the given limits 2θ_{max} (ENRAF-Nonius CAD-4 diffractometers, monochromatic Mo Kα radiation λ = 0.7106₉ Å, conventional θ–2θ scan mode), yielding N independent reflections; of these N₀ with |F| > 3σ|F₀| (chloride), I > 3σ(I) (bromide) were considered "observed" and used in the full-matrix least squares refinements on |F|, minimizing ΣwΔ|F|² after absorption correction (empirical, chloride; Gaussian, bromide) and solution of the structures by vector and direct methods. Anisotropic thermal parameters were refined for the non-hydrogen atoms; (x, y, z, U_{iso})_H were

Table II. Non-Hydrogen Atom Coordinates for [(TMPP)AgX]

atom	X = Cl			X = Br		
	x	y	z	x	y	z
Ag	0.36143 (2)	0.22732 (2)	0.0 ^a	0.36280 (3)	0.22493 (3)	0.0 ^a
X	0.49267 (7)	0.20361 (8)	-0.0927 (1)	0.50134 (5)	0.19914 (5)	-0.09280 (9)
P	0.23533 (6)	0.25774 (6)	0.10587 (8)	0.2366 (1)	0.2558 (1)	0.1040 (2)
C(11)	0.2012 (2)	0.1642 (2)	0.1875 (3)	0.2025 (4)	0.1620 (4)	0.1850 (5)
C(12)	0.2688 (2)	0.1194 (2)	0.2435 (4)	0.2688 (4)	0.1170 (4)	0.2402 (6)
O(12)	0.3482 (2)	0.1584 (2)	0.2387 (3)	0.3488 (3)	0.1565 (3)	0.2355 (5)
C(121)	0.4208 (3)	0.1157 (3)	0.2841 (4)	0.4221 (5)	0.1124 (6)	0.2799 (9)
C(13)	0.2535 (3)	0.0430 (3)	0.2992 (3)	0.2551 (5)	0.0412 (4)	0.2942 (6)
C(14)	0.1704 (3)	0.0076 (3)	0.2981 (3)	0.1712 (5)	0.0054 (5)	0.2949 (6)
O(14)	0.1609 (2)	-0.0693 (2)	0.3552 (3)	0.1624 (4)	-0.0707 (3)	0.3511 (5)
C(141)	0.0833 (4)	-0.1162 (3)	0.3445 (5)	0.0816 (6)	-0.1159 (6)	0.3391 (9)
C(15)	0.1024 (2)	0.0483 (2)	0.2459 (4)	0.1039 (4)	0.0477 (4)	0.2447 (7)
C(16)	0.1193 (3)	0.1259 (3)	0.1903 (3)	0.1193 (4)	0.1251 (4)	0.1885 (5)
O(16)	0.0531 (2)	0.1628 (2)	0.1313 (3)	0.0544 (3)	0.1631 (4)	0.1306 (5)
C(161)	-0.0315 (3)	0.1575 (3)	0.1675 (5)	-0.0306 (5)	0.1561 (6)	0.1654 (9)
C(21)	0.2661 (2)	0.3502 (2)	0.1911 (3)	0.2667 (4)	0.3474 (4)	0.1873 (6)
C(22)	0.3013 (2)	0.4222 (3)	0.1355 (3)	0.3022 (4)	0.4202 (4)	0.1335 (5)
O(22)	0.2999 (2)	0.4149 (2)	0.0245 (2)	0.3014 (3)	0.4125 (3)	0.0237 (4)
C(221)	0.3371 (3)	0.4827 (3)	-0.0377 (3)	0.3381 (6)	0.4806 (5)	-0.0401 (7)
C(23)	0.3348 (3)	0.4934 (3)	0.1888 (3)	0.3351 (5)	0.4914 (4)	0.1865 (6)
C(24)	0.3347 (3)	0.4952 (3)	0.3007 (3)	0.3331 (5)	0.4939 (4)	0.2964 (6)
O(24)	0.3698 (2)	0.5684 (2)	0.3449 (2)	0.3686 (4)	0.5665 (3)	0.3413 (4)
C(241)	0.3878 (3)	0.5702 (3)	0.4573 (3)	0.3844 (6)	0.5685 (5)	0.4529 (7)
C(25)	0.2989 (3)	0.4272 (3)	0.3587 (3)	0.2981 (5)	0.4249 (5)	0.3555 (6)
C(26)	0.2642 (2)	0.3560 (3)	0.3040 (3)	0.2641 (4)	0.3544 (4)	0.3004 (6)
O(26)	0.2257 (2)	0.2882 (2)	0.3560 (2)	0.2258 (3)	0.2869 (3)	0.3528 (4)
C(261)	0.2271 (4)	0.2871 (4)	0.4702 (4)	0.2267 (8)	0.2847 (7)	0.4644 (7)
C(31)	0.1433 (2)	0.2971 (2)	0.0279 (3)	0.1448 (4)	0.2953 (4)	0.0256 (5)
C(32)	0.1439 (3)	0.2914 (3)	-0.0854 (3)	0.1444 (4)	0.2869 (4)	-0.0854 (6)
O(32)	0.2130 (2)	0.2494 (2)	-0.1318 (2)	0.2132 (3)	0.2431 (3)	-0.1309 (4)
C(321)	0.2277 (3)	0.2623 (3)	-0.2428 (4)	0.2283 (6)	0.2545 (6)	-0.2405 (9)
C(33)	0.0759 (3)	0.3249 (3)	-0.1474 (3)	0.0769 (5)	0.3190 (5)	-0.1472 (6)
C(34)	0.0082 (3)	0.3650 (3)	-0.0968 (4)	0.0092 (5)	0.3610 (5)	-0.0973 (7)
O(34)	-0.0556 (2)	0.3951 (3)	-0.1664 (3)	-0.0540 (4)	0.3904 (4)	-0.1683 (5)
C(341)	-0.1274 (3)	0.4391 (4)	-0.1240 (4)	-0.1246 (6)	0.4355 (7)	-0.1268 (8)
C(35)	0.0037 (2)	0.3741 (2)	0.0158 (3)	0.0068 (4)	0.3718 (4)	0.0121 (7)
C(36)	0.0733 (3)	0.3406 (3)	0.0758 (3)	0.0747 (4)	0.3394 (4)	0.0729 (6)
O(36)	0.0775 (2)	0.3459 (2)	0.1860 (2)	0.0793 (3)	0.3458 (4)	0.1811 (4)
C(361)	0.0082 (3)	0.3839 (3)	0.2434 (4)	0.0108 (5)	0.3857 (6)	0.2389 (8)

^a Defines origin.

included constrained at estimated values. An extinction parameter was refined for the bromide ($g = 0.003$) but not for the chloride. Statistical weights, derivative of $\sigma^2(I_{\text{diff}}) + 0.000n\sigma^4(I_{\text{diff}})$, were used. For both complexes, agreement factors were higher in the enantiomeric space group $P4_3$. Neutral atom complex scattering factors were employed,³³ computation using SHELXS-86³⁴ (chloride) or the XTAL 2.6³⁵ (bromide) program systems. Final atom coordinates are given in Table II. The structure of the bromide complex is shown in Figure 1.

Results and Discussion

Single Crystal X-ray Diffraction. The [(TMPP)AgCl] and [(TMPP)AgBr] complexes are isomorphous with each other, and with the corresponding copper(I) complexes.³² They are monomeric, with the silver atom in a nearly linear two-coordinate environment (Figure 1). For the chloro complex, Ag-P is 2.379 (1) Å and Ag-Cl is 2.342 (1) Å, while for the bromo complex, Ag-P is 2.374 (2) Å, and Ag-Br is 2.448 (1) Å. These are apparently the first two-coordinate phosphine silver(I) halide complexes to be completely characterized structurally. Normally the 1:1 complexes of tertiary phosphines with silver(I) halides crystallize as tetramers [(PR₃)AgX]₄ with a "cubane" (R = Et, Ph; X = Cl, Br, I)³⁶⁻⁴⁰ or a "step" (R = Ph; X = I)⁴⁰ structure.

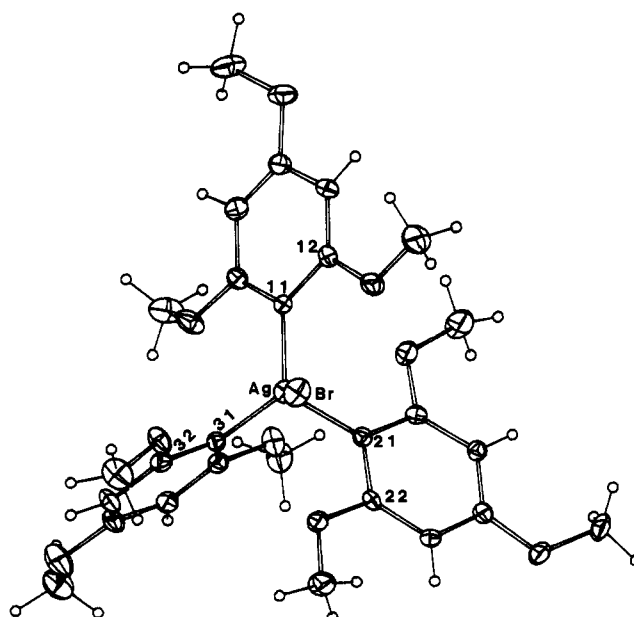


Figure 1. Structure of [(TMPP)AgBr] projected down P-Ag. The 20% thermal ellipsoids are shown for the non-hydrogen atoms. Hydrogen atoms have an arbitrary radius of 0.1 Å.

(33) Ibers, J. A.; Hamilton, W. C., Eds.; *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. 4.

(34) Sheldrick, G. M. SHELXS-86. Program for Crystal Structure Solution. Göttingen, 1986.

(35) Hall, S. R.; Stewart, J. M. XTAL Users' Manual: Version 2.6. Universities of Western Australia and Maryland, 1989.

(36) Churchill, M. R.; Donahue, J.; Rotella, F. J. *Inorg. Chem.* **1976**, *15*, 2752.

(37) Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* **1975**, *14*, 2502.

(38) Teo, B.-K.; Calabrese, J. C. *Inorg. Chem.* **1976**, *15*, 2467.

(39) Teo, B.-K.; Calabrese, J. C. *J. Chem. Soc., Chem. Commun.* **1976**, 185.

(40) Teo, B.-K.; Calabrese, J. C. *Inorg. Chem.* **1976**, *15*, 2474.

The Ag-P bond lengths in the present compounds are similar in magnitude to those in the corresponding cubane tetramers for which the average values are 2.39 and 2.38 Å (X = Cl, R = Et, Ph)^{36,38} and 2.40 and 2.42 Å (X = Br, R = Et, Ph).^{36,39} The Ag-X bond lengths, however, are considerably shorter than those in the tetramer molecules for which the average values are 2.82 and 2.65 Å (X = Cl, R = Et, Ph)^{36,38} and 2.66 and 2.82 Å (X = Br, R = Et, Ph).^{36,39} This change in bond length with the change in bonding mode of the halogen atoms from triply bridging in the tetramers to terminal in the monomers is entirely as expected. In contrast to this, the Ag-P bond length remains largely unaffected by the change in the coordination environment about the silver atom and is relatively insensitive to the nature of the halide or the tertiary phosphine involved. However, both the Ag-P and the Ag-Cl bond lengths in [(TMPP)AgCl] are considerably shorter than those in [(PPh₃)₃AgCl] (average Ag-P = 2.54 Å; Ag-Cl = 2.55 Å).⁴¹

In both complexes, the P-Ag-X fragment lies approximately in the plane of phenyl ring 3 [Ag-P-C(31)-C(32) = 11 (Cl), 15° (Br)] with the silver atom approached by the *o*-methoxy oxygen O(32). The resulting Ag...O distances are 2.818 (3) Å (Cl) and 2.826 (5) Å (Br). This interaction may be associated with the observed slight deviation of the P-Ag-X angles from linearity; P-Ag-Cl = 175.0 (1)°, and P-Ag-Br = 174.40 (6)°. The phenyl rings 1 and 2 are located above and below the P, Ag, X, O(32) plane and are twisted in opposite directions to accommodate the bulky methoxy groups [Ag-P-C(11)-C(12) = 56 (Cl), 45° (Br); Ag-P-C(21)-C(22) = 42 (Cl), 52° (Br)] with distances to the two next nearest *o*-methoxy oxygen atoms of 3.038 (3) and 3.140 (3) Å (X = Cl) and 3.038 (5) and 3.119 (6) Å (X = Br). This conformation is similar to that observed in the corresponding CuX complexes,³² but is less regular than the quasi C₃ conformation of the trimesitylphosphine ligand, PMes₃,⁴² and its CuBr complex.⁴³ The deviation of the P-Ag-X units from linearity in the present complexes is slightly less than that in the corresponding CuX complexes (P-Cu-Cl = 172.97 (6)°, P-Cu-Br = 172.00 (9)°) and comparable to that in [PMes₃CuBr] (P-Cu-Br = 173.7 (1)°) where it is attributed to intramolecular packing effects.⁴³ Thus, while a secondary interaction between the Ag atom and the nearest *o*-methoxy oxygen in the present complexes may be related to the slight deviation from linearity, this deviation is comparable to that which would be expected from crystal packing effects and so must be relatively weak. The Ag...O distances are all considerably greater than the Ag-O bond lengths in other silver(I) complexes with oxygen donor ligands, such as [CF₃-CO₂Ag]₂ (Ag-O = 2.2 Å)⁴⁴ or [(H₂O)₄Ag]⁺ (Ag-O = 2.3 Å).⁴⁵

Another complex of TMPP for which a crystal structure has been reported is [(TMPP)₂Rh]²⁺. In this complex the Rh atom is bound to the P atom and to two *o*-methoxy O atoms on two of the three phenyl rings of each ligand molecule. The structure is best described as a distorted octahedron with two strong axial Rh-P bonds and four much weaker equatorial Rh-O bonds.⁴⁶ The Rh...O distances involved (ca. 2.2, 2.4 Å) are nevertheless significantly shorter than those in the Ag complexes reported here (ca. 2.8 Å), further emphasizing the weakness of the Ag...O interaction.

Far-Infrared Spectra. The far-infrared spectra of [(TMPP)-AgX] (X = Cl, Br) are shown in Figure 2. The strong bands at

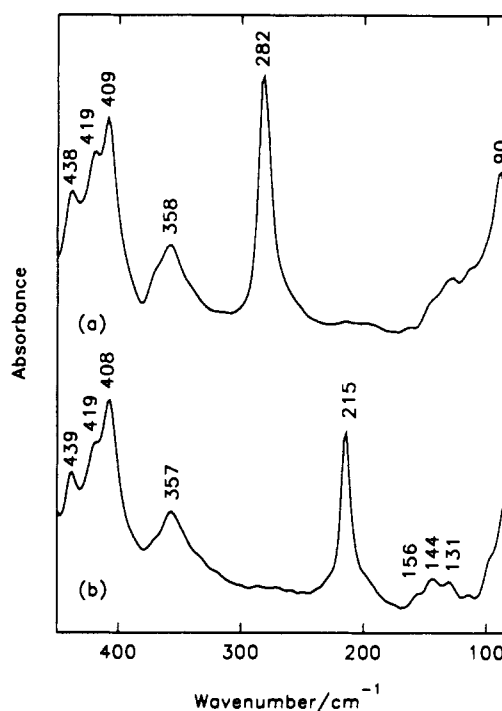


Figure 2. Far-IR spectra of (a) [(TMPP)AgCl] and (b) [(TMPP)AgBr].

Table III. Metal-Halogen Vibrational Wavenumbers, $\nu(\text{MX})$, Force Constants, f_r , and Bond Lengths, $d(\text{M-X})$, for [(TMPP)AgX] (X = Cl, Br) and Related Species

compound	$\nu(\text{MX})/\text{cm}^{-1}$		$f_r/\text{N m}^{-1}$		ref	$d(\text{M-X})/\text{Å}$		ref
	Cl	Br	Cl	Br		Cl	Br	
[(TMPP)AgX]	282	215	125	125	<i>a</i>	2.342	2.45	<i>a</i>
AgX (vapor)	341	246	183	164	47	2.281	2.393	49
[AgX ₂] ⁻ (ν_3)	333	253	145	129	5	2.329		8
[(PPh ₃) ₃ AgX]	192	138	58	52	48	2.54	2.69	41
[(TMPP)CuX]	355	262	169	143	32	2.118	2.259	32

^a This work.

282 (X = Cl) and 215 cm⁻¹ (X = Br) can be readily assigned as the terminal silver-halogen stretching frequencies $\nu(\text{AgX})$. The wavenumbers of these bands are compared with the $\nu(\text{MX})$ wavenumbers for a number of related complexes in Table III. The ratios of the $\nu(\text{AgX})$ wavenumbers for the two compounds are almost the same as those for vapor-phase diatomic AgX,⁴⁷ for the complexes [(PPh₃)₃AgX],⁴⁸ and for the IR active asymmetric stretching mode ν_3 of [AgX₂]⁻.⁵ For the X = Cl members of this series the Ag-Cl bond lengths are all known (Table III), and there is a monotonic decrease in $\nu(\text{AgCl})$ with $d(\text{Ag-Cl})$ for this series. The relationship between $\nu(\text{AgX})$ and $d(\text{Ag-X})$ for the members of this series which contain only a single terminal Ag-X unit is shown in Figure 3. These curves have the same form as those which have been reported previously for CuX complexes, although in the CuX cases the relationships are rather better defined due to the existence of many more complexes containing a single terminal CuX unit.⁵⁰ Also listed in Table III are Ag-X force constants f_r , which can be calculated exactly for AgX and [AgX₂]⁻ and which have been calculated by using a diatomic approximation^{48,50} for [(TMPP)AgX] and [(PPh₃)₃AgX]. This allows the vibrational results to be used to compare the Ag-X bond strengths by removing the effects of the different atomic masses which affect the vibrational frequencies. These results

(41) Engelhardt, L. M.; Healy, P. C.; Patrick, V. A.; White, A. H. *Aust. J. Chem.* **1987**, *40*, 1873.

(42) Blount, J. F.; Maryanoff, C. A.; Mislow, K. *Tetrahedron Lett.* **1975**, *11*, 913.

(43) Alyea, E. C.; Ferguson, G.; Malito, J.; Ruhl, B. L. *Inorg. Chem.* **1985**, *24*, 3719.

(44) Griffin, R. G.; Ellet, J. D., Jr.; Mehring, M.; Bullitt, J. G.; Waugh, J. S. *J. Chem. Phys.* **1972**, *57*, 2147.

(45) Yamaguchi, T.; Johansson, G.; Holmberg, B.; Maeda, M.; Ohtaki, H. *Acta. Chem. Scand.* **1984**, *38A*, 437.

(46) Dunbar, K. R.; Haefner, S. C.; Pence, L. E. *J. Am. Chem. Soc.* **1989**, *111*, 5504.

(47) Herzberg, G. *Spectra of Diatomic Molecules*; D. Van Nostrand: Princeton, NJ, 1950. Huber, K. P.; Herzberg, G. *Constants of Diatomic Molecules*; D. Van Nostrand: New York, 1979.

(48) Teo, B.-K.; Barnes, D. M. *Inorg. Nucl. Chem. Lett.* **1976**, *12*, 681.

(49) Hoefl, J.; Nair, K. P. R. *Z. Naturforsch.* **1979**, *34A*, 1290.

(50) Bowmaker, G. A.; Healy, P. C.; Kildea, J. D.; White, A. H. *Spectrochim. Acta* **1988**, *44A*, 1219.

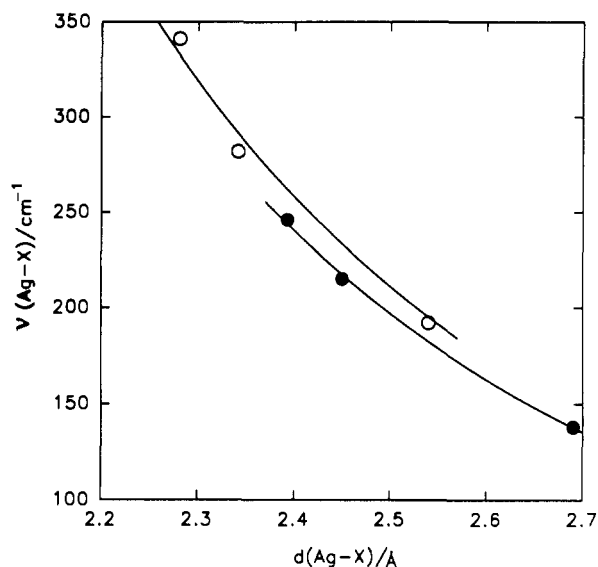


Figure 3. Dependence of $\nu(\text{AgX})$ on the Ag-X bond length in AgX (vapor), $[(\text{TMPP})\text{AgX}]$, and $[(\text{PPH}_3)_3\text{AgX}]$ for X = Cl (O) and X = Br (●).

show the expected decrease in bond strength with increasing coordination number. Somewhat surprisingly, they also show equal bond strengths for $[(\text{TMPP})\text{AgX}]$ (X = Cl, Br), whereas the other AgX species in Table III show a ca. 10% decrease in force constant from the Cl to the Br species. Comparison with the results for the corresponding copper(I) complexes $[(\text{TMPP})\text{CuX}]$ shows that the expected reduction in force constant from Cl to Br does occur in this case and that the Ag-X bonds are weaker than the Cu-X bonds.

On the basis of the relationships discussed above and using the known vibrational frequencies for AgI vapor (206 cm^{-1})⁴⁷ and $[\text{AgI}_2]^-$ ($\nu_3 = 215\text{ cm}^{-1}$),⁵ $\nu(\text{AgI})$ for $[(\text{TMPP})\text{AgI}]$ would be expected to lie at ca. 180 cm^{-1} . The far-IR spectrum of the product obtained in the attempted synthesis of this complex is shown in Figure 4a, and this shows no band in this region, suggesting that this complex has a structure different from that of the Cl and Br analogues. Further evidence in support of this conclusion comes from the form of the far-IR spectra in the region $400\text{--}450\text{ cm}^{-1}$, where strong bands due to the coordinated ligand occur. For the Cl and Br complexes, three bands are observed in this region, with very nearly the same wavenumbers and relative intensities for both compounds. For the iodo complex only a single band is observed at 422 cm^{-1} , the same as the wavenumber of the corresponding band in $[(\text{TMPP})_2\text{Ag}][\text{ClO}_4]$ (Figure 4b). This suggests that the iodo complex is ionic, containing the cationic $[(\text{TMPP})_2\text{Ag}]^+$ species. In order to correspond to the overall 1:1 TMPP:AgI stoichiometry which is implied by the analytical data, the complex must also contain iodide ions and AgI or, since the colorless product does not contain any unreacted yellow AgI, an iodoargentate(I) complex anion. In order to obtain more information on this point, an X-ray crystallographic study was carried out on a small crystal taken from this sample. Despite the poor quality of the crystal, this was shown with reasonable certainty to be the salt $[(\text{TMPP})_2\text{Ag}]_2[\text{Ag}_5\text{I}_7]$, containing a novel polymeric iodoargentate(I) anion.⁵¹ The product cannot consist entirely of this latter compound, as it corresponds to a TMPP:AgI ratio of 2:7, whereas the analytical results are close to 1:1. The product must therefore also contain another ionic compound (or compounds) with a higher TMPP:AgI ratio. The presence of a bridged iodoargentate complex anion would explain the absence of a terminal $\nu(\text{AgI})$ band in the far-IR spectrum of the product. Further evidence in support of the presence of the

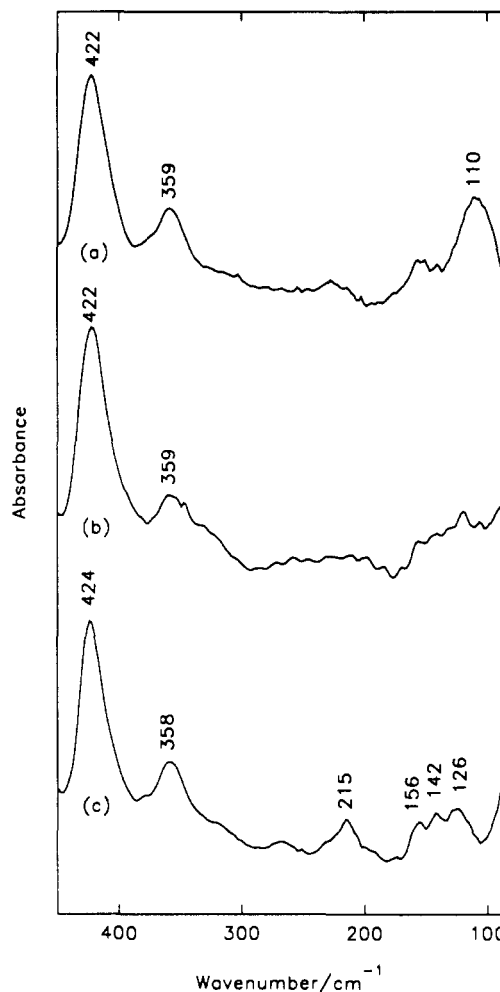


Figure 4. Far-IR spectra of (a) solid product obtained from 1:1 TMPP + AgI reaction, (b) $[(\text{TMPP})_2\text{Ag}][\text{ClO}_4]$, and (c) solid product obtained from 1:1 TMPP + $[(\text{TMPP})\text{AgBr}]$ reaction.

Table IV. Solution ^{31}P NMR Parameters

complex	solvent	$\delta(^{31}\text{P})/\text{ppm}$	$^1J(^{109}\text{Ag}-^{31}\text{P})/\text{Hz}$	$^1J(^{107}\text{Ag}-^{31}\text{P})/\text{Hz}$
$[(\text{TMPP})\text{AgCl}]$	CHCl_3	-67.2	821	711
$[(\text{TMPP})\text{AgBr}]$	CHCl_3	-66.4	796	690
$[(\text{TMPP})\text{AgI}]$	CHCl_3	-64.6	745	646
$[(\text{TMPP})_2\text{Ag}]\text{Cl}$	CHCl_3	-74.2	666	577
$[(\text{TMPP})_2\text{Ag}]\text{Br}$	CHCl_3	-74.2	666	577
$[(\text{TMPP})_2\text{Ag}]\text{I}$	CH_3CN	-67.8	662	579
$[(\text{TMPP})_2\text{Ag}][\text{ClO}_4]$	DMSO	-70.9	665	576

complex cation $[(\text{TMPP})_2\text{Ag}]^+$ in this compound was obtained from its solid-state ^{31}P CP/MAS NMR spectrum (see below).

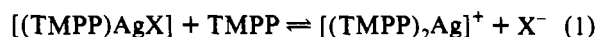
The ^{31}P NMR spectra of solutions containing equimolar amounts of TMPP and the 1:1 $[(\text{TMPP})\text{AgX}]$ complexes indicate that the main species present are $[(\text{TMPP})_2\text{Ag}]^+$ and X^- (see below). The far-IR spectra of the solids obtained by removal of the solvent from such solutions contain no $\nu(\text{AgX})$ bands (example shown for TMPP + $[(\text{TMPP})\text{AgBr}]$ in Figure 4c). Moreover, the bands due to the coordinated ligand are almost identical in appearance to those for the 1:1 AgX complex, and for $[(\text{TMPP})_2\text{Ag}][\text{ClO}_4]$. These observations indicate that the 2:1 complexes are the ionic compounds $[(\text{TMPP})_2\text{Ag}]^+\text{X}^-$.

^{31}P NMR Spectra. The ^{31}P NMR spectra of the $[(\text{TMPP})\text{AgX}]$ complexes in chloroform solution at ambient temperature show a superposition of two doublets due to coupling of the phosphorus nucleus with the two magnetic isotopes of silver (^{107}Ag , ^{109}Ag). The ^{31}P NMR parameters are listed in Table IV. The ratios of $^1J(^{109}\text{Ag}-^{31}\text{P})/^1J(^{107}\text{Ag}-^{31}\text{P})$ for all of the complexes are in good agreement with the theoretical ratio of 1.15. The

(51) Baker, L.-J.; Bowmaker, G. A.; Effendy, Skelton, B. W.; White, A. H. *Aust. J. Chem.*, submitted for publication.

observation of splitting due to $^1J(\text{AgP})$ coupling for phosphine complexes of Ag(I) in solution at ambient temperature is unusual; the rapid exchange of the phosphine ligands causes this coupling to be averaged to zero, and it is normally necessary to slow down the ligand exchange by cooling the solution to ca. -80°C in order to observe it.^{28,52,53} However the observation of $^1J(\text{AgP})$ at ambient temperature has been reported previously in cases where the phosphine ligand is chelating⁵⁴ or is strongly sterically hindered^{25,26} as in the present case.

Addition of excess TMPP to the $[(\text{TMPP})\text{AgX}]$ solutions results in the appearance of a second signal to higher field to those of $[(\text{TMPP})\text{AgX}]$ which also shows $^1J(\text{Ag-P})$ coupling at ambient temperature. This second signal is assigned to $[(\text{TMPP})_2\text{Ag}]^+$, formed according to the equilibrium:



This is supported by the observation that the ^{31}P NMR parameters for this second signal are essentially independent of X and by the fact that they are the same as those for $[(\text{TMPP})_2\text{Ag}][\text{ClO}_4]$ (Table IV). The spectra show that the equilibrium lies well to the right, as only relatively weak signals due to $[(\text{TMPP})\text{AgX}]$ and uncomplexed TMPP are observed in solutions containing a 1:1 mole ratio of TMPP to $[(\text{TMPP})\text{AgX}]$. In the case of the iodo compounds these results imply that, although the solid 1:1 complex does not contain discrete monomeric $[(\text{TMPP})\text{AgI}]$ molecules (see discussion of the far-IR results above), it dissolves in CHCl_3 in the monomeric molecular form, but can readily be converted to an ionic form containing $[(\text{TMPP})_2\text{Ag}]^+$ by addition of excess TMPP.

Addition of TMPP to $[(\text{TMPP})\text{AgX}]$ in a greater than 1:1 mole ratio simply results in the disappearance of the signal due to $[(\text{TMPP})\text{AgX}]$ and an increase in the intensity of the signal due to uncomplexed TMPP. This implies that the maximum coordination number which is achievable in this system is 2, and this is most likely to be due to the great steric bulk of the ligand.

The present system shows some similarities in its behavior to that of previously reported complexes of PBU_3 .²⁵ The ^{31}P NMR spectra of $[(\text{PBU}_3)\text{AgX}]$ (X = Cl, Br, I) showed $^1J(\text{Ag-P})$ splitting at ambient temperature, but addition of 2 mol equiv of excess PBU_3 resulted in the appearance of only a single peak due to ligand exchange processes. The spectra of the solutions at -90°C , however, showed the presence of $[(\text{PBU}_3)_2\text{Ag}]^+$ and uncomplexed PBU_3 only. Thus, in this case also, the steric bulk of the ligand is sufficient to limit the coordination number of the silver atom to 2 in solution.

The $^1J(^{107}\text{Ag}-^{31}\text{P})$ coupling constants for the compounds of the present study are compared with those for some related systems Table V. The values observed for $[(\text{TMPP})\text{AgX}]$ and $[(\text{TMPP})_2\text{Ag}]^+$ are all significantly greater than those for the corresponding complexes of the other ligands listed. This is probably a consequence of the high base strength of TMPP, for which there is other evidence.³¹ The trend of decreasing $^1J(\text{Ag-P})$ from the chloro to the iodo complex in $[(\text{TMPP})\text{AgX}]$ is similar to that which has been observed previously for $[(\text{PBU}_3)\text{AgX}]$ ²⁴ and $[(\text{PTol}_3)_3\text{AgX}]$ ⁵² and has been attributed to a variation in the strength of the AgP bond.²⁵ Presumably a higher value for the coupling constant indicates a stronger bond, and this could be rationalized in terms of the donor strengths of the halide ligands. Thus, as Br⁻ is a stronger σ donor than Cl⁻, it should cause a greater degree of weakening of the Ag-P bond trans to it. This agrees with the trend in the coupling constants, but the effect is not large enough to cause a significant difference in the Ag-P bond lengths, which are equal within experimental error in $[(\text{TMPP})\text{AgX}]$. A more likely explanation (suggested by one of

Table V. $^1J(^{107}\text{Ag}-^{31}\text{P})$ Coupling Constants (Hz) for Complexes $[\text{L}_n\text{AgX}]$ of Ag(I) with Tertiary Phosphines

L	X	n = 1	n = 2	n = 3	n = 4	ref
TMPP	Cl	711	577			a
	Br	690	577			
	I	646	579			
	ClO_4		576			
PBU_3	Cl	593				25
	Br	561				
	I	544				
	PF_6		437			
PMes_3	PF_6		513			
PPh_3	PF_6	755	507	319	224	53
PTol_3	Cl		378	280	225	52
	Br			278	230	
	I			226		
	PF_6		496	321	225	
$\text{P}(\text{Me}_2\text{N})_3$	Cl		535			28
	I		597			
	BF_4	910				

^a This work.

the reviewers) is that the Ag 4s orbital is more contracted in the Cl complex as a consequence of the greater positive charge on the Ag atom (Cl more electronegative than Br), so that the coupling constant is greater in this case.

In order to obtain further information about the relationship between the species present in solutions of these complexes and those present in the solid state, the ^{31}P CP/MAS NMR spectra of the solid complexes were obtained. The spectra of $[(\text{TMPP})\text{AgX}]$ (X = Cl, Br) consist of a double doublet due to coupling of the phosphorus nucleus to the two magnetic isotopes of silver (^{107}Ag , ^{109}Ag). Although less well resolved than in the solution spectrum, the isotopic splitting is clearly visible and represents the first observation of such splitting in the solid state. The chemical shifts are -67 (Cl) and -66 ppm (Br), which are very close to the solution values (Table IV). The $^1J(^{107,109}\text{Ag}-^{31}\text{P})$ values are 697 and 785 Hz (Cl) and 675 and 763 Hz (Br), which are about 3% less than the solution values (Table IV). Thus the structures of these complexes in solution must be very similar to those determined in the X-ray diffraction studies of the solids.

Under some conditions the spectra of the solids obtained from the 1:1 TMPP + AgX reactions were more complex. Thus, we recorded the ^{31}P CP/MAS NMR spectra of solid samples obtained by dissolution of 1 mmol of each of TMPP and the appropriate silver halide in 20 mL of refluxing acetonitrile followed by cooling to room temperature. The spectrum of the AgBr complex is shown in Figure 5a. This consists of a double doublet centered at -66 ppm due to the monomeric molecular species $[(\text{TMPP})\text{AgBr}]$ and an envelope of several overlapping doublets centered at ca. -82 ppm with $^1J(^{107,109}\text{Ag}-^{31}\text{P}) \approx 600$ Hz. These parameters are in reasonable agreement with the corresponding values for $[(\text{TMPP})_2\text{Ag}]^+$ in solution (Table IV) and are in excellent agreement with the values obtained for solid $[(\text{TMPP})_2\text{Ag}][\text{PF}_6]$ (-84 ppm and 600 Hz). This result indicates that the product obtained under these conditions contains a number of ionic compounds involving the $[(\text{TMPP})_2\text{Ag}]^+$ complex, in addition to the molecular $[(\text{TMPP})\text{AgBr}]$ species. Similar results were obtained for the AgCl product prepared under these conditions. We have found that the relative amounts of neutral and ionic products obtained are sensitive to the detailed recrystallization procedures used. This is consistent with the chemistry of other phosphine-copper/silver halide systems where dependence of the nature of the products obtained from stoichiometric solutions on both kinetic and thermodynamic factors is well-known,⁵⁵ and we are continuing to explore the chemistry of these systems with the aim of isolating crystalline samples of the ionic species suitable for structural analysis.

(52) Muetterties, E. L.; Alegrianti, C. W. *J. Am. Chem. Soc.* **1972**, *94*, 6386.
 (53) Alyea, E. C.; Malito, J.; Nelson, J. H. *Inorg. Chem.* **1987**, *26*, 4294.
 (54) Berners Price, S. J.; Brevard, C.; Pagelot, A.; Sadler, P. J. *Inorg. Chem.* **1985**, *24*, 4278.

(55) Costa, G.; Reisenhofer, E.; Stefani, L. *J. Inorg. Nucl. Chem.* **1965**, *27*, 2581.

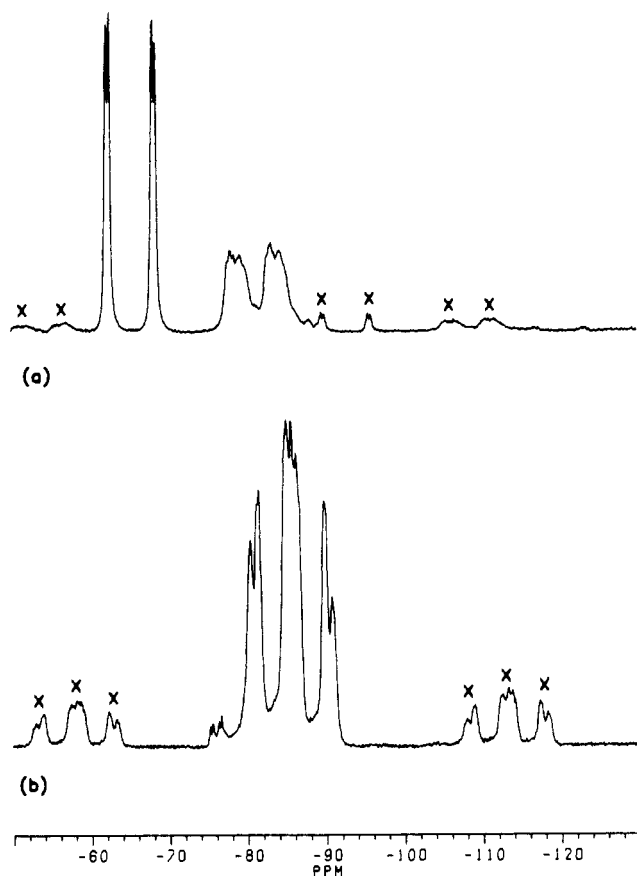


Figure 5. Solid-state ^{31}P CP/MAS NMR spectra of solid products obtained from (a) 1:1 TMPP + AgBr and (b) 1:1 TMPP + AgI (bands labeled "x" are spinning sidebands).

In the case of the AgI complex, the ^{31}P CP/MAS NMR spectrum of the solid shows no evidence for the presence of the monomeric molecular compound. The spectrum consists of at least four overlapping doublets assignable to $[(\text{TMPP})_2\text{Ag}]^+$ species (Figure 5b). This spectrum can be interpreted as being due either to several A_2X spin systems ($\text{A} = ^{31}\text{P}$; $\text{X} = ^{107,109}\text{Ag}$) with slightly different ^{31}P chemical shifts in the range -83 to -88 ppm and $^1J_{\text{AX}} \approx 600$ Hz or to a single ABX system (A , $\text{B} =$ two crystallographically inequivalent ^{31}P moieties within the same

cation) with $\delta_{\text{A}} = -83$ and $\delta_{\text{B}} = -88$ ppm, $^1J_{\text{AX}} \approx ^1J_{\text{BX}} \approx 600$ Hz and $^2J_{\text{AB}} \approx 100$ Hz (similar spectra showing $^2J(\text{P-P})$ coupling of about 100 Hz between crystallographically inequivalent P atoms bound to the same Ag atom have been reported recently).⁵⁶ In either case, the chemical shifts and $^1J(^{107,109}\text{Ag}-^{31}\text{P})$ values are in good agreement with those for $[(\text{TMPP})_2\text{Ag}]^+$ in solution (Table IV) and in solid $[(\text{TMPP})_2\text{Ag}][\text{PF}_6]$ (see above). The absence of any signal due to the molecular species $[(\text{TMPP})\text{AgI}]$ in the solid is consistent with the far-IR results (see above). It is clear from the solution NMR results, however, that this species does exist in solution and is formed by dissolution of the ionic solid in CHCl_3 ; in due course it is likely that circumstances where crystalline $[(\text{TMPP})\text{AgI}]$ can be obtained will be achieved.

Conclusions

The present study provides the first structural and spectroscopic data for complexes with a two-coordinate P-Ag-X ($\text{X} = \text{Cl}, \text{Br}$) grouping. The structural results complement those which have been reported recently for compounds containing linear P-Ag-P²⁷ and Cl-Ag-Cl,⁸ and will provide a good basis for the theoretical investigation of the electronic structure and bonding in two-coordinate complexes of silver(I). The present study also provides data for members of an isostructural and valence-isoelectronic series of compounds containing two-coordinate P-M-X ($\text{M} = \text{Cu}, \text{Ag}, \text{Au}$), which will likewise be useful for comparative studies of electronic structure in compounds of the group 11 metals, something which is not normally possible due to the different coordination numbers which these metals prefer. Although it has not yet been possible to obtain complete structural data for a species with a linear P-Ag-I grouping, it is clear from the present study that such species exist in solution.

Acknowledgment. We acknowledge support of this work by grants from the New Zealand University Grants Committee, the University of Auckland Research Committee, and the Australian Research Council. We thank the Brisbane NMR Center for the use of solid-state NMR facilities.

Supplementary Material Available: For the crystal structure studies, listings of crystal and refinement data, H atom coordinates, thermal parameters, and bond distances and angles (8 pages). Ordering information is given on any current masthead page.

(56) Attar, S.; Alcock, N. W.; Bowmaker, G. A.; Frye, J. S.; Bearden, W. H.; Nelson, J. H. *Inorg. Chem.* **1991**, *30*, 4166.