

Full experimental details for each compound are given in the supplementary material.

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Supplementary Material Available: Details of the structural determination and Table S-I, listing full crystal data and details of data collections and refinements for both $L_nPd(PPh_3)_m$ and $[L_nPdAg(PPh_3)]_2(ClO_4)_2$, Tables S-II-S-V, listing hydrogen atom parameters, thermal parameters, equations of least-squares planes, and intermolecular contacts for $L_nPd(PPh_3)_m$, and Tables S-VI-S-IX, listing the same data for $[L_nPdAg(PPh_3)]_2(ClO_4)_2$ solvate (15 pages); Tables S-X and S-XI, listing structure factors for the two compounds (82 pages). Ordering information is given on any current masthead page.

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Phosphole Complexes of Silver(I). Investigations of Structure and Bonding by X-ray Crystallography, Infrared Spectroscopy, and CP/MAS and Solution ^{31}P NMR Spectroscopy

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A series of complexes of 1-phenyl-3,4-dimethylphosphole (DMPP) and 1-phenyldibenzophosphole (DBP), of the type $[L_nAgX]_m$ ($n = 1, m = 4, L = DMPP; n = 2, m = 2, L = DMPP, DBP; n = 3, m = 1, L = DBP; X = Cl, Br, I$), have been prepared and characterized. The structure of $[(DBP)_2AgCl]_2$ has been determined by X-ray crystallography. It crystallizes in the space group $P\bar{1}$ with $a = 10.831(3) \text{ \AA}$, $b = 11.683(3) \text{ \AA}$, $c = 11.243(3) \text{ \AA}$, $\alpha = 82.73(2)^\circ$, $\beta = 89.39(2)^\circ$, $\gamma = 78.01(2)^\circ$, and $Z = 1$. The structure was refined by least-squares methods with $R_F = 0.066$ for 2273 unique reflections with $I/\sigma(I) \geq 3.0$. The complex crystallizes as a dimer with a structure similar to that which has previously been observed for 2:1 complexes of PPh_3 with silver(I) halides. In this structure both of the silver atoms are tetracoordinated through bonds to the P atoms of two phosphole ligands and two μ_2 -chlorine atoms, which bridge the two silver atoms. The dimer lies on a crystallographic inversion center. The bond lengths in the $P_2Ag_2Cl_2$ core are $Ag-P = 2.504(3), 2.525(4), Ag-Cl = 2.643(3), 2.634(4)$, and $Ag \cdots Ag = 3.750 \text{ \AA}$, and the bond angles are $Ag-Cl-Ag = 90.5(1), Cl-Ag-Cl = 89.4(1), P-Ag-Cl = 108.5(1), 122.4(1), 121.5(1), 102.6(1)$, and $P-Ag-P = 111.5(1)^\circ$. The Ag_2Cl_2 unit in this complex is thus almost perfectly square, with a difference of less than 0.01 \AA between the symmetrically inequivalent $Ag-Cl$ bond lengths. This contrasts with the structure of the corresponding PPh_3 complex, $[(PPh_3)_2AgCl]_2$, where the $Ag-Cl$ bond lengths differ by nearly 0.15 \AA . The structures of the other members of the phosphole/AgX series were deduced from their far IR and cross-polarization magic-angle-spinning (CP/MAS) ^{31}P NMR spectra. Thus, the 1:1 complexes ($n = 1$), which exist only for $L = DMPP$, are shown to have the tetrameric cubane structure. The 2:1 complexes all have the halogen-bridged dimeric structures, $[L_2AgX]_2$, which was proved for the $L = DBP, X = Cl$ case by X-ray diffraction. Their far-IR spectra appear to be very sensitive to distortion of the Ag_2X_2 core. The 3:1 complexes, which exist only for $L = DBP$, have mononuclear $[L_3AgX]$ structures. The CP/MAS ^{31}P NMR spectra show splitting due to $^1J(Ag-P)$ coupling, which progressively decreases in magnitude from the 1:1 complexes (450–580 Hz) to the 3:1 complexes (ca. 250 Hz). A further splitting of about 100 Hz was observed for some of the 2:1 and 3:1 complexes, and this is assigned to $^2J(P-P)$ coupling between crystallographically inequivalent phosphorus atoms that are bound to a common silver atom in the complex. The ionic 4:1 complexes $[L_4Ag]BF_4$ ($L = DMPP, DBP$) were also prepared and characterized by CP/MAS ^{31}P NMR spectroscopy. The $Ag-P$ bond length r may be estimated with reasonable accuracy from $^1J(Ag-P)$ via the empirical relation $1/(r/\text{\AA})^3 = (3.707 \times 10^{-5})J/\text{Hz} + 4.788 \times 10^{-2}$. The solution ^{31}P NMR spectrum of $[LAgCl]_4$ ($L = DMPP$) in CH_2Cl_2 at $-80^\circ C$ shows a signal due to $[L_4Ag]^+$, as well as that due to the parent $[LAgCl]_4$. Likewise, $[L_2AgX]_2$ complexes ($L = DMPP; X = Cl, Br$) show signals due to $[LAgCl]_4$, $[L_3AgCl]$, and $[L_4Ag]^+$. Solutions of $[L_3AgX]$ ($L = DBP; X = Cl, Br, I$) show signals due to $[L_4Ag]^+$ and uncoordinated L, as well as to the parent $[L_3AgX]$. Thus, although the binuclear complexes $[L_2AgX]_2$ are the prevalent ones in the solid state, they do not exist in solution in detectable amounts. The nonexistence of $[LAgX]_4$ ($L = DBP$) and $[L_3AgX]$ ($L = DMPP$) in the solid state is consistent with the absence or, in the latter case, high lability of these species in solution.

Introduction

Tertiary phosphine complexes of silver(I) of the type $[L_nAgX]$ ($L =$ tertiary phosphine; $n = 1-4; X =$ coordinating or noncoordinating anion) were first prepared in 1937 by Mann, Wells, and Purdie.² Their general method of preparation involves the reaction of stoichiometric amounts of the phosphine ligand with the appropriate silver(I) salt. These complexes display a diversity of structural types, and several reviews on this topic have been published.³⁻⁶ The established structural chemistry of the $[L_nAgX]$

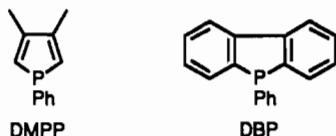
complexes is quite similar to that of the copper(I) analogues, although fewer X-ray crystallographic studies have appeared in the case of silver(I). The similarities and differences between the silver(I) and copper(I) cases are well illustrated by the complexes with $L =$ triphenylphosphine, PPh_3 . Thus, for $n = 1$, tetramers $[L_nAgX]_4$ with both the "cubane" and "step" structures have been characterized,⁷⁻⁹ and these have close parallels in the corresponding

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copper complexes.¹⁰⁻¹⁵ However, only in the case of copper have complexes with $n = 1.5$ been reported, which have a binuclear halogen-bridged structure with one three-coordinate and one four-coordinate copper atom.^{13,16,17} For $n = 2$, the silver complexes have dimeric halogen-bridged structures $[L_2AgX]_2$,^{8,18} whereas the corresponding copper complexes are all monomeric, with trigonal-planar coordination at the copper atom.¹⁹ For $n = 3$, monomeric complexes $[L_3AgX]$ with four-coordinate silver are found,²⁰ and this again parallels to the corresponding copper compounds.²¹

Phospholes, such as 1-phenyl-3,4-dimethylphosphole (DMPP)²²⁻²⁶ and 1-phenyldibenzophosphole (DBP),^{27,28} are



phosphorus donor ligands with unusual donor properties. Recent studies of their complexes of gold(I)²⁹ and copper(I)³⁰ halides showed that these ligands have coordination properties significantly different from those of PPh_3 . As part of a continuing program of investigation of the structures and properties of transition-metal phosphole complexes,^{23,24,27,28,31-33} we now report the results of a study of a number of silver(I) complexes with the phospholes DMPP and DBP. No silver(I) complexes of these ligands have previously been isolated. Apart from X-ray diffraction, there are several useful techniques for characterizing compounds in the solid state that have not been explored to a very great extent for silver(I) complexes. Thus, vibrational spectroscopy has proved to be useful for the determination of structures in silver(I) halide complexes,³⁴⁻³⁷ although it has not been as extensively applied to silver

Table I. Elemental Analyses and Melting Point Data for the (Phosphole)_nAgX Complexes

complex	mp/deg	% C		% H		yield
		calc	found	calc	found	
$[(DMPP)AgCl]_4^a$	192-194	43.47	43.90	3.96	3.98	64.6
$[(DMPP)AgBr]_4^c$ 1.25CH ₂ Cl ₂ ^b	200-202	33.00	33.01	3.24	2.99	70.0
$[(DMPP)AgI]_4^c$ 2.7CH ₂ Cl ₂ ^b	154-156	27.06	26.98	2.85	2.54	28.7
$[(DBP)_2AgCl]_2^c$	201-204	65.13	65.53	3.95	3.95	97.5
$[(DBP)_2AgBr]_2$	224-226	61.04	60.49	3.71	3.80	96.8
$[(DBP)_2AgI]_2$	208-210	57.24	57.53	3.48	3.52	89.0
$[(DMPP)_2AgCl]_2^c$ 0.1CH ₂ Cl ₂ ^{b,d}	140-142	54.79	54.81	5.01	5.08	93.5
$[(DMPP)_2AgBr]_2^c$ 0.1CH ₂ Cl ₂ ^b	120-122	50.54	50.55	4.62	4.75	98.1
$[(DMPP)_2AgI]_2^c$ 0.5CH ₂ Cl ₂ ^b	90-93	45.10	45.07	4.17	4.32	71.0
$[(DBP)_3AgCl]$	200-202	70.18	70.44	4.26	4.38	83.0
$[(DBP)_3AgBr]$	199-201	66.95	67.13	4.07	4.15	95.4
$[(DBP)_3AgI]$	177-179	61.67	61.40	3.74	3.83	93.5
$[(DBP)_4Ag]BF_4$	dec 235	69.97	70.26	4.25	4.35	64.0
$[(DMPP)_4Ag]BF_4$	158-160	60.84	60.20	5.54	5.58	94.8

^a% Cl: calc, 10.70; found, 10.70. ^bThe presence of CH₂Cl₂ was confirmed by ¹H NMR spectroscopy, $\delta = 5.3$ ppm. ^c% Cl: calc, 5.34; found, 5.14. ^d% Cl: calc, 6.82; found, 7.06.

as it has been to copper complexes.^{19,34-42} More recently, the technique of cross-polarization magic-angle-spinning (CP/MAS) ³¹P NMR spectroscopy has been shown to yield useful information about the structure and bonding in silver(I) complexes with phosphine ligands,⁴³ although again the number of studies of analogous copper(I) complexes by this technique is much greater.^{10,11,19,21,41,42,44-47} In order to investigate the usefulness of these techniques, we have applied them to the series of new phosphole complexes prepared in the present study and have checked the structural conclusions reached in one case by means of X-ray crystallography.

Because of the different nuclear spin properties of copper and silver, the solution chemistry of phosphine complexes of silver(I) is more amenable to study by NMR methods than is that of the analogous copper(I) complexes. Thus, the species $[(DBP)_nAg]^+$ ($n = 1-4$) have been observed in solution by means of ³¹P NMR spectroscopy,⁴⁸ and these are the only phosphole complexes of silver that have been reported to date. Further information about the solution chemistry of phosphole/silver(I) systems has been obtained here by studying the ³¹P NMR spectra of solutions of the new complexes prepared in the present work.

Experimental Section

Reagents and Physical Measurements. All chemicals were reagent grade and were used as received or synthesized as described below. When necessary, solvents were dried by standard procedures and stored over

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Table II. Abbreviated Crystal and Refinement Data for $[(DBP)_2AgCl]_2$

fw	1327.8	space group	$P\bar{1}$
$a/\text{\AA}$	10.831 (3)	Z	1
$b/\text{\AA}$	11.683 (3)	$d(\text{calc})/\text{g cm}^{-3}$	1.53
$c/\text{\AA}$	11.243 (3)	linear abs coeff/ cm^{-1}	9.18
α/deg	82.73 (2)	temp/K	290
β/deg	89.39 (2)	final R_F	0.066
γ/deg	78.01 (2)	final R_{wF}	0.069

Linde 4- \AA molecular sieves. All reactions involving phospholes were conducted under a dry N_2 atmosphere. Silver(I) chloride was purchased from J. T. Baker Chemical Co., Phillipsburg, NJ. Silver(I) bromide and iodide were prepared by metathetical reactions between aqueous solutions of $AgNO_3$ and $NaBr$ or NaI , respectively. 1-Phenyl-3,4-dimethylphosphole⁴⁰ (DMPP) and 1-phenyldibenzophosphole³¹ (DBP) were prepared by literature methods. All reactions involving the silver halides were conducted with minimum exposure to light.

Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. Melting points were determined on a Meltemp apparatus and are uncorrected. 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.

Solid-state cross-polarization magic-angle-spinning (CP/MAS) ^{31}P - ^1H NMR spectra were obtained on Nicolet NT-150 (^{31}P at 60.745 MHz), JEOL GX-270 (^{31}P at 109.25 MHz), and Chemagnetics CMC-300 (^{31}P at 120.61 MHz) wide-bore spectrometers using 20- and 40-kHz sweep widths, recycle delay times of 1–30 s, and proton decoupling fields of 10 G. Between 200 and 300 mg of the compounds were spun at 3–4.5 kHz in Delrin or Kel-F rotors. The chemical shifts were referenced to 85% H_3PO_4 via an external sample of solid PPh_3 ($\delta = -6.0$ ppm). The uncertainties in chemical shifts and coupling constants are estimated to be ± 0.5 ppm and ± 10 Hz, respectively. Spectral simulations were performed on a JEOL JEC 980B computer with the program FASNO3-760812 supplied by JEOL for this purpose. Solution $^{31}\text{P}\{^1\text{H}\}$ NMR were recorded at 40.26 MHz on a JEOL FX-100 spectrometer with ^7Li external lock. The chemical shifts were referenced to 85% H_3PO_4 via external PPh_3 in $CDCl_3$ ($\delta = -6.0$ ppm) with shifts to low field (high frequency) positive. Variable-temperature spectra were measured by using a commercially available temperature regulator (± 1 °C), and temperatures were monitored with both an alcohol thermometer and a thermocouple inserted directly into the probe.

Syntheses. All preparations were carried out under an atmosphere of dry nitrogen in flasks that were protected from light with aluminum foil. The $[L_nAgX]_m$ compounds were prepared by reacting the appropriate silver halide with a slight excess of the phosphorus ligand in acetonitrile or chloroform. The following are exemplary.

$[(DBP)_2AgCl]_2$. A mixture containing 0.230 g (1.59 mmol) of $AgCl$ and 0.910 g (3.5 mmol) of DBP in 50 mL of CH_3CN was heated at reflux overnight. After cooling of the reaction mixture to ambient temperature, the resulting colorless crystals were collected by filtration, washed with a small volume of anhydrous diethyl ether, and vacuum dried (yield 1.03 g, 97.5%).

$[(DBP)_3AgBr]$. A mixture containing 0.410 g (2.17 mmol) of $AgBr$ and 2.27 g (8.73 mmol) of DBP in 50 mL of $CHCl_3$ was stirred magnetically at ambient temperature overnight. The resulting colorless solution was filtered and the volume of the filtrate reduced to a few milliliters on a rotary evaporator. Hexane was added, and the mixture was kept in a refrigerator at 5 °C overnight. The colorless crystals that formed were collected by filtration, washed with hexane, and vacuum dried (yield 2.01 g, 95.4%).

$[(DBP)_4AgBF_4]$. A mixture containing 0.21 g (1.06 mmol) of $AgBF_4$ and 1.23 g (4.73 mmol) of DBP in 50 mL of CH_3CN was heated at reflux overnight. After cooling of the reaction mixture to ambient temperature, the resulting off-white microcrystals were collected by filtration, washed with a small volume of anhydrous diethyl ether, and vacuum dried (yield 0.84 g, 64%).

The elemental analyses, melting points, and yields of the complexes are given in Table I.

X-ray Crystal Structure Determinations. Colorless plates of bis(μ_2 -chloro)tetrakis(5-phenyldibenzophosphole)disilver(I) were isolated from a $CHCl_3$ /petroleum ether (70–100 °C) solution. Crystal data and additional details of data collection and refinement are given in Table II. Intensity data were taken with a Syntex P2, four-circle diffractometer in the θ - 2θ scan mode and were corrected for Lorentz, polarization, and

Table III. Atom Coordinates ($\times 10^4$) and Temperature Factors ($\text{\AA}^2 \times 10^3$) for $[(DBP)_2AgCl]_2$

atom	x	z	y	U^a
Ag	4457.9 (10)	4003.3 (9)	1192.6 (8)	46
Cl	4553 (3)	4108 (3)	-1068 (3)	53
P(1)	5659 (4)	2021 (3)	2058 (3)	57
P(2)	2421 (3)	4622 (4)	2230 (3)	69
C(11)	7058 (13)	1999 (9)	2959 (9)	45
C(12)	7989 (16)	998 (11)	3205 (10)	72
C(13)	8968 (18)	1044 (14)	3866 (12)	91
C(14)	9054 (15)	2031 (14)	4375 (12)	72
C(15)	8106 (14)	3003 (12)	4130 (12)	56
C(16)	7122 (13)	3031 (11)	3422 (11)	53
C(17)	6278 (17)	875 (11)	1136 (12)	68
C(18)	7020 (18)	913 (13)	237 (12)	85
C(19)	7381 (17)	-117 (14)	-349 (12)	94
C(110)	6815 (19)	-1077 (12)	0 (13)	102
C(111)	6115 (18)	-1119 (12)	908 (12)	91
C(112)	5767 (18)	-132 (12)	1512 (13)	78
C(113)	4956 (18)	-38 (11)	2511 (12)	78
C(114)	4311 (19)	-890 (13)	3020 (13)	92
C(115)	3579 (20)	-664 (13)	3952 (14)	102
C(116)	3431 (19)	433 (13)	4359 (12)	99
C(117)	4051 (17)	1289 (12)	3848 (12)	79
C(118)	4787 (17)	1066 (11)	2917 (11)	75
C(21)	2534 (12)	4261 (13)	3785 (11)	59
C(22)	3666 (13)	4266 (11)	4305 (11)	56
C(23)	3799 (16)	3973 (12)	5511 (15)	68
C(24)	2839 (15)	3649 (14)	6166 (13)	83
C(25)	1713 (17)	3697 (17)	5635 (12)	103
C(26)	1558 (14)	3937 (16)	4472 (13)	94
C(27)	1561 (14)	6152 (12)	2130 (2)	67 (4)
C(28)	1910 (16)	7092 (13)	2383 (13)	81 (5)
C(29)	1068 (19)	8208 (18)	2282 (17)	119 (7)
C(210)	-180 (18)	8154 (16)	1853 (15)	99 (6)
C(211)	-505 (20)	7206 (16)	1614 (17)	120 (7)
C(212)	241 (16)	6106 (114)	1738 (14)	84 (5)
C(213)	34 (17)	5099 (15)	1552 (15)	91 (5)
C(214)	-1195 (19)	4750 (17)	1143 (16)	106 (6)
C(215)	-1067 (21)	3648 (17)	1109 (17)	118 (7)
C(216)	-205 (19)	2746 (18)	1336 (17)	120 (7)
C(217)	953 (19)	2993 (17)	1745 (15)	103 (6)
C(218)	994 (17)	4121 (15)	1807 (14)	88 (5)

^a Average isotropic 10^3U given for anisotropic atoms.

Table IV. Core Geometries for the Complexes $[L_2AgCl]_2$ (L = DBP, PPh_3)

parameter	$[(DBP)_2AgCl]_2^a$	$[(PPh_3)_2AgCl]_2^b$
bond length/ \AA		
Ag–P(1)	2.504 (3)	2.467 (2)
Ag–P(2)	2.525 (3)	2.472 (2)
Ag–Cl	2.643 (3)	2.596 (2)
Ag–Cl'	2.634 (4)	2.741 (2)
Ag–Ag'	3.750 (2)	3.840 (2)
angle/deg		
Cl–Ag–Cl'	89.4 (1)	88.03 (6)
Ag–Cl–Ag'	90.5 (1)	91.97 (6)
P(1)–Ag–Cl	108.5 (1)	112.97 (7)
P(1)–Ag–Cl'	121.5 (1)	103.59 (7)
P(2)–Ag–Cl	122.4 (1)	113.92 (7)
P(2)–Ag–Cl'	102.6 (1)	108.70 (7)
P(1)–Ag–P(2)	111.5 (1)	122.91 (7)

^a This work. ^b Reference 18.

absorption effects, the last by the Gaussian method. Slight crystal decomposition (2% maximum) was corrected for by a sliding scale factor. No systematic absences were found. The heavy atoms were located by Patterson techniques, and the light atoms were then found on successive Fourier syntheses. Anisotropic temperature factors were used for all non-H atoms, with the exception of those on the phosphole ring 2, for which isotropic values were used. Hydrogen atoms were given fixed isotropic temperature factors, $U = 0.07 \text{\AA}^2$, and were inserted at calculated positions and not refined. Final refinement was by cascaded least-squares methods (minimizing $\sum w(F_o - F_c)^2$). The largest positive and negative peaks on final difference Fourier syntheses were of height ($e/\text{\AA}^3$) ± 1.3 . Weighting schemes of the form $1/(\sigma^2(F) + gF^2)$ were

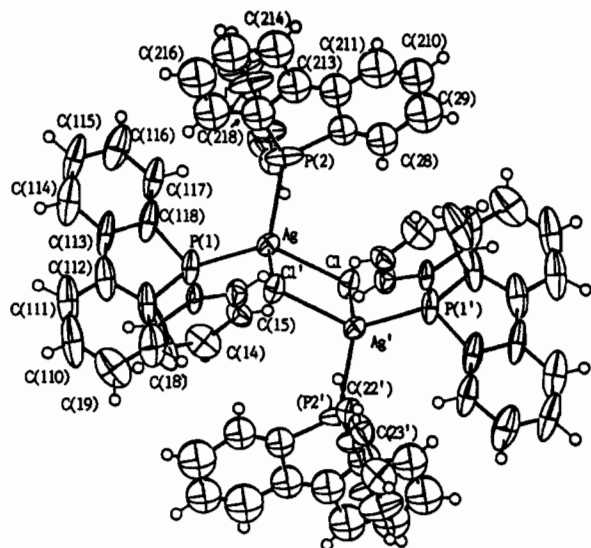


Figure 1. Structure of $[(\text{DBP})_2\text{AgCl}]_2$, showing 50% thermal ellipsoids. Hydrogen atoms have an arbitrary radius of 0.1 Å.

shown to be satisfactory by weight analysis. Three standard reflections monitored every 200 reflections showed slight changes during data collection, so the data were rescaled to correct for this. Computing was done with the SHEXTL system⁵⁰ on a Data General NOVA3 computer, following initial processing (absorption correction) on a Burroughs B6700 computer. Scattering factors were taken from ref 51. Final atom coordinates are given in Table III, and selected bond lengths and angles in Table IV.

Results and Discussion

The phosphole ligands 1-phenyl-3,4-dimethylphosphole (DMPP) and 1-phenyldibenzophosphole (DBP) were reacted with the silver(I) halides AgX ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) in mole ratios of $n:1$ ($n = 1-4$) and with silver tetrafluoroborate, AgBF_4 , in a 4:1 ratio. In the latter case complexes of the type $[\text{L}_4\text{Ag}]\text{BF}_4$ were obtained, and this contrasts with the case of the corresponding copper(I) system,³⁰ where no such compounds could be isolated. In the case of the silver halides, no complexes of 4:1 stoichiometry were obtained with either ligand, and this parallels the behavior of phosphines with tertiary aryl groups, such as PPh_3 , but contrasts with the situation for PMe_3 , where the existence of the 4:1 adducts has been established.^{52,53} In the case of DMPP, complexes with $n = 1$ and $n = 2$ were isolated, whereas with DBP the $n = 2$ and $n = 3$ compounds were obtained. Reaction mixtures containing a 1:1 DBP:AgX ratio or a 3:1 DMPP:AgX ratio yielded only the corresponding 2:1 complexes.

Crystal Structure of $[(\text{DBP})_2\text{AgCl}]_2$. The crystal structure of the 2:1 complex of DBP with AgCl shows that this complex crystallizes as a dimer $[(\text{DBP})_2\text{AgCl}]_2$ with a structure analogous to those previously observed for 2:1 complexes of PPh_3 with silver(I) halides.^{8,18} The structure of the molecule is shown in Figure 1. In this structure each of the two silver atoms is tetracoordinated by P atoms of the two independent phosphole ligands and the two doubly bridging chlorine atoms. This compound is isostructural with the corresponding triphenylphosphine complex $[(\text{PPh}_3)_2\text{AgCl}]_2$,¹⁸ and the important structural parameters for these two compounds are compared in Table IV. Both contain a nearly square Ag_2Cl_2 arrangement. However, the two symmetrically inequivalent Ag-Cl bond lengths differ by nearly 0.15 Å in the PPh_3 complex, whereas they are nearly equal (difference less than 0.01 Å) in the case of the DBP complex; this perhaps arises from the different packing constraints of the two ligands. The Ag-P bond lengths in the two complexes are similar, although

Table V. Silver-Halogen Vibrational Frequencies (cm^{-1}) for $[\text{L}_n\text{AgX}]_m$ Complexes

L	X	$[\text{LAgX}]_4$			
		step	cubane	$[\text{L}_2\text{AgX}]_2$	$[\text{L}_3\text{AgX}]$
DBP	Cl			154, 144	200
	Br			128, 118	143
	I			123	125
DMPP	Cl		188, 140	201, 130	
	Br		152, 114	145, 129	
	I			129	
PPh_3^a	Cl		178, 140	179, 128	192
	Br		131, 116		138
	I	130, 110, 93	109, 82		107

^aData for $[(\text{Ph}_3\text{P})\text{AgX}]_4$ and $[(\text{Ph}_3\text{P})_3\text{AgX}]$ from ref 35. Data for $[(\text{Ph}_3\text{P})_2\text{AgCl}]_2$ from this work; the structures of the 2:1 PPh_3/AgX complexes for which data are reported in ref 35 are uncertain (see text).

the mean value for the DBP complex (2.515 Å) is about 0.05 Å longer than that in the PPh_3 complex (2.470 Å), this being indicative of slightly stronger Ag-P bonds in the latter case. The P-Ag-P angle, however, is much smaller for the DBP complex than for the PPh_3 analogue. This can be attributed to the fact that DBP is sterically less demanding than PPh_3 , thus allowing the ligands to approach each other more closely.

Infrared Spectra. The far-infrared spectra of all of the phosphole/silver halide complexes showed halogen-sensitive bands that could be assigned to silver-halogen stretching modes $\nu(\text{AgX})$ (Table V). The assignments are straightforward in the case of the $[(\text{DBP})_2\text{AgX}]_2$ complexes, since only a single $\nu(\text{AgX})$ band is expected in the spectrum if the structure of these complexes is the same as those of the PPh_3 analogues,²⁰ i.e. mononuclear, with four-coordinate silver and a single terminal Ag-X bond. Single $\nu(\text{AgX})$ bands are in fact observed in the spectra at wavenumbers close to those of the corresponding PPh_3 complexes (Table V), and this supports the proposed mononuclear four-coordinate structure for these complexes.

The 1:1 complexes of PPh_3 with silver(I) halides are tetramers $[(\text{PPh}_3)\text{AgX}]_4$ with either the cubane⁷⁻⁹ or the step structure.⁹ The ideal cubane structure has T_d symmetry, and two IR-active $\nu(\text{AgX})$ modes of T_2 symmetry are predicted for this structure, as observed experimentally for all three AgX complexes. The step structure has only been found for the AgI complex.⁹ This has lower symmetry than the cubane structure, so that a larger number of $\nu(\text{AgX})$ bands can occur in principle, and three bands have been assigned for the step form of $[(\text{PPh}_3)\text{AgI}]_4$ (Table V). The wavenumbers of the bands for the cubane and step structures for $[(\text{PPh}_3)\text{AgI}]_4$ are quite similar, although those for the step structure are significantly higher than the ones for the cubane structure. Two strong halogen-sensitive bands have been assigned to $\nu(\text{AgX})$ modes for the 1:1 (DMPP)AgX complexes, and the wavenumbers of these bands are close to those of the corresponding PPh_3 complexes (Table V). These complexes are thus assigned tetrameric structures $[(\text{DMPP})\text{AgX}]_4$. It is not so easy to distinguish between the cubane and step structures on the basis of the far-IR results alone. The observation of only two $\nu(\text{AgX})$ bands fits the cubane structure better (see discussion above), but in this connection it should be mentioned that only two $\nu(\text{CuX})$ bands have been assigned for the step structures of the analogous copper(I) complexes $[(\text{PPh}_3)\text{CuX}]_4$.^{35,38} Definitive evidence for the cubane as opposed to the step structure has been obtained, however, from the CP/MAS ³¹P NMR spectra of these complexes (see below).

The 2:1 complexes of PPh_3 with silver(I) halides are dimers $[(\text{PPh}_3)_2\text{AgX}]_2$.^{8,18} The ideal symmetry of an isolated complex with this structure is D_{2h} , and two IR-active $\nu(\text{AgX})$ modes of B_{2u} and B_{3u} symmetry are predicted for this structure. However, in a previously reported IR study of these complexes,³⁵ only a single $\nu(\text{AgX})$ band was found for each compound, and this was assigned to the B_{2u} and/or B_{3u} modes, thus leaving open the question of whether both of these modes are coincident or whether only one of the two possible bands has been observed. In order to investigate

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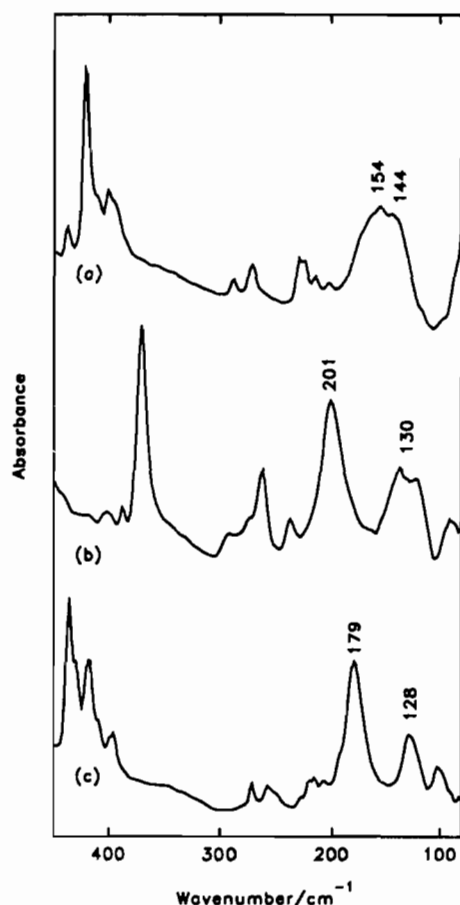


Figure 2. Far-infrared spectra of (a) $[(\text{DBP})_2\text{AgCl}]_2$, (b) $[(\text{DMPP})_2\text{AgCl}]_2$, and (c) $[(\text{PPh}_3)_2\text{AgCl}]_2$. The bands due to silver-halogen vibrations are labeled with their wavenumber.

this question further, the three complexes $[(\text{PPh}_3)_2\text{AgX}]_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) were prepared by the literature method³⁵ and their far-IR spectra were recorded. The chloro complex shows two bands that are assigned to $\nu(\text{AgCl})$ at 179 and 128 cm^{-1} . These are considerably lower in wavenumber than the single band at 208 cm^{-1} previously reported for this compound.³⁵ The spectrum of $[(\text{PPh}_3)_2\text{AgCl}]_2$ is compared in Figure 2 with those of the corresponding DBP and DMPP complexes. $[(\text{DBP})_2\text{AgCl}]_2$ also shows two $\nu(\text{AgCl})$ bands, but the separation between these (27 cm^{-1}) is considerably smaller than that in the corresponding PPh_3 complex (51 cm^{-1}). Since it has been established by X-ray crystallography that these complexes have essentially the same structure, this difference is rather surprising and warrants further investigation. Since the vibrational modes concerned involve the Ag_2Cl_2 core, it is likely that differences in the structure of this unit are responsible for the observed differences in the IR spectra. As pointed out above, the Ag_2Cl_2 group in both complexes is nearly square, with $\text{Cl}-\text{Ag}-\text{Cl}$ and $\text{Ag}-\text{Cl}-\text{Ag}$ angles near 90° . In the DBP complex, however, the $\text{Ag}-\text{Cl}$ bonds are very nearly equal, whereas there is a difference of nearly 0.15 Å in the case of the PPh_3 complex. For a perfectly square Ag_2X_2 unit (x parallel to the $\text{X}-\text{X}$ diagonal, y parallel to the $\text{Ag}-\text{Ag}$ diagonal) the two IR-active normal modes involve displacement of X and Ag along the positive and negative x directions, respectively, (B_{3u}) or a similar vibration in the y direction (B_{2u}). For an isolated square Ag_2X_2 unit, these two modes would have the same frequency. A distortion in which two bonds on opposite sides of the square are shortened and the other two are lengthened results in a lowering of the symmetry from D_{2h} to C_{2h} , and the two IR-active $\nu(\text{AgX})$ modes both have B_u symmetry. The forms of these modes are such that one mainly involves stretching of the two short $\text{Ag}-\text{X}$ bonds, while the other mainly involves stretching of the two long $\text{Ag}-\text{X}$ bonds, so that the two modes should give rise to bands at significantly different wavenumbers. This leads to the expectation

that the larger splitting of the $\nu(\text{AgX})$ bands should occur for the less symmetrical complex, in agreement with the experimental observations. Elsewhere it has been shown that the dependence of $\nu(\text{AgCl})$ on the $\text{Ag}-\text{Cl}$ bond length is such that a difference of 0.15 Å in the bond length corresponds to a difference in the vibrational frequency of up to 50 cm^{-1} .⁵⁴ Thus, the splitting observed for $[(\text{PPh}_3)_2\text{AgCl}]_2$ is of the right order of magnitude for the observed bond length difference.

The 2:1 complex of PPh_3 with AgBr showed a single strong band at 170 cm^{-1} , in agreement with the literature.³⁵ This appears to be too high in relation to the values found in this work for the AgCl complex, and this suggests that the two complexes have different structures. The AgI complex could not be prepared in pure form, in agreement with a statement in the original report.³⁵ We note that the $\nu(\text{AgI})$ wavenumbers (130, 107 cm^{-1}) reported in that work are the same as those for $[(\text{PPh}_3)_3\text{AgI}]_4$ (step isomer) and $[(\text{PPh}_3)_3\text{AgI}]$, respectively.

Despite the lack of well-characterized $[(\text{PPh}_3)_2\text{AgX}]_2$ model compounds, all of the 2:1 phosphole/ AgX complexes prepared in this work are assigned dimeric halogen-bridged structures $[\text{L}_2\text{AgX}]_2$. In the case of $[(\text{DMPP})_2\text{AgCl}]_2$, the separation between the two $\nu(\text{AgCl})$ bands (71 cm^{-1}) is greater than that in the corresponding PPh_3 complex. According to the argument given above, this implies that this complex has a structure with two sets of bridging $\text{Ag}-\text{Cl}$ bonds of unequal length, as has been observed in the PPh_3 complex. The splitting of the $\nu(\text{AgX})$ bands is much less in the bromo than in the chloro complexes, and this suggests that the symmetry of the Ag_2Br_2 core in these complexes is closer to D_{2h} . Only a single $\nu(\text{AgI})$ band was observed for the iodo complexes.

CP/MAS ^{31}P NMR Spectra. The naturally occurring isotopes of silver (^{107}Ag , 51.82% natural abundance; ^{109}Ag , 48.18%) both have nuclear spin $I = 1/2$, and their magnetogyric ratios are similar in magnitude ($\gamma(^{109}\text{Ag})/\gamma(^{107}\text{Ag}) = 1.15$). Thus, the ^{31}P NMR spectra of complexes of silver(I) with phosphorus donor ligands may show splitting due to $^1J(\text{Ag}-\text{P})$ coupling, and such splitting has been observed in several studies of such complexes in solution (see below). The resulting spectra normally show two doublets in which the separate couplings of ^{31}P to the ^{107}Ag and ^{109}Ag nuclei are resolved. Despite the large number of ^{31}P NMR studies of silver(I) complexes of phosphorus donor ligands in solution, the only solid-state study reported to date for such compounds is one on the series of complexes $[(\text{PPh}_3)_n\text{AgNO}_3]$ ($n = 1-4$).⁴³ The CP/MAS ^{31}P NMR spectra of these complexes show splitting due to $^1J(\text{Ag}-\text{P})$ coupling, although the separate splitting due to the ^{107}Ag and ^{109}Ag nuclei are not resolved due to the greater line widths ($\Delta\nu_{1/2} \approx 40$ Hz) that are observed in the solid-state spectra.

The far-IR results (see above) indicate that the 1:1 complexes of DMPP with the silver(I) halides are tetramers $[(\text{DMPP})\text{AgX}]_4$ in the solid state. The CP/MAS ^{31}P NMR spectra of these complexes are shown in Figure 3. The chemical shifts and coupling constants determined from the spectra are listed in Table VI. For the chloride and the bromide, the spectra consist of doublets due to $^1J(\text{Ag}-\text{P})$ coupling as described above. The presence of only one doublet in each of these spectra implies that there is only one kind of phosphorus and silver environment in these compounds. This confirms that they have the cubane rather than the step structure, as there are two different phosphorus and silver environments in the step structure. The spectrum of the iodide contains two doublets with nearly equal $^1J(\text{Ag}-\text{P})$ coupling but with chemical shifts that differ by 1.8 ppm. The distinction between the two different possible tetrameric structures is therefore not quite so clear in this case. The cubane structure cannot be ruled out, as such a structure can be distorted from ideal T_d symmetry in the solid state in such a way that it gives rise to two different phosphorus and silver environments. This is exactly what happens in the case of the analogous copper(I) complex, $[(\text{DMPP})\text{CuI}]_4$, which has C_2 crystal symmetry and which gives rise to two ^{31}P chemical shifts that differ by 2.3 ppm.³⁰ On this

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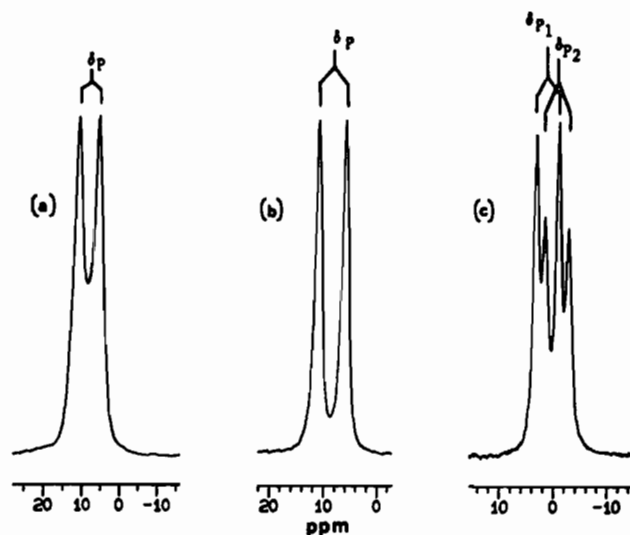


Figure 3. 109.25-MHz $^{31}\text{P}\{^1\text{H}\}$ CP/MAS solid-state NMR spectra of $[(\text{DMPP})\text{AgX}]_4$: (a) X = Cl; (b) X = Br; (c) X = I.

Table VI. CP/MAS ^{31}P NMR Parameters

complex	δ/ppm	$^1J(\text{Ag-P})/\text{Hz}$	$^2J(\text{P-P})/\text{Hz}$
$[(\text{DMPP})\text{AgCl}]_4$	8.6	581	
$[(\text{DMPP})\text{AgBr}]_4$	8.6	542	
$[(\text{DMPP})\text{AgI}]_4$	1.3, -0.5	458, 483	
$[(\text{DMPP})_2\text{AgCl}]_2$	8.1, 3.1	346, 371	90
$[(\text{DMPP})_2\text{AgBr}]_2$	12.1, 7.2	346, 356	
$[(\text{DMPP})_2\text{AgI}]_2$	-0.3, -3.9	264, 322	118
$[(\text{DBP})_2\text{AgCl}]_2$	-1.0, -5.0	308, 324	173
$[(\text{DBP})_2\text{AgBr}]_2$	3.5 ^a		
$[(\text{DBP})_2\text{AgI}]_2$	-3.0, -9.5	276, 327	
$[(\text{DBP})_3\text{AgCl}]$	1.6, -7.7	235, 251	74
$[(\text{DBP})_3\text{AgBr}]$	0.6, -9.5	262, 249	
$[(\text{DBP})_3\text{AgI}]$	-5.4, -11.3	245, 267	
$[(\text{DMPP})_4\text{Ag}]\text{BF}_4$	15.1	244	
$[(\text{DMPP})_4\text{Ag}]\text{BF}_4$	1.4	249	

^aChemical shift at center of spectrum; resolution insufficient to allow further analysis.

basis we conclude that the silver iodide complex has a similar structure. It can be noted that the details of the structures proposed here for the $[(\text{DMPP})\text{AgX}]_4$ complexes parallel exactly those that have been observed in the X-ray crystal structures of the cubane $[(\text{Et}_3\text{P})\text{AgX}]_4$ series, for which the X = Cl and Br members have exact T_d symmetry, while for the iodo analogue the symmetry is reduced to D_{2d} .

The $^1J(\text{Ag-P})$ coupling constants for $[(\text{DMPP})\text{AgX}]_4$ show a progressive decrease from X = Cl to X = I. This parallels the behavior already observed for the corresponding CuX complexes.³⁰ This suggests that there is a progressive weakening of the Ag-P bond along this series, and this conclusion is supported by the observation that the Ag-P bond lengths in the cubane $[(\text{Et}_3\text{P})\text{AgX}]_4$ series increase in the order 2.290 Å (Cl) < 2.402 Å (Br) < 2.438 Å (I). The most likely reason for this trend is that the donor strengths of the halide ligands are in the order $\text{Cl}^- < \text{Br}^- < \text{I}^-$, so that the phosphorus donor ligand is able to form the strongest dative bond (with least competition from the halide) in the chloride case. An equivalent way of stating this is to say that the Ag-P bond strength increases with increasing electronegativity of the X atom that is bonded to Ag.

The 109.25-MHz CP/MAS ^{31}P NMR spectra of the $[(\text{DMPP})_2\text{AgX}]_2$ complexes are shown in Figure 4. The observed patterns arise from the superposition of two doublets due to two inequivalent P atoms (the AM part of an AMX spin system where X represents the Ag nucleus). The high-field component of the low-field doublet overlaps with the low-field component of the high-field doublet so that the spectra appear roughly as 1:2:1 triplets. In the case of the iodo complex a further splitting is

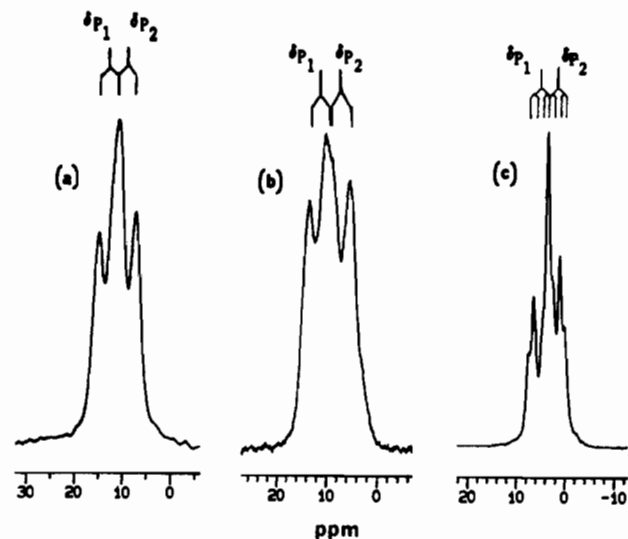


Figure 4. 109.25-MHz $^{31}\text{P}\{^1\text{H}\}$ CP/MAS solid-state NMR spectra of $[(\text{DMPP})_2\text{AgX}]_2$: (a) X = Cl; (b) X = Br; (c) X = I.

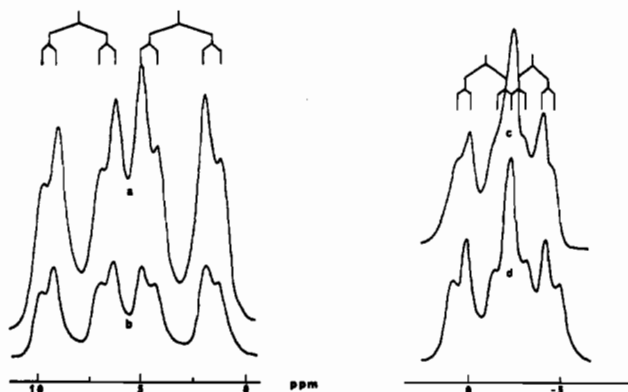


Figure 5. 120.61-MHz $^{31}\text{P}\{^1\text{H}\}$ CP/MAS solid-state NMR spectra of $[(\text{DMPP})_2\text{AgX}]_2$: (a) X = Cl, experimental spectrum; (b) X = Cl, simulated spectrum using parameters in Tables VI and $\Delta\nu_{1/2} = 40$ Hz; (c) X = I, experimental spectrum; (d) X = I, simulated spectrum using parameters in Table VI and $\Delta\nu_{1/2} = 40$ Hz.

evident, and this is assigned to $^2J(\text{P-P})$ coupling between the two inequivalent P atoms (i.e. to J_{AM} in the AMX spin system). The origin of the splitting patterns is indicated by the stick diagrams above the spectra in Figure 4. Confirmation of this interpretation was obtained by running the spectra at a higher applied magnetic field strength. The spectra obtained at 120.61 MHz are shown in Figure 5. At the higher field strength the frequency separation between the signals due to the two inequivalent P atoms is increased, so that the two doublets become more clearly resolved. Moreover, the smaller splitting due to the $^2J(\text{P-P})$ coupling is better resolved in these spectra. In the chloro complex, this splitting is clearly evident in the 120.61-MHz spectrum, whereas it is not evident at all in the 109.25-MHz spectrum. The corresponding DBP complexes $[(\text{DBP})_2\text{AgX}]_2$ gave similar, but generally less well-resolved spectra. The NMR parameters obtained from the spectra of both series of $[\text{L}_2\text{AgX}]_2$ complexes (L = DMPP, DBP) are given in Table VI. The interpretation of these spectra is that the two L_2Ag units in the dimer are identical and there is no observable coupling across the halogen bridges. The inequivalence of the two P atoms in the L_2Ag units is consistent with the crystal structure of $[(\text{DBP})_2\text{AgCl}]_2$ (see above) and has also been observed for the corresponding PPh_3 complexes $[(\text{PPh}_3)_2\text{AgCl}]_2$ (X = Cl, Br).^{8,18} The $^1J(\text{Ag-P})$ values for $[\text{L}_2\text{AgX}]_2$ (L = DMPP, DBP) show a progressive decrease from X = Cl to X = Br, as was observed in the case of $[(\text{DMPP})\text{AgX}]_4$, and the possible reasons for this are discussed above.

The CP/MAS ^{31}P NMR spectrum of $[(\text{DBP})_3\text{AgCl}]$ is shown in Figure 6. The origin of the observed splitting pattern is illustrated by the stick diagram above the spectrum. There are

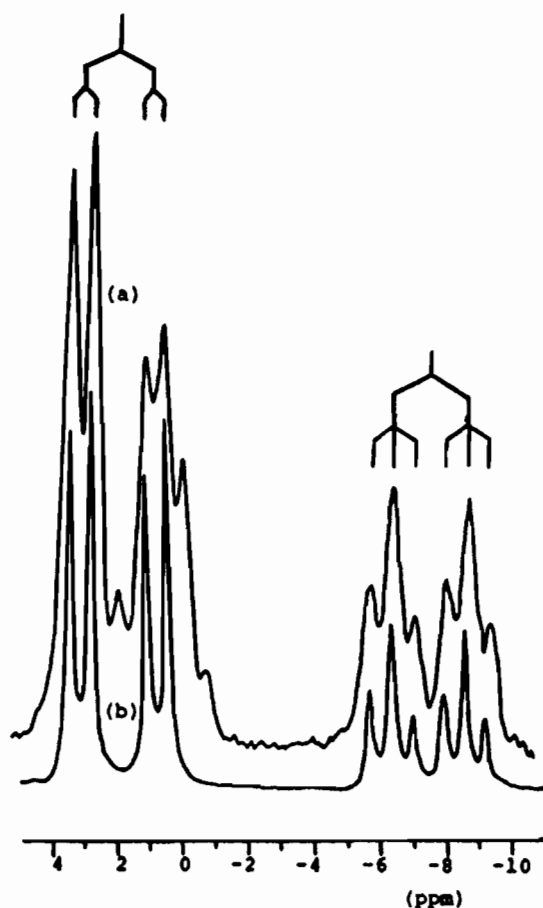


Figure 6. 109.25-MHz $^{31}\text{P}\{^1\text{H}\}$ CP/MAS solid-state NMR spectra of $[(\text{DBP})_3\text{AgCl}]$: (a) experimental spectrum; (b) simulated spectrum using parameters in Table VI and $\Delta\nu_{1/2} = 40$ Hz.

two ^{31}P chemical shifts, indicating that two of the three phosphorus atoms in the molecule are equivalent. The spin system that gives rise to this spectrum is A_2MX , where the A_2M part refers to the phosphorus nuclei and X is the silver nucleus. The ^{31}P spectrum thus consists of an A_2M pattern that exhibits splitting due to $J_{\text{AM}} = {}^2J(\text{P-P})$ (a doublet due to the two equivalent phosphorus nuclei and a triplet due to the third phosphorus nucleus), the components of which show a further splitting due to $J_{\text{AX}}, J_{\text{MX}} = {}^1J(\text{Ag-P})$. The NMR parameters obtained from this analysis are given in Table VI, and a simulation of the spectrum using these parameters is given in Figure 6. The fit is very good except for the high-field component of the multiplet arising from the two equivalent phosphorus nuclei (A_2), which is more complex than the doublet predicted for the A_2MX system. This suggests that these two nuclei are not exactly equivalent and that the spin system might be more accurately described as ABMX , but the analysis is given here in terms of the simpler spin system to which it closely approximates. The crystal structure of the corresponding gold(I) complex $[(\text{DBP})_3\text{AuCl}]$ shows that two of the three DBP ligands are related by symmetry,²⁹ so that two of the three phosphorus atoms in this complex are symmetrically equivalent in the solid. In the monoclinic PPh_3 complex $[(\text{PPh}_3)_3\text{AgCl}]$ there are four molecules in the unit cell, each of which has three inequivalent phosphorus atoms and thus three inequivalent bond lengths: $\text{Ag-P}(1) = 2.552 \text{ \AA}$, $\text{Ag-P}(2) = 2.556 \text{ \AA}$, and $\text{Ag-P}(3) = 2.520 \text{ \AA}$.²⁰ Since the first two of these differ by only 0.004 \AA , and both differ by an average of 0.034 \AA from the third, this compound might be expected to show a solid-state ^{31}P NMR spectrum similar to that observed for $[(\text{DBP})_3\text{AgCl}]$. In order to investigate this point, we prepared $[(\text{PPh}_3)_3\text{AgCl}]$ and recorded its CP/MAS ^{31}P NMR spectrum, and this is shown in Figure 7. Contrary to the expectation stated above, the signals do not separate into two clearly defined regions but show a non-first-order pattern as might be expected for an ABCX spin system. The CP/MAS NMR ^{31}P

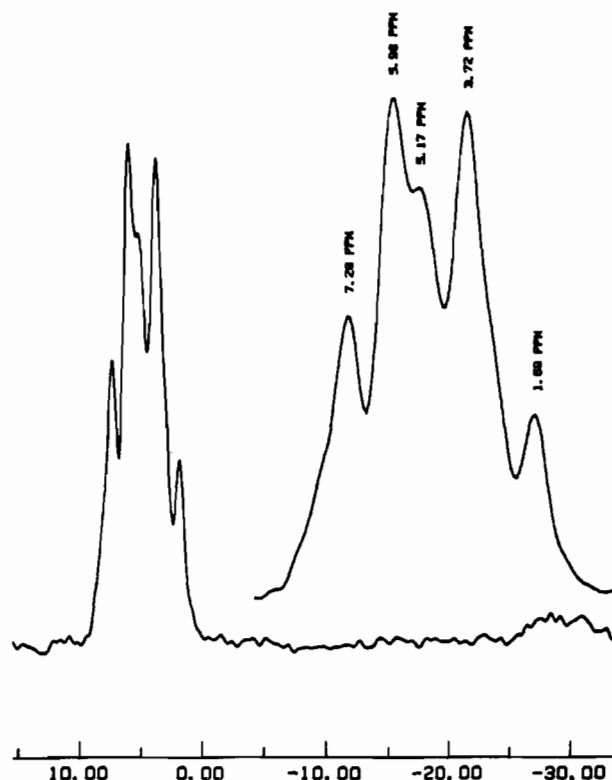


Figure 7. 120.61-MHz $^{31}\text{P}\{^1\text{H}\}$ CP/MAS solid-state NMR spectrum of $[(\text{PPh}_3)_3\text{AgCl}]$.

NMR spectrum of $[(\text{DBP})_3\text{AgBr}]$ is similar to that of the chloride in that it shows two well-separated signals of relative intensity 2:1, each of which is split by ${}^1J(\text{Ag-P})$ coupling (Table VI). However, the resolution is insufficient to allow any ${}^2J(\text{P-P})$ coupling to be seen in this case. The resolution in the spectrum of $[(\text{DBP})_3\text{AgI}]$ is poorer, but an analysis similar to that of the bromide complex is still possible. The resulting parameters are given in Table VI.

From these results it can be seen that the strong dependence of ${}^1J(\text{Ag-P})$ on X which is observed for the 1:1 and 2:1 phosphole/AgX complexes (see above) is not evident in the case of the 3:1 complexes. This is similar to the situation that has been observed previously for complexes of PPh_3 with CuX . Thus, for the cubane complexes $[(\text{PPh}_3)_3\text{CuX}]_4$, there is approximately a 20% reduction in ${}^1J(\text{Cu-X})$ from $\text{X} = \text{Cl}$ to $\text{X} = \text{I}$,^{10,11} as is observed in the present series of $[(\text{DMPP})\text{AgX}]_4$ complexes, whereas for the series $[(\text{PPh}_3)_3\text{CuX}]$ there is almost no variation in ${}^1J(\text{Cu-X})$ with X.²¹

Also evident in the results in Table VI is a progressive decrease in the magnitude of ${}^1J(\text{Ag-P})$ with increasing number of coordinated phosphole ligands. This parallels observations made for the corresponding phosphole CuX complexes,³⁰ and for the compounds $[(\text{PPh}_3)_n\text{AgNO}_3]$ ($n = 1-4$),⁴³ which are the only other silver/phosphine complexes to have been studied by solid-state CP/MAS ^{31}P NMR spectroscopy to date. Similar observations have also been made for complexes of silver(I) with phosphine ligands in solution,^{48,55,56} and this trend has been attributed to a decrease in the Ag 4s character in the Ag-P bonds with an increase in the number of coordinated phosphorus ligands.^{55,56}

The CP/MAS ^{31}P NMR spectra of the 4:1 complexes $[\text{L}_4\text{-Ag}]\text{BF}_4$ ($\text{L} = \text{DMPP}, \text{DBP}$) were also measured and are shown in Figure 8. Crystal structure studies on related PPh_3 complexes $[(\text{PPh}_3)_4\text{Ag}]^+\text{Y}^-$ ($\text{Y} = \text{NO}_3, \text{PF}_6, \text{ClO}_4$)^{43,53,57} show that these are ionic as formulated, with no significant interactions between the anions Y^- and the silver atom. In addition, the cations in all three

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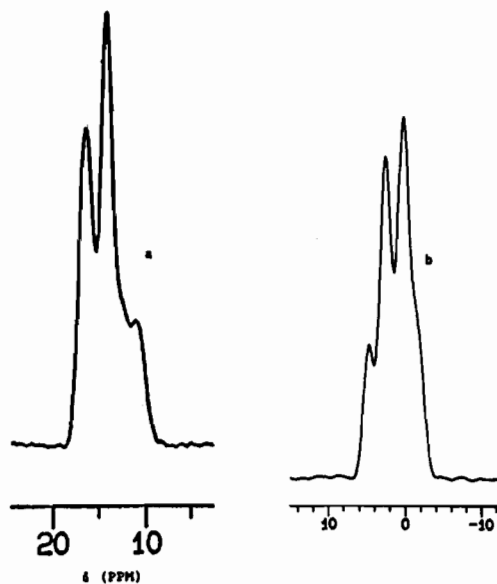


Figure 8. 109.25-MHz $^{31}\text{P}\{^1\text{H}\}$ CP/MAS solid-state NMR spectra of (a) $[(\text{DMPP})_4\text{Ag}]\text{BF}_4$ and (b) $[(\text{DBP})_4\text{Ag}]\text{BF}_4$.

compounds possess C_3 molecular symmetry with a very nearly tetrahedral environment about the silver atom. In the case of the nitrate complex, the P–Ag–P angles are 109.4 and 109.5° and the Ag–P distances are 2.643 and 2.671 Å. The CP/MAS ^{31}P NMR spectrum of this complex shows a single doublet (the A part of an A_4X spin system) with $^1J(\text{Ag–P}) = 190$ Hz.⁴³ Likewise, the spectra of $[(\text{DMPP})_4\text{Ag}]\text{BF}_4$ and $[(\text{DBP})_4\text{Ag}]\text{BF}_4$ show a strong doublet, but there are additional peaks present that cannot be fully explained as yet. This probably indicates that the four phosphorus atoms are not equivalent in these solids. Nevertheless, the separation between the two main peaks in the spectra is taken to be $^1J(\text{Ag–P})$, yielding values of 244 and 249 Hz, respectively (Table VI). These coupling constants are not very different in magnitude from those of the 3:1 complexes $[(\text{DBP})_3\text{AgX}]$, but otherwise they fit in well with the general trend of decreasing $^1J(\text{Ag–P})$ with increasing number of coordinated phosphorus donor ligands as discussed above. The fact that they are significantly larger in magnitude than the value 190 Hz previously reported for $[(\text{PPh}_3)_4\text{Ag}]\text{NO}_3$ ⁴³ suggests that the phosphole ligands bind more strongly than PPh_3 to the silver(I) center in $[\text{L}_4\text{Ag}]^+$.

We have recently shown that a good correlation exists between the $^1J(\text{Cu–P})$ coupling constant obtained from CP/MAS ^{31}P solid-state NMR spectroscopy for a range of copper(I) complexes with phosphorus donor ligands and the inverse cube of the Cu–P bond length in these complexes.³⁰ The number of silver(I) complexes for which both solid-state ^{31}P NMR and X-ray crystal structure data have been reported is much less, being restricted to the series $[(\text{PPh}_3)_n\text{AgNO}_3]$ ($n = 1-4$)⁴³ and the complex $[(\text{DBP})_2\text{AgCl}]_2$ studied in the present work. A plot of $1/r^3$ vs J (where r is the Ag–P bond length and J is the $^1J(\text{Ag–P})$ coupling constant) for the $[(\text{PPh}_3)_n\text{AgNO}_3]$ ($n = 1-4$) series is shown in Figure 9. The line of best fit through the four points is

$$1/(r/\text{Å})^3 = (3.707 \times 10^{-5})J/\text{Hz} + 4.788 \times 10^{-2} \quad (1)$$

with a correlation coefficient of 0.94. As discussed above, the solid-state ^{31}P NMR spectrum of $[(\text{DBP})_2\text{AgCl}]_2$ shows two separate signals with different $^1J(\text{Ag–P})$ splittings due to the inequivalence of the two phosphorus atoms bound to each silver atom. Thus, two points can be plotted for this compound, and this has been done in Figure 9 by assuming that the shorter of the two Ag–P bonds is associated with the larger $^1J(\text{Ag–P})$ value. It is seen that these points lie close to the line of best fit for the $[(\text{PPh}_3)_n\text{AgNO}_3]$ complexes, nearest to the point for the $n = 3$ compound.

The results of the present study and those of the previous study of the analogous copper(I) complexes³⁰ provide CP/MAS ^{31}P NMR data for a number of isostructural copper(I) and silver(I)

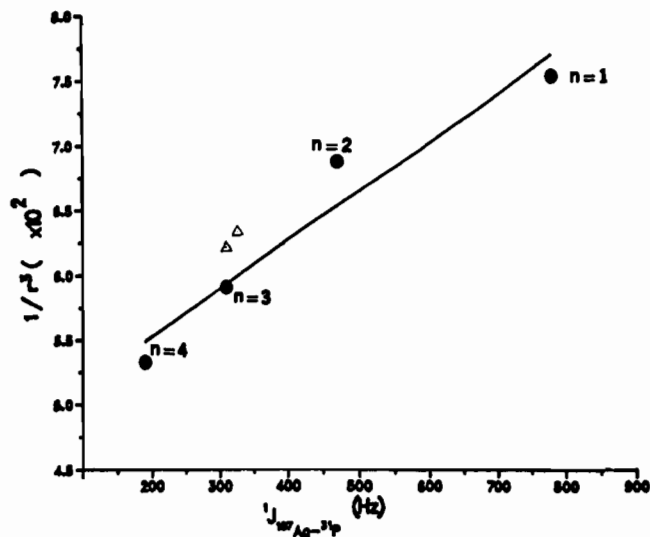


Figure 9. Graph of the inverse cube of the Ag–P bond length r vs the $^1J(\text{Ag–P})$ coupling constant for $[(\text{PPh}_3)_n\text{AgNO}_3]$ ($n = 1-4$; ●) and $[(\text{DBP})_2\text{AgCl}]_2$ (Δ).

Table VII. Comparison of $^1J(\text{M–P})$ Values from CP/MAS ^{31}P NMR Spectra of Isostructural Copper(I) and Silver(I) Complexes with Phosphorus Donor Ligands^a

complex	J/Hz		$10^6 J_r/T^b$		R^c
	M = Cu	M = Ag	M = Cu	M = Ag	
$[(\text{DMPP})\text{MCl}]_4$	1802	581	24.9	50.0	2.01
$[(\text{DMPP})\text{MBr}]_4$	1594	542	22.0	46.7	2.12
$[(\text{DMPP})\text{MI}]_4$	1358	471	18.7	40.6	2.17
$[(\text{DMPP})_2\text{MBr}]_2$	1060	351	14.6	30.2	2.07
$[(\text{DMPP})_2\text{MI}]_2$	1003	293	13.8	25.2	1.83
$[(\text{DBP})_3\text{MI}]$	886	256	12.2	22.1	1.81
$[(\text{DMPP})_4\text{M}]^+$	749	244	10.3	21.0	2.04
$[(\text{PPh}_3)_2\text{MNO}_3]$	1400	470	19.3	40.5	2.10

^aData for phosphole/silver(I) complexes from this work; data for phosphole/copper(I) complexes from ref 30; data for $[(\text{PPh}_3)_2\text{MNO}_3]$ from refs 19 (M = Cu) and 43 (M = Ag). Mean values of the coupling constants are given in cases where more than one value is obtained due to crystallographic inequivalence. ^b $J_r = |J/\gamma|$. $\gamma/10^7 \text{ T}^{-1} \text{ s}^{-1} = 7.2466$ ($^{63,65}\text{Cu}$), -1.1609 ($^{107,109}\text{Ag}$); the weighted mean of the values for the two isotopes was used in each case (see text). ^c $R = J_r(\text{Ag})/J_r(\text{Cu})$.

complexes, and this allows a comparison to be made of the $^1J(\text{M–P})$ coupling constants for these complexes. These parameters are listed in Table VII. In order to eliminate the effect of the different magnetic moments of the metal nuclei on these coupling constants, they have been divided by the magnetogyric ratio γ of the metal nucleus concerned (the γ values that were used for each metal nucleus are the weighted means of those for the naturally occurring isotopes ^{63}Cu , ^{65}Cu and ^{107}Ag , ^{109}Ag , since separate signals for the two isotopes were not resolved in most cases). This yields a reduced coupling constant J_r , which is essentially the magnitude of the magnetic field at the metal nucleus, which is induced by the magnetic moment of the phosphorus nucleus by means of the Fermi contact interaction between the nuclei and the electrons in the M–P bond. Since this arises from the Fermi contact interaction, it depends on the contributions of the phosphorus and the metal s orbitals to the M–P bonds. The copper and silver complexes that are compared in Table VII have the same phosphorus donor ligand, so the phosphorus s-orbital contribution should be similar in both cases. Thus, the values of J_r should be dominated by the metal s-orbital involvement in the M–P bond. The results in Table VII show that the J_r values for the Ag complexes are a factor of 2.0 ± 0.2 greater than those of the corresponding Cu complexes. This suggests that the metal s-orbital involvement in the M–P bond is greater for M = Ag than for M = Cu. Assuming that for these d^{10} complexes the metal orbitals involved in the bonding are the s and p orbitals, the factor that is most likely to determine the degree of s-orbital involvement

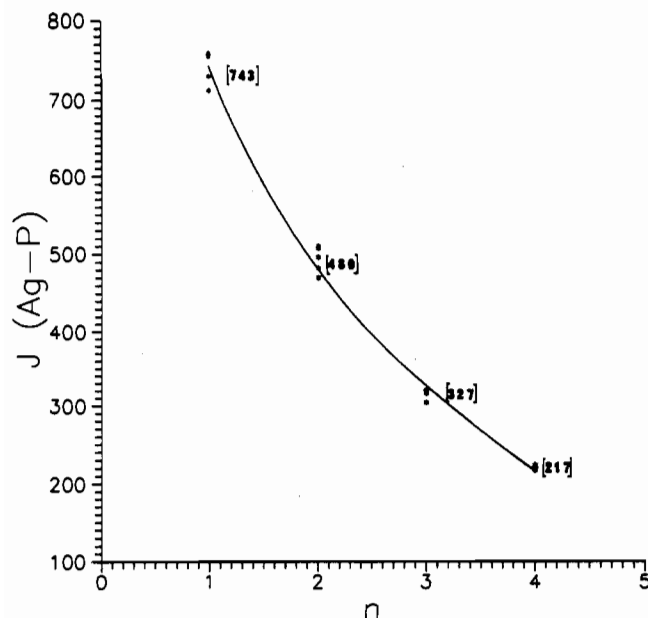


Figure 10. Graph of $^1J(^{107}\text{Ag}-\text{P})$ versus n for $[\text{L}_n\text{Ag}]\text{X}$ ($\text{L} = \text{DBP}, \text{PPh}_3, \text{Et}_3\text{P}, (p\text{-tol})_3\text{P}$; $\text{X} = \text{BF}_4, \text{PF}_6$). Data are for CH_2Cl_2 solutions at -80°C (Table VIII). $^1J(^{107}\text{Ag}-\text{P}) = -379.48 \ln(n) + 743.37$. Predicted values are in brackets.

is the s-p orbital energy separation.⁵⁸ A large energy separation should lead to greater participation of the s orbitals in the bonding. For the group 11 metal atoms, this energy difference is 3.79, 3.66, and 4.63 eV for Cu, Ag, and Au, respectively.⁵⁸ Thus, the expected order of s-orbital participation is $\text{Au} \gg \text{Cu} > \text{Ag}$. The order deduced from the $^1J(\text{M}-\text{P})$ values for Cu and Ag appears to be the reverse of this and is consistent with a general increase in s-electron density of MP bonds with an increase in the mass of M.⁵⁹

Solution ^{31}P NMR Studies. It is well-known that the solution and solid-state structures of transition-metal complexes are not necessarily the same. This is particularly true for substitutionally labile complexes such as $(\text{R}_3\text{P})_n\text{AgX}$, where it is possible for several species to exist in solution through fast ligand-exchange equilibria. Complexes of this type have been extensively studied in solution by ^{31}P NMR spectroscopy^{28,56,61-66} following the initial reports by Muettterties and Alegranti.^{55,60} Singlets are normally observed in ambient temperature spectra due to rapid exchange equilibria, but at low temperatures exchange is stopped and the typical pair of doublets due to coupling of ^{31}P to both ^{107}Ag and ^{109}Ag is resolved. Typical data are given in Table VIII. The magnitude of $^1J(\text{Ag}-\text{P})$ is diagnostic of the number n of coordinated phosphorus ligands, as shown in Figure 10. For the series L_nAgX complexes ($\text{L} = \text{DBP}, \text{PPh}_3, \text{Et}_3\text{P}, \text{Bu}^n_3\text{P}, (p\text{-tol})_3\text{P}$; $\text{X} = \text{BF}_4, \text{PF}_6, \text{NO}_3$) we find a useful empirical relation between $^1J(\text{Ag}-\text{P})$ and n that is of the form

$$^1J(^{107}\text{Ag}-\text{P}) = -379.48 \ln(n) + 734.37 \quad (2)$$

If X is a coordinating anion, $^1J(\text{Ag}-\text{P})$ is also a function of the coordinating ability of X in all but the $n = 4$ case, as is illustrated in Figure 11 and the data in Table VIII. This is due to the fact that silver(I) shows a strong tendency toward tetrahedral four-

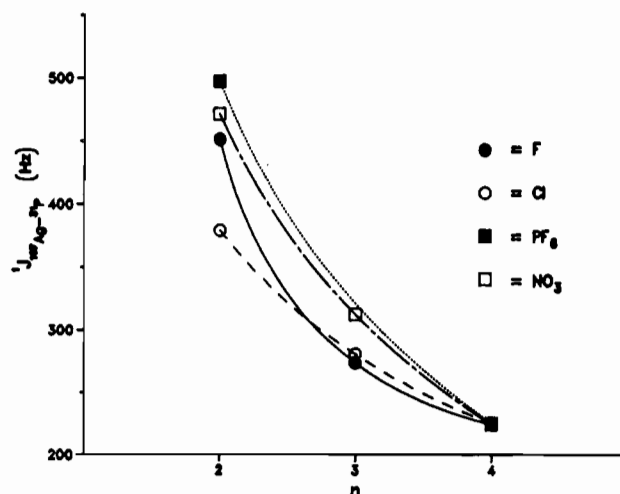


Figure 11. Plot of $^1J(^{107}\text{Ag}-\text{P})$ versus n for $\{(p\text{-tol})_3\text{P}\}_n\text{AgX}$ (Table VIII).

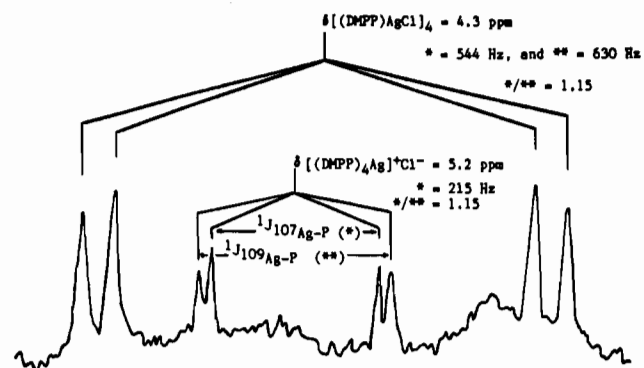


Figure 12. 40.26-MHz $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[(\text{DMPP})\text{AgCl}]_4$ in CH_2Cl_2 at -80°C . $J = ^1J(^{107}\text{Ag}-\text{P})$.

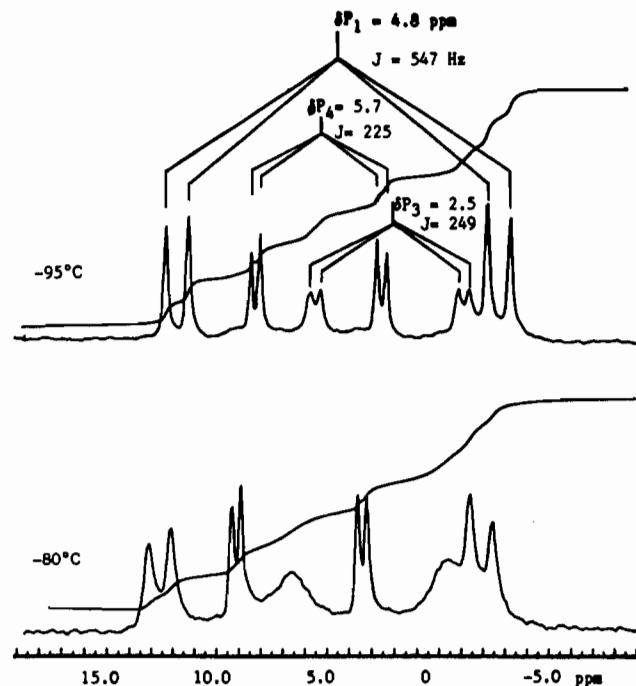


Figure 13. 40.26-MHz $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[(\text{DMPP})_2\text{AgCl}]_2$ in CH_2Cl_2 at -80 and -95°C . $\text{P}_1 = [(\text{DMPP})\text{AgCl}]_4$, $\text{P}_3 = [(\text{DMPP})_3\text{AgCl}]$, $\text{P}_4 = [(\text{DMPP})_4\text{Ag}]^+$, and $J = ^1J(^{107}\text{Ag}-\text{P})$.

coordination so that for $n < 4$ the X atom is coordinated to Ag and $^1J(\text{Ag}-\text{P})$ is X dependent, but for $n = 4$ the coordination requirements of the Ag atom are satisfied by the four phosphorus ligands so that the complex is ionic, $[\text{L}_4\text{Ag}]^+\text{X}^-$, and $^1J(\text{Ag}-\text{P})$ is just that for $[\text{L}_4\text{Ag}]^+$.

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Table VIII. ^{31}P NMR Chemical Shifts (δ/ppm) and One-bond ^{107}Ag - ^{31}P Spin-Spin Coupling Constants ($^1J/\text{Hz}$) for Selected L_nAgX Complexes^a

L	X	$\delta(^{31}\text{P})/^1J_{^{107}\text{Ag-P}}$				ref
		$n = 1$	$n = 2$	$n = 3$	$n = 4$	
Ph ₃ P	Cl	3.3/282	3.0/277	3.0/277		61
	I				b/262	62
	PF ₆	15.8/755	15.3/507	11.5/319	5.6/224	28
	BF ₄			b/318	7.5/222	56
	NO ₃			b/309		62
	OH				5.9/221	61
	SnCl ₃			8.3/300 ^d 5.9/223 ^d		61
DBP	Cl			-4.7/262	-1.4/222	TW
	Br			-6.9/259	-2.2/222	TW
	I			-10.4/247	-2.1/222	TW
	PF ₆	3.0/730	4.9/510	2.7/316	1.9/223	28
	NO ₃				b/225	28
DMPP	Cl	4.3/544		2.5/249	5.2/215	TW
	Br	2.2/505		1.3/247	5.3/217	TW
	I	2.6/460		-0.5/232	5.5/215	TW
	BF ₄				4.6/215	TW
Et ₃ P	BF ₄	10.3/712	8.9/470	1.9/304	7.7/218	56
	BF ₄				-31.6/212	56
Me ₂ PhP	BF ₄				-16.0/230	56
	BF ₄				15.5/219	56
MePh ₂ P	BF ₄	b/759	32.9/470	26.6/304		56
	CH ₃	-6.8/279				64
(n-Bu) ₃ P ^r	Cl	82.5/593				63
	Br	73.8/561				63
	I	74.5/544				63
(t-Bu) ₃ P ^r	PF ₆		79.9/437			63
	BF ₄		80.0/444			63
	NO ₃	86.3/683	79.8/442			63
	ClO ₄		79.7/442			63
	CN	79.7/498				63
	SCN	83.3/635				63
(MeS) ₃ P ^r	OAc		-28.4/513			63
	PF ₆		-28.4/513	2.5/273	5.3/224	65
	F		8.1/450	2.7/280	5.3/225	55
	Cl		1.4/378	1.7/278	5.5/230	55
	Br			-1.2/266		55
	I			10.6/321	5.6/225	55
	PF ₆		13.4/496	7.3/312	5.5/224	55
	NO ₃		9.8/470		5.6/225	55
	ClO ₄		13.1/503	4.2/230		55
	CN		3.8/278	5.0/270		55
	SCN			7.3/310	5.7/230	55
	F ₃ OAc ^h		9.5/451			55
	(Me ₂ N) ₃ P	Cl		121.2/535		
I			119.3/597			66
BF ₄		121.5/910				66
BPh ₄			115.4/610	122.1/393		66
NO ₃			118.6/592			66
CN			124.3/437			66

^a For $^1J_{^{109}\text{Ag-P}} = 1.15 (^1J_{^{107}\text{Ag-P}})$, the values have not been reported and/or not listed here. The $\delta(^{31}\text{P})$ and $^1J_{\text{Ag-P}}$ values have been obtained in common NMR solvents (CH_2Cl_2 , CD_2Cl_2 , CDCl_3) at temperatures ranging from -80 to -100 °C, unless specified otherwise. TW = this work. ^b $\delta(^{31}\text{P})$ not reported. ^c From ref 61. ^d The major species is the ionic $[(\text{Ph}_3\text{P})_3\text{Ag}]^+\text{SnCl}_3^-$ ($J = 223$ Hz). ^e All parameters obtained at ambient temperature. ^f $(\text{Mes})_3\text{P}$ = trimesitylphosphine, where mesityl = 2,4,6-trimethylphenyl. ^g $(p\text{-Tol})_3\text{P}$ = tris(*p*-tolyl)phosphine = $(p\text{-CH}_3\text{C}_6\text{H}_4)_3\text{P}$. ^h $\text{F}_3\text{OAc} = \text{F}_3\text{CCO}_2^-$.

The ^{31}P NMR spectra of the phosphole complexes of the silver(I) halides in dichloromethane solution at ambient temperature show single, exchange-averaged signals. At lower temperatures (-50 to -80 °C), however, the spectra show signals from several distinct species, each characterized by two doublets due to coupling of the phosphorus nucleus with the two magnetic isotopes of silver (^{107}Ag , ^{109}Ag) as described above. Typical spectra obtained on CH_2Cl_2 solutions at -80 to -95 °C are shown in Figures 12–15, and the parameters obtained from these spectra are given in Table VIII.

The spectrum of $[(\text{DMPP})_4\text{AgCl}]_4$ is shown in Figure 12. This shows signals due to two distinct species with an approximately 3:1 intensity ratio. The assignment of each set of signals is based on their relative intensities and on a calculation of the ratio $^1J(^{109}\text{Ag-P})/^1J(^{107}\text{Ag-P})$, which should equal the theoretical ratio $\gamma(^{109}\text{Ag})/\gamma(^{107}\text{Ag}) = 1.15$. These assignments are shown as stick diagrams in Figure 12. The major species corresponding to the

signal at $\delta = 4.3$ ppm with $^1J(^{107}\text{Ag-P}) = 544$ Hz and $^1J(^{109}\text{Ag-P}) = 630$ Hz can be assigned to the 1:1 tetrameric complex $[(\text{DMPP})_4\text{AgCl}]_4$. This assignment is justified by comparison with the solid-state ^{31}P NMR spectrum, which showed $^1J(\text{Ag-P}) = 581$ Hz (Table V). Since the separate splittings due to the two isotopes of silver are not resolved in the solid-state spectrum, the value obtained in this case is the weighted mean of the values for the two isotopes. The weighted mean calculated from the solution values is $0.5182 \times 544 + 0.4818 \times 630 = 585$ Hz, which agrees very closely with the solid-state value. The second (minor) species in solution has $\delta = 5.2$ ppm and $^1J(^{107}\text{Ag-P}) = 215$ Hz and is assigned to the ionic complex $[(\text{DMPP})_4\text{Ag}]^+$. This assignment is based on the fact that the $^1J(^{107}\text{Ag-P})$ value is close to those of several other $[\text{L}_4\text{Ag}]^+$ complexes, including $[(\text{DMPP})_4\text{Ag}]^+\text{BF}_4^-$ (Table VIII). The existence of the ionic species $[(\text{DMPP})_4\text{Ag}]^+$ in solution is rather surprising, as the 4:1 complex $[(\text{DMPP})_4\text{Ag}]^+\text{Cl}^-$ does not exist in the solid state. Indeed, as

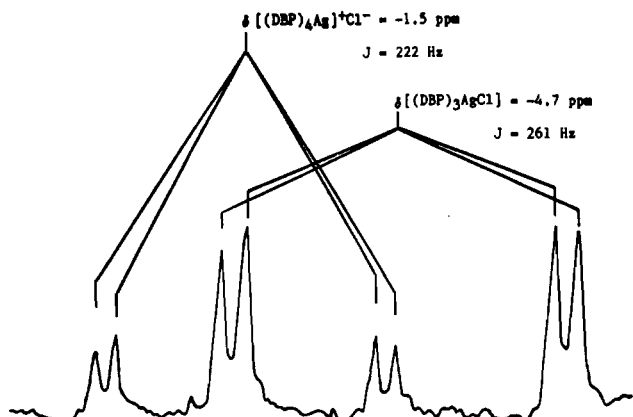


Figure 14. 40.26-MHz $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[(\text{DBP})_2\text{AgCl}]_2$ in CH_2Cl_2 at -80°C . $\delta = \delta(^{31}\text{P})$, and $J = {}^1J(^{107}\text{Ag}-\text{P})$.

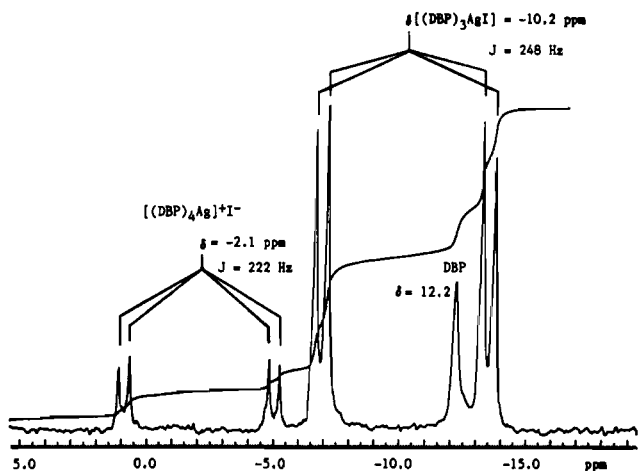


Figure 15. 40.26-MHz $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $(\text{DBP})_3\text{AgI}$ in CH_2Cl_2 at -80°C . $\delta = \delta(^{31}\text{P})$, and $J = {}^1J(^{107}\text{Ag}-\text{P})$.

has been discussed above, not even the 3:1 complex $[(\text{DMPP})_3\text{AgCl}]$ can be isolated as a solid. The 2:1 complex, with a proposed chloride-bridged dimeric structure, is the only complex with a DMPP:AgCl ratio greater than 1:1 that has been isolated in the solid state. Such a complex should have a ${}^1J(\text{Ag}-\text{P})$ value of about 360 Hz, as was observed in the solid-state spectrum, but the solution spectrum shows no evidence for the presence of such a species. Solutions of $[(\text{DMPP})\text{AgX}]_4$ ($\text{X} = \text{Br}, \text{I}$) similarly contain only $[(\text{DMPP})\text{AgX}]_4$ and $[(\text{DMPP})_4\text{Ag}]^+$ in ratios similar to that found for the $\text{X} = \text{Cl}$ case.

The spectra of $[(\text{DMPP})_2\text{AgCl}]_2$ at -80 and -95°C are shown in Figure 13. In this case signals due to three separate species are observed, and all of the peaks (especially the broader ones) sharpen considerably as the temperature is reduced. The signals are assigned to the species $[(\text{DMPP})\text{AgCl}]_4$ ($\delta = 4.8$ ppm, ${}^1J(^{107}\text{Ag}-\text{P}) = 547$ Hz), $[(\text{DMPP})_3\text{AgCl}]$ ($\delta = 2.5$ ppm, ${}^1J(^{107}\text{Ag}-\text{P}) = 249$ Hz), and $[(\text{DMPP})_4\text{Ag}]^+$ ($\delta = 5.7$ ppm, ${}^1J(^{107}\text{Ag}-\text{P}) = 225$ Hz), which are present in an approximately 2:1:1 ratio. $[(\text{DMPP})_3\text{AgCl}]$ is the most labile of the three species, consistent with previous observations on complexes of $(\text{EtO})_3\text{P}$ and $(p\text{-tol})_3\text{P}$.⁵⁵ There is no evidence for the presence of a species of 2:1 stoichiometry in solution, despite the fact that this is the stoichiometry of the solid complex which was used to prepare the solution. Thus, in this case, the complex completely dissociates

upon dissolution to form a range of complexes of stoichiometry different from that of the parent solid. Similarly, solutions of $[(\text{DMPP})_2\text{AgX}]_2$ ($\text{X} = \text{Br}, \text{I}$) contain $[(\text{DMPP})\text{AgX}]_4$, $[(\text{DMPP})_3\text{AgX}]$, and $[(\text{DMPP})_4\text{Ag}]^+$ in similar ratios, with the relative ligand exchange rates increasing in the order $\text{Cl} < \text{Br} < \text{I}$.

Solutions of $[(\text{DBP})_2\text{AgX}]_2$ contain only $[(\text{DBP})_3\text{AgX}]$ and $[(\text{DBP})_4\text{Ag}]^+$, as illustrated in Figure 14 for the chloro complex. Thus, as in the case of the corresponding DMPP complexes, no species of 2:1 stoichiometry are observed in solution. For these three complexes, the amount of $[(\text{DBP})_4\text{Ag}]^+$ decreases in the sequence $\text{Cl} > \text{Br} > \text{I}$ and is present in only trace amounts for the iodide.

Solutions of $[(\text{DBP})_3\text{AgX}]$ contain $[(\text{DBP})_3\text{AgCl}]$ and $[(\text{DBP})_4\text{Ag}]^+$ ($\text{X} = \text{Cl}$); $[(\text{DBP})_4\text{Ag}]^+$ and free DBP ($\text{X} = \text{Br}$); and $[(\text{DBP})_3\text{AgI}]$, $[(\text{DBP})_4\text{Ag}]^+$, and free DBP ($\text{X} = \text{I}$; Figure 15). The situation for $\text{X} = \text{Cl}$ contrasts with that for the corresponding PPh₃ complex, $[(\text{PPh}_3)_3\text{AgCl}]$, which showed signals due to this species only ($\delta = 3.4$ ppm, ${}^1J(^{107}\text{Ag}-\text{P}) = 275$ Hz) in the present study, the measured parameters being in good agreement with those reported previously for this complex ($\delta = 3.0$ ppm, ${}^1J(^{107}\text{Ag}-\text{P}) = 277$ Hz).⁶¹

Solutions of $[\text{L}_4\text{Ag}]^+\text{BF}_4^-$ ($\text{L} = \text{DMPP}, \text{DBP}$) show signals due to $[\text{L}_4\text{Ag}]^+$ only. Hence, for these two compounds, the solution and solid-state structures are the same.

The solution behavior of the phosphole complexes of the silver halides is obviously quite complicated, and some aspects of this behavior, such as the differences in the distribution of species, that are observed with changes from one halide to another are not easily explained at present. The differences in the distribution of species that are observed upon changing the ligand are also somewhat unexpected. Thus, although the binuclear complexes $[\text{L}_2\text{AgX}]_2$ can be isolated in the solid state for $\text{L} = \text{DMPP}$ and DBP , these species do not exist at all in CH_2Cl_2 solution. However, the species that are observed in the solution studies do bear some relationship to ones that were isolated as solids. Thus, the nonexistence of $[\text{LAgX}]_4$ ($\text{L} = \text{DBP}$) and $[\text{L}_3\text{AgX}]$ ($\text{L} = \text{DMPP}$) in the solid state is consistent with the absence or, in the latter case, high lability of these species in solution. A further surprising feature of the results of the solution studies is the formation of the ionic complexes $[\text{L}_4\text{Ag}]^+$ even when the ligand to silver halide ratio is as low as 1:1. This implies the concomitant formation of halogenoargentate(I) ions in solution, which are not detected in the ^{31}P NMR studies. None of the solid complexes isolated from such solutions appear to contain an $[\text{L}_4\text{Ag}]^+$ complex. However, it is relevant to note in this connection that, in the corresponding copper(I) system, the solid which is isolated from CH_2Cl_2 solutions containing a 2:1 mixture of DMPP and CuCl is the ionic complex $[(\text{DMPP})_4\text{Cu}]^+[\text{CuCl}_2]^-$.³⁰ It thus appears that the neutral and corresponding ionic complexes have similar stabilities but that lattice energy considerations result in the formation of the neutral complexes in the solid state in most cases.

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Supplementary Material Available: For the crystal structure study, listings of crystal and refinement data, H atom coordinates, thermal parameters, and bond distances and angles (4 pages); a listing of observed and calculated structure factors (14 pages). Ordering information is given on any current masthead page.