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Two-, Three-, and Four-Coordinate Ag(I) Coordination Polymers Formed by the Novel Phosphinite $PPh_2(3\text{-}OCH_2C_5H_4N)$

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The novel phosphinite $PPh_2(3\text{-}OCH_2C_5H_4N)$ (**1**) has been synthesized, and its coordination properties to Ag(I) have been studied. When reacted in a 1:1 ratio with Ag(I), coordination polymers with different coordination numbers about the Ag are found depending on the anion. For $PPh_2(3\text{-}OCH_2C_5H_4N)AgBF_4$ (**2**), a two-coordinate Ag is observed with a P–Ag–N angle of 167°. Mixed three and four coordination about Ag is observed for $PPh_2(3\text{-}OCH_2C_5H_4N)$-AgOTf (**3**), and for the trifluoroacetate derivative, $PPh_2(3\text{-}OCH_2C_5H_4N)$Agtfa (**4**), only a four-coordinate Ag is produced. X-ray crystal-structure determinations for compounds **2**–**4** have been carried out. The X-ray structures show a wide range of Ag–Ag distances in the polymers, which are dependent on the conformation of the bridging ligand.

Introduction

Silver-based coordination polymers have received great attention lately.[1−11] This is owed to the rich chemistry that is available to this versatile metal. Silver phosphine/silver pyridine complexes have repeatedly demonstrated interesting electronic, medicinal, and structural properties.[1−33] Part of what gives silver the ability to produce such intriguing structural motifs is the ease with which it varies its

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coordination number, generally from two to four.[22] Thus far, the vast majority of silver coordination polymers employ ligands that are symmetric, very often using some isomer of bipyridine.[6]

Pyridyl-substituted phosphines, which were first reported nearly 60 years ago, have become commonplace and have been thoroughly explored since their introduction.[9,23,25−30,32−53] They are an interesting family of ligands because they have the potential to display both the hard- and soft-donating abilities of the nitrogen and phosphorus, respectively, in a single moiety. The majority of reports in this area have been of 2-pyridylphosphines, with their chelating or bimetallic/biligand ring-forming abilities.[23,25−38,43−49,51−56] Relatively little work has been reported for 3- and 4-pyridylphosphines, most likely because of the difficulty with which they are synthesized.[34,37,49] Using only 2-pyridyl substituents, the arrangement of the complexes formed is inherently limited to those discrete structures that can be obtained with the acute angles present. This excludes a vast array of complexes that could be formed by separating the nitrogen and phosphorus to the point of minimal interaction.

To provide an easier entry into new pyridyl-containing phosphines and in an attempt to open a new area of coordination-polymer chemistry using ligands with different binding functionalities, an OCH_2 "spacer" has been inserted between the P and 3-pyridyl components, thereby achieving the goal of P−N isolation with an added benefit of inherent flexibility in the P−N distance. From this, several new coordination compounds of silver that have been prepared with a novel pyridylcarbinol-substituted phosphine ligand are now reported.

Experimental Section

General Procedures. All of the experiments were carried out under an argon atmosphere, using a Schlenk line and standard Schlenk techniques. All of the glassware was dried at 120 °C for several hours prior to use. All of the reagents were stored in an inert-atmosphere glovebox; solvents were distilled under nitrogen from the appropriate drying agent immediately before use. Triethylamine was purchased from Aldrich and purged with argon before use. 3-Pyridylcarbinol was purchased from Aldrich and used as received. Chlorodiphenylphosphine, silver(I) trifluoroacetate, silver(I) triflate, and silver(I) tetrafluoroborate were purchased from Strem Chemicals Inc. and used as received. Celite was purchased from Aldrich and dried at 120 °C prior to use. ^1H and room-temperature ^{31}P NMR spectra were recorded at 300.13 and 121.49 MHz, respectively, on a Bruker Spectrospin 300 MHz spectrometer. Low-temperature ^{31}P NMR spectra were recorded at 145.78 MHz on a Bruker Spectrospin 360 MHz spectrometer. Elemental analyses were performed by Atlantic Microlabs Inc., Norcross, GA.

Synthesis of Diphenylphoshino-3-pyridylcarbinol, $PPh_2(3\text{-}OCH_2C_5H_4N)$ (1). In an argon-purged addition funnel, 1.3 mL of degassed triethylamine (9.33 mmol) was added via a syringe to a stirred solution of 1.00 g of 3-pyridylcarbinol (9.16 mmol) in 20 mL of toluene at room temperature. The solution was then cooled to 0 °C and shielded from light with aluminum foil. A solution of 2.02 g (9.16 mmol) of chlorodiphenylphosphine in 20 mL of toluene was then added dropwise over 10 min. The solution was stirred for 1 h, then allowed to warm to room temperature, and stirred for an additional 1 h. The resultant cloudy mixture was reduced to $^3/_4$ of its original volume under vacuum and immediately filtered through Celite. The triethylammonium chloride salts were washed with an additional 5 mL of cold toluene, and the solvent was removed from the yellow liquid at reduced pressure to leave a pale yellow oil in 96% yield. The oil was then extracted several times with hexanes. Drying of the hexane wash in vacuo yielded the clear, colorless oil, **1**, in 81% yield (2.18 g, 7.44 mmol). ^1H NMR ($CDCl_3$, 298 K) δ: 4.93 d, 2H, $J(PH) = 9.10$ Hz; 7.28 m, 1H; 7.39 m, 6H; 7.53 m, 4H; 7.68 dt, 1H; 8.56 d, 1H; 8.63 s, 1H. ^{31}P NMR δ: 116.2 m, $J(PH) = 8.1$ Hz.

Synthesis of $PPh_2(3\text{-}OCH_2C_5H_4N)AgBF_4$ (2). To a stirred solution of 0.300 g of $AgBF_4$ (1.54 mmol) in 5 mL of CH_2Cl_2 was added 0.452 g (1.54 mmol) of **1** in 5 mL of CH_2Cl_2. The resulting solution remained clear and colorless, and the solvent was removed by vacuum after 5 min of stirring. Upon drying, the white powder, **2**, was reclaimed in 91% yield (0.686 g, 1.406 mmol). Crystals of **2** were obtained by vapor diffusion of ether into a CH_2Cl_2 solution at 5 °C. ^1H NMR (CD_3CN, 298 K) δ: 5.05 d, 2H; 7.37 m, 7H; 7.58 t, 4H; 7.78 d, 1H; 8.43 d, 1H; 8.69 s, 1H. ^{31}P NMR (238 K) δ: 111.9 dd, $J(^{107}Ag-P) = 790.1$ Hz, $J(^{109}Ag-P) = 685.1$ Hz. Elem anal. Calcd: C, 44.31; H, 3.30; N, 2.87. Found: C, 45.11; H, 3.39; N, 3.16.

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Table 1. Crystallographic Data for **2**−**4**

	2	**3**	**4**
formula	$C_{18}H_{16}AgBF_4NOP(CH_2Cl_2)_{1.5}$	$C_{76}H_{64}Ag_4F_{12}N_4O_{16}P_4S_4(CH_2Cl_2)_2$	$C_{40}H_{32}Ag_2F_6N_2O_6P_2$
formula weight	615.36	2370.76	1028.36
a (Å)	29.399(5)	17.972(5)	8.991(1)
b (Å)	11.204(2)	10.191(3)	9.103(1)
c (Å)	14.189(2)	27.936(8)	25.965(4)
α (deg)			96.721(2)
β (deg)	94.266(9)	115.441(4)	95.492(2)
γ (deg)			105.485(2)
V (Å^3)	4660.7(11)	4620(2)	2015.9(5)
Z	8	2	2
space group	$C2/c$	Pc	$P\bar{1}$
T (K)	110	110	110
λ (Å)	0.710 73	0.710 73	0.710 73
D_{calcd} (g cm^{-3})	1.754	1.704	1.694
μ (mm^{-1})	1.323	1.198	1.127
$2\theta_{max}$ (deg)	66	55	55
reflns measured	34 150	47 570	27 968
reflns used (R_{int})	8789	18 852	8965
restraints/parameters	0/285	201/1106	125/546
R1 [$I > 2\sigma(I)$]	0.0301	0.0624	0.0531
wR2 [$I > 2\sigma(I)$]	0.0812	0.1531	0.1260
$R(F_o^2)$ (all of the data)	0.0402	0.0693	0.0567
$R_w(F_o^2)$ (all of the data)	0.0834	0.1531	0.1278
GOF on F^2	1.073	1.088	1.105
instrument	X8 Apex	SMART 1000	Apex

Synthesis of $PPh_2(3\text{-}OCH_2C_5H_4N)AgOTf$ (3). To a stirred solution of 0.088 g (0.342 mmol) of AgOTf in 10 mL of THF was added 0.100 g (0.341 mmol) of **1** in 5 mL of THF. This solution was stirred for 5 min, and then the solvent was removed in vacuo to leave a white solid, **3**, in 92% yield (0.172 g, 0.312 mmol). Crystals of **3** were grown by slow diffusion of diethyl ether into a solution of **3** in CH_2Cl_2 at 5 °C. ^1H NMR (CD_3CN, 298 K) δ: 5.07 d, 2H; 7.34 m, 7H; 7.57 t, 4H; 7.86 d, 1H; 8.46 d, 1H; 8.66 s, 1H. ^{31}P NMR (238 K) δ: 112.1 dd, $J(^{107}Ag-P) = 788.7$ Hz, $J(^{109}Ag-P) = 688.1$ Hz. Elem anal. Calcd: C, 41.47; H, 2.93; N, 2.55. Found: C, 40.90; H, 2.82; N, 2.69.

Synthesis of $PPh_2(3\text{-}OCH_2C_5H_4N)Agtfa$ (4). To a stirred suspension of 0.076 g (0.344 mmol) of Agtfa in 10 mL of CH_2Cl_2 was added 0.100 g (0.341 mmol) of **1** in 5 mL of CH_2Cl_2. The solid Agtfa dissolved immediately upon introduction of the ligand. After approximately 5 min of vigorous stirring, a precipitate formed. The brown-yellow solvent was removed via cannula, and the solid **4** was washed with another 5 mL aliquot of CH_2Cl_2. The residual solvent was then removed in vacuo to leave a white solid, **4**, in 98% yield (0.172 g, 0.334 mmol). Crystals of **4** were obtained by slow diffusion of diethyl ether into a solution of **4** in CH_2Cl_2 at 5 °C. ^1H NMR ($CDCl_3$, 298 K) δ: 5.05 d, 2H; 7.43 m, 7H; 7.58 t, 4H; 7.83 d, 1H; 8.51 d, 1H; 8.59 s, 1H. ^{31}P NMR (219 K) δ: 117.5 d, $J(Ag-P) = 519.0$ Hz. Elem anal. Calcd: C, 46.72; H, 3.14; N, 2.72. Found: C, 46.67; H, 3.10; N, 2.90.

X-ray Crystallographic Analysis. Crystallographic data were collected on crystals with the dimensions 0.29 × 0.28 × 0.25 mm for **2**, 0.22 × 0.17 × 0.13 mm for **3**, and 0.26 × 0.22 × 0.15 mm for **4**. Data for **3** and **4** were collected at 110 K on a SMART 1000 and Bruker Apex diffractometer, respectively. Data for **2** was collected on a Bruker X8 Apex at 110 K. All of the structures were solved by direct methods after the correction of the data using SADABS.[57] Crystal data are presented in Table 1, and selected interatomic distances, angles, torsion angles, and other important distances are given in Table 2. All of the data were processed using the Bruker AXS SHELXTL software, version 6.10.[58] Unless otherwise noted, all of the non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed in calculated positions. The structure of **3** is a racemic twin, which was refined using the TWIN command in SHELX.

Results and Discussion

Synthesis and NMR Spectroscopy. Compound **1** is made by the S_N2-type substitution of a chlorophosphine with an alkoxypyridine in a modified version of the phenol-derived analogue reported by Bedford and Welch.[59] Deprotonation of the carbinol to make the $^{-}OCH_2C_5H_4N$ nucleophile is facile in toluene with the base triethylamine. Great care must be taken for the synthesis of **1** as a result of the observations that in the intermediate stages of the reaction all of the reaction components are extremely sensitive to factors such as temperature, light, addition rate, concentration, and solvent. High temperatures, rapid or extremely slow addition rates, and ion-stabilizing solvents, such as THF, tend to favor the production of the well-known phosphorus/phosphine oxide byproduct $PPh_2P(O)Ph_2$.[60] Exposure to light at any stage of the synthesis leads to the accelerated formation of the yellow decomposition product. Once isolated, **1** is stable to moisture but unstable to air, heat, or light. Decomposition can be slowed, though not completely halted, by keeping it shielded from light and refrigerated under an inert atmosphere. ^1H and ^{31}P NMR spectra of **1** were obtained in $CDCl_3$ and demonstrate the very pronounced three-bond coupling of phosphorus to the phenyl and methylene protons. A defined phosphorus septet is found centered at $\delta = 116.3$, which is in the region expected for aromatic-substituted phosphinites.[35]

The silver compounds **2**−**4** were synthesized by the reaction with simple silver salts under ambient conditions

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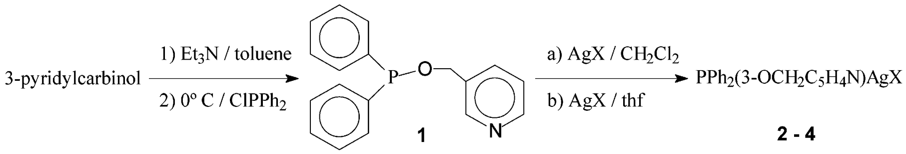
Scheme 1. General Synthetic Scheme for the Carbinol-Substituted Phosphine Coordination Complexes of Silver(I) Salts[a]



[a] In a, X = BF_4 or Tfa, and in b, X = OTf.

Table 2. Selected Bond Lengths (Å), Angles (deg), Torsion Angles (deg), and Important Distances for **2**−**4**[a]

	Compound **2**		
Ag1−N1	2.171(1)	Ag1−P1	2.3543(5)
Ag1−Ag1#1	7.1914(9)	Ag1#2−F2	2.785(1)
P1#1−N1	5.569(2)	P1#1−C2	3.883(2)
N1−Ag1−P2	167.28(4)	P1#1−O1−C1−C2	−155.1(1)
	Compound **3**		
Ag1−N2#1	2.232(7)	Ag1−P1	2.334(2)
Ag1−O5	2.494(8)	Ag2−N1	2.217(7)
Ag2−P2	2.341(2)	Ag2−O8	2.470(7)
Ag3−N4#2	2.255(7)	Ag3−P3	2.355(2)
Ag3−O11	2.490(6)	Ag3−O9	2.524(7)
Ag4−N3	2.241(7)	Ag4−P4	2.359(2)
Ag4−O14	2.515(6)	Ag1−Ag2	9.165(2)
Ag1−Ag3	10.678(3)	Ag1−Ag4	4.460(1)
Ag2−Ag3	4.806(1)	Ag2−Ag4	8.912(2)
Ag3−Ag4	9.265(2)	P1−N1	5.933(7)
P2−N2	6.119(7)	P3−N3	5.979(7)
P4−N4	6.014(7)	P1−C2	3.902(8)
P2−C21	3.866(9)	P3−C40	3.891(8)
P4−C59	3.865(8)	N2#1−Ag1−P1	142.8(2)
N2#1−Ag1−O6	86.5(3)	P1−Ag1−O6	119.4(2)
N1−Ag2−P2	145.5(2)	N1−Ag2−O8	83.8(3)
P2−Ag2−O8	119.9(2)	N4#2−Ag3−P3	140.2(2)
N4#2−Ag3−O11	86.7(2)	P3−Ag3−O11	119.9(2)
N4#2−Ag3−O9	82.3(2)	P3−Ag3−O9	124.1(2)
O11−Ag3−O9	88.2(2)	N3−Ag4−P4	146.9(2)
N3−Ag4−O14	83.3(2)	P4−Ag4−O14	119.9(2)
P1−O1−C1−C2	−169.4(5)	P2−O2−C20−C21	166.7(6)
P3−O3−C39−C40	−169.6(5)	P4−O4−C58−C59	167.3(5)
	Compound **4**		
Ag1−N1#1	2.269(4)	Ag1−P1	2.356(1)
Ag1−O2#2	2.375(4)	Ag1−O2	2.549(4)
Ag2−N2#3	2.264(5)	Ag2−P2	2.368(1)
Ag2−O5#4	2.419(4)	Ag2−O5	2.576(4)
Ag1−Ag1#1	3.8686(9)	Ag1−Ag1#2	6.068(1)
Ag2−Ag2#4	3.9404(9)	Ag2−Ag2#3	5.937(1)
P1−N1	5.370(4)	P1−C2	3.794(5)
P2−N2	5.337(4)	P2−C22	3.784(5)
N1#1−Ag1−P1	133.4(1)	N1#1−Ag1−O2#2	103.1(2)
P1−Ag1−O2#2	119.7(1)	N1#1−Ag1−O2	91.6(1)
P1−Ag1−O2	114.5(1)	O2#2−Ag1−O2	76.5(1)
N2#3−Ag2−P2	136.3(1)	N2#3−Ag2−O5#4	107.2(2)
P2−Ag2−O5#4	112.7(1)	N2#3−Ag2−O5	92.2(1)
P2−Ag2−O5	113.91(9)	O5#4−Ag2−O5	75.9(1)
P1−O1−C1−C2	−136.7(3)	P2−O2−C21−C22	−134.4(3)

[a] Symmetry transformations used to generate the equivalent atoms for **2**: #1 = $x, -y + 2, z + {}^1/_2$; #2 = $x, y - 1, z$. For **3**: #1 = $x + 1, y, z$; #2 = $x - 1, y, z$. For **4**: #1 = $-x, -y + 2, -z$; #2 = $-x, -y + 1, -z$; #3 = $-x + 1, -y + 2, -z + 1$; #4 = $-x + 2, -y + 2, -z + 1$.

in an inert atmosphere as outlined in Scheme 1. Upon coordination, all of the silver compounds reported herein are white powders that noticeably decompose within several hours upon exposure to light. Solutions of the metal compounds **2**−**4** in organic solvents undergo reduction of silver to precipitate metallic silver and an oily black phosphorus byproduct. Compounds **2**−**4** appear to be stable indefinitely in the solid state when kept in the absence of light and refrigerated under an inert atmosphere.

Compound **2** is the most robust of the coordination complexes presented. Though it still suffers from decomposition in solution, under conditions similar to those of **3** and **4**, it is at a notably slower rate, while the rapid rate of decomposition of **3** and **4** may be due to having a counterion bound to the silver, which makes reduction of the metal more facile. Compound **2** is prepared from the mixing of 1 equiv of $AgBF_4$ in CH_2Cl_2 with a solution of **1**. The two-coordinate coordination polymer is collected as a white solid by removal of CH_2Cl_2 under vacuum after less than 5 min of reaction. The precipitation of metallic silver from solutions of **2** is at such a rate that after 24 h, layered in a crystallization tube at 5 °C, there is only a slightly dark appearance to the tube, whereas under similar conditions, compounds **3** and **4** would have released the majority of their solute as a black precipitate. ^{31}P NMR spectra of **2** were recorded in CD_3CN down to 238 K. At room temperature, ^{31}P NMR spectra show a doublet of broad peaks centered at 114.0 ppm, owing to the silver−phosphorus coupling. This indicates at least some degree of coordination of the ligand to silver in room-temperature solutions, though the process does appear to be dynamic on the NMR time scale. Slowing of the dissociation of the Ag−P bond by lowering the temperature causes the doublet peaks to sharpen, move slightly upfield, and eventually split, revealing the coupling of the separate isotopes of Ag.

A solution of silver triflate in THF added to 1 equiv of **1** in THF yields the mixed coordination complex **3** as a white powder upon drying. Stirring for longer than a few minutes, however, results in a precipitate of metallic silver from an unknown redox reaction. Saturated CH_2Cl_2 solutions of **3** turn dark, form a brown precipitate within hours, but still manage to grow X-ray quality crystals over several days when layered with diethyl ether at 5 °C. ^{31}P NMR spectra of this compound were obtained using $CDCl_3$ and collected to 238 K. Again, some degree of coordination of phosphorus to silver is seen at room temperature, though dissociation is rapid. After the cooling of the sample to 238 K, the isotopic coupling of silver can be observed to form a doublet of doublets that is centered slightly upfield of the original doublet's 114.6 ppm position.

All of the attempts to synthesize the coordination compound **4** using the ligand **1** and completely dissolved silver trifluoroacetate were unsuccessful; the results of such reactions consistently are brown solutions with a rapid precipitation of silver in the flask. It was found that the most productive route to compound **4** was to allow the ligand **1** to solubilize the silver trifluoroacetate directly into a solution from its solid state. The dissolved ligand, upon addition to a CH_2Cl_2 suspension of the silver salt, immediately draws the silver salt into the solution. Following several minutes of vigorous stirring, the slightly soluble complex **4** precipitates from the solution. The precipitate is collected and washed with several aliquots of CH_2Cl_2. The product is a white solid that noticeably decomposes in solution within minutes at room temperature. Single crystals of **4** were grown with some difficulty from the saturated solutions of CH_2Cl_2, layered with diethyl ether at 5 °C. ^1H and ^{31}P NMR spectra were obtained in $CDCl_3$ by keeping the sample in an ice bath until the injection into the spectrometer. ^{31}P NMR spectra were recorded to 219 K. The ^{31}P NMR spectrum of **4** indicates a P−Ag bond that is considerably more labile than those of compounds **2** and **3**, with the room-temperature resonance showing no sign of Ag coupling. A single peak is observed at 116.9 ppm that, upon cooling to 219 K, first broadens and then splits to form a doublet centered at 117.5 ppm.

X-ray Crystal Structure. The coordination of the silver centers in each of the compounds **2**−**4** is notably different. We were able to achieve compounds demonstrating each of the common coordination numbers of silver, 2−4, by changing only the counterion in each case. Variations in coordination have also been observed by changing the crystallization solvent; for instance, a different structural isomer of compound **3**, obtained by crystallization from THF, has been observed that contains only three-coordinate silver centers. The crystal structure data for this isomer are of very poor quality and therefore are not included in this report; there are continuing efforts to crystallize the compound from THF. As the coordination number about the silver center increases, there is a concomitant increase in the Ag−N and Ag−P bond lengths; all of these bond lengths fall well within the expected ranges.[3,5] For compounds **2**−**4**, varying only the anion between the structures, we can see the N−Ag−P bond angle increase from 133.4° in **4** to a nearly linear 167.3° angle in the two-coordinate BF_4^- complex, **2**. All of the compounds have one structural feature in common in that the phosphinite-ligand coordinates head-to-tail, P−Ag−N, rather than in a head-to-head fashion, which would form different P−Ag−P and N−Ag−N localities in the polymer. In each of the structures, the phosphinite ligand is able to adopt different conformations in the polymer. The P−N distance across the ligand varies from 5.33 to 6.11 Å; this ability to adapt the distance between the bonding moieties in the ligand allows the Ag−Ag distances bridged by the same ligand to vary from 5.93 to 9.26 Å.

Compound **2** makes use of the noncoordinating BF_4 anion to display nearly exclusive ligand−metal interactions. A thermal ellipsoid plot of the one-dimensional polymeric structure of the zigzag chains of **2** is presented in Figure 1, and selected bond lengths and angles are given in Table 2. Without a coordinating counterion, the silver centers take on a near-linear geometry with respect to the head-to-tail linking by **1**. The N−Ag−P angle is slightly off linear at 167.3°; the distortion from 180° is likely caused by the long-range interaction of BF_4^- with Ag^+. The shortest contact is Ag1−F2 with a distance of 2.785(1) Å, slightly longer than the sum of the van der Waals radii for the ions. The Ag−P bond length is 2.3543(5) Å, and the N−Ag distance is 2.171(1) Å. All of the other bond lengths and angles fall well within the expected ranges. The Ag−Ag distance across the bridging ligand is 7.1914(9) Å. One and a half molecules of CH_2Cl_2 are present per asymmetric unit.

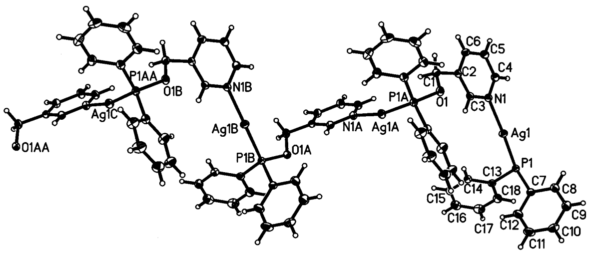


Figure 1. Thermal ellipsoid plot of the polymeric cation of **2** with an atomic numbering scheme. Ellipsoids are shown at the 50% level.

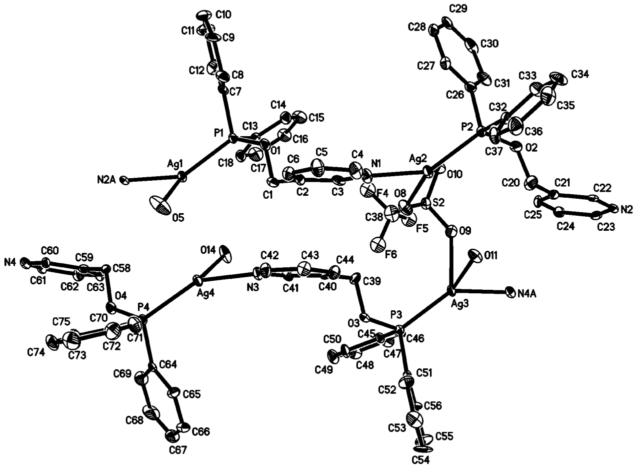


Figure 2. Thermal ellipsoid plot of **3** with an atomic numbering scheme. Ellipsoids are shown at the 30% level. Hydrogen atoms and the CF_3SO_2 portion of three of the triflates have been removed for clarity.

The X-ray crystal structure of compound **3** reveals the triflate anion playing an integral part in deciding the geometry of the silver ions. A thermal ellipsoid plot is shown in Figure 2, and selected bond lengths and angles are given in Table 2. The asymmetric unit of **3** contains four unique silver centers, which upon further inspection reveals a cross-linked polymer structure. Cross-linking is achieved by the bridging of Ag2 and Ag3 through a triflate (S2). Each phosphinite ligand acts as a bridge that connects two silver cations as in **2**. Ag1, Ag3, and Ag4 each have a terminal triflate bound through a single sulfonate oxygen. The triflate bound to Ag2 also forms a bridge to Ag3, resulting in four coordination about Ag3. The other three silvers display a distorted trigonal arrangement resulting from the single anion and two ligands coordinating to each other, giving an O, P, N environment. The cross-linked polymer structure contains six repeating Ag-containing rings as shown in Figure 3. The Ag−Ag distances range from 4.806(1) Å in the triflate-bridged atoms, Ag2 and Ag3, to the more than doubled distance of 10.678(3) Å in the diagonal silvers, Ag1 and Ag3. While not bridged by triflate, the Ag1−Ag4 distance is only 4.460(1) Å, probably as a result of packing or a pseudo-π-stacking interaction of the pyridine rings. The Ag−N bonds range from 2.217(7) to 2.255(7) Å, slightly longer than that observed in **2**, and the Ag−P bonds average 2.34 Å, nearly

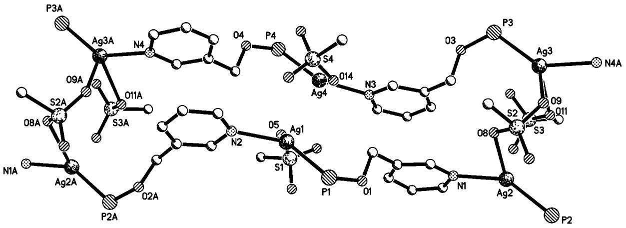


Figure 3. Ball and stick diagram of **3** showing the six Ag-containing rings. Triflate oxygens that are bound to Ag are labeled. Phenyl rings and hydrogen atoms are removed for clarity.

the same as that in **2**. The intraligand P−N distances range from 5.933(7) Å for P1−N1 to 6.119(7) Å for P2−N2, about 0.4 Å longer than that observed in **2**. This observation helps to account for the much longer Ag−Ag distances across the same ligand, which range from 9.164(2) Å for Ag1−Ag2 to 9.265(2) Å for Ag3−Ag4. The N−Ag−O bond angles around the Ag centers range from 82.3° to 86.5°, and the P−Ag−O angles for Ag1, Ag2, and Ag4 are all near the ideal trigonal-planar angle of 120°, ranging from 119.4(1)° to 119.9(2)°; the exception is the P−Ag−O angle for Ag3, which is a bit wider at 124.1(2)°. The N−Ag−P angle is consistently the widest in the structure, from 140.1(2)° for Ag3 to 146.9(2)° for Ag4. For the three-coordinate Ag centers, the sum of the angles averages 349°, showing the distortion from the trigonal-planar geometry. The polymer chains are continued to the next unit by the pendent N2 and N4 pyridine rings. The fluorine atoms of the triflate groups are highly disordered about the C−S axis; because of this disorder, they were refined isotropically, and each group was restrained to have the same C−F bond lengths, angles, and thermal parameters. There are two molecules of the CH_2Cl_2 solvent in the lattice, of which one (C78) is disordered. This carbon was refined isotropically.

The crystal structure of compound **4** reveals a diamond-like binuclear silver center with each Ag bridged by two trifluoroacetate ions. There are two independent Ag centers in the structure, with only minor differences between the two; a thermal ellipsoid plot of one of the independent units is shown in Figure 4. Each silver has near-tetrahedral geometry with a Ag1−Ag1A distance of 3.8686(9) Å and slightly longer for Ag2−Ag2A at 3.9404(9) Å. Each Ag is also bound by two ligands with opposing ends facing each other in a head-to-tail fashion. The pendent ends of the ligands are bound to the Ag^+ and then to another Ag^+, making a ring as shown in Figure 5. The Ag−Ag distance across this ring is 6.068(1) Å for Ag1−Ag1B and 5.937(1) Å for Ag2−Ag2B. Therefore, for **4**, the coordination polymer formed is not from the linkage through the phosphinite ligand but through the trifluoroacetate-bridged Ag^+ centers. The coordination about the Ag ions in **4** is the most electron rich of those presented here, being ligated by two O's, a N, and a P. The Ag−N bonds of **4** reflect the effect of increased coordination by lengthening to 2.269(4) Å for Ag1−N1 and 2.264(5) Å for Ag2−N2, which is nearly a 0.1 Å increase from **2**. The Ag−P bond lengths are less impacted, being at 2.356(1) Å for Ag1−P1 and 2.368(1) Å for Ag2−P2. In the adoption of the conformation for the ring structure, the P−N distance displays its shortest distance observed at 5.370(4) Å for P1−N1 and 5.337(4) Å for P2−N2. The P−Ag−N angles are the most acute of the examples presented here, being 133.4(1)° for N1−Ag−P1 and 136.3(1)° for N2−Ag2−P2. The fluorine atoms of the trifluoroacetate groups are disordered about the C−C axis, and the fluorine atoms of each group are restrained to have the same C−F bond lengths and thermal parameters.

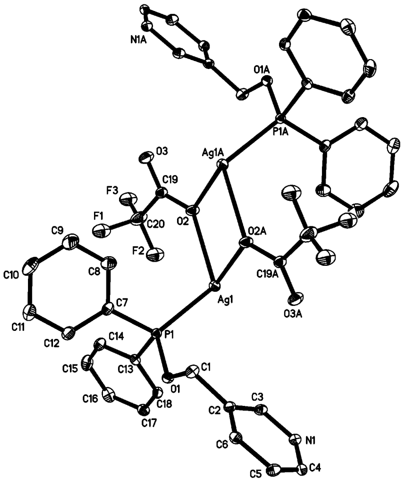


Figure 4. Thermal ellipsoid plot of **4** with an atomic numbering scheme. Hydrogen atoms have been removed for clarity, and ellipsoids are shown at the 30% level.

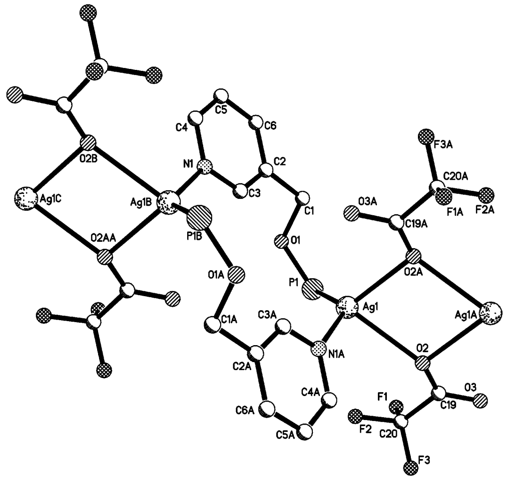


Figure 5. Ball and stick diagram of the ring formed by **1** and Ag, which is linked by the trifluoroacetate ions forming an infinite chain. Phenyl groups and hydrogens have been removed for clarity.

Conclusions

We have reported the synthesis of a novel pyridyl-containing phosphinite, which shows the ability to bind silver ions through both the phosphorus and nitrogen moieties. Several new coordination polymers of Ag(I) have been characterized using X-ray crystallography, which reveals a structure dependence on the anion used for crystallization. The inherent flexibility of the ligand is manifested in the wide-ranging difference in Ag−Ag distances across the ligand from 5.937(1) to 9.265(2) Å. We are continuing to study the coordination properties of **1** with other metals and are also actively pursuing the bi- and trisubstituted

3-pyridylcarbinol derivatives, which have initially shown increased diversity of coordination to Ag(I). We are also exploring the chemistry of the 4-pyridylcarbinol derivatives, which thus far exhibit even more diverse coordination modes to Ag(I) than the 3-pyridylcarbinol species. Competition studies of these various ligands toward different metals are also underway.

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Supporting Information Available: A listing of the final atomic coordinates, anisotropic thermal parameters, and complete bond lengths and angles for complexes **2**−**4** is available. This material is available free of charge via the Internet at http://pubs.acs.org.

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