

Polymeric Complexes of Silver(I) with Diphosphine Ligands: Self-Assembly of a Puckered Sheet Network Structure

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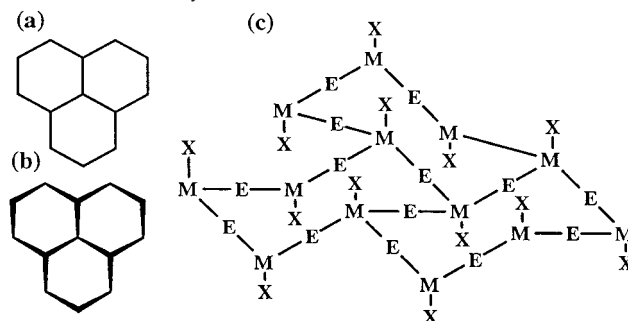
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Abstract: The syntheses and structures of polymeric silver(I)–diphosphine complexes are reported, in which the silver(I) center is surrounded by 1, 2, or 3 phosphorus atoms. When rigid diphosphine ligands are used in combination with weakly coordinating anions, linear polymers are obtained that contain both diphosphine and anion bridges. However, with excess of a diphosphine with a long, flexible, spacer group, a remarkable puckered sheet structure, comprised of fused giant 54-membered rings, is obtained that is a coordination polymer analogue of laminated materials such as micas and clays. The polymeric chain and sheet structures may be considered to be formed by ring-opening polymerization of cyclic precursors.

Introduction

The self-assembly of polymers and nanostructures through coordination chemistry has become a very topical field, since the metal centers can act as nodes to control the self-assembly process, often using bidentate spacer ligands as connecting units, and the metals offer a natural functional group in the resulting material. For polymer synthesis, metals having two (linear), three (T-shaped or trigonal planar), or four (tetrahedral) or more available sites tend to give 1D, 2D, or 3D polymers, respectively.¹ In designing these structures it is often useful to compare the overall architecture to that of a known material. For example, two-dimensional networks based on trigonal planar coordination have been characterized and they exist as planar sheets, such as the honeycomb or chickenwire structure that is a structural analogue of graphite [Chart 1a].¹ Another possible 2D structure is the puckered sheet network, which exists in the elemental structures of arsenic, antimony, and bismuth, as well as in some metal silicides and related materials, and which is based on trigonal pyramidal nodes [Chart 1b].² Related but more complex structures exist with edge bridging groups E and capping groups X, based on tetrahedral nodes as shown in Chart 1c, and these are important in many laminated materials such as micas and clays that contain $[\text{Si}_2\text{O}_5]^{2-}$ repeating units [Chart 1c, M = Si, E = X = O].² This article reports the simple self-assembly of a puckered sheet material [Chart 1c, M = Ag, E = bridging diphosphine, X = trifluoroacetate] prepared through the coordination chemistry approach. It also reports two one-dimensional polymers that demonstrate the versatility of the combination of silver(I) and diphosphine units in forming different types of coordination polymer. Previous related work on silver(I)

Chart 1. The Honeycomb and Puckered Network Structures

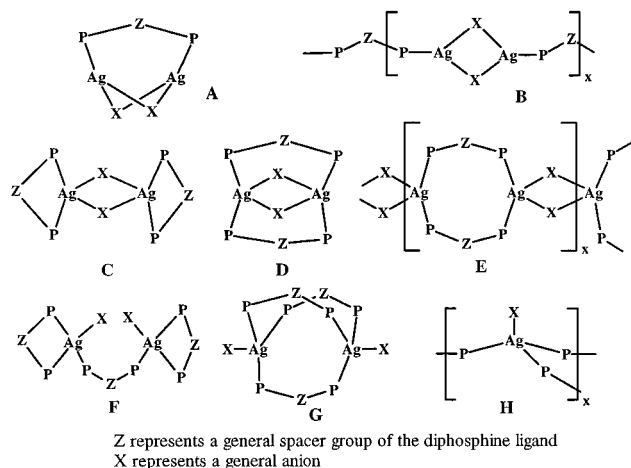


coordination polymers has concentrated on the use of nitrogen-donor ligands,³ but the use of phosphine ligands either alone or in combination with oxygen- and nitrogen-donor ligands has much promise in the synthesis of robust polymers and networks.^{4–6} Silver(I) complexes have potential as emissive or medically active materials.^{4,7} In some cases, the polymers reported here may be considered to be formed by ring-opening polymerization of cyclic precursors.

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Chart 2



Silver(I) can have a coordination number ranging from 2 to 4, and diphosphine ligands may bind in several different ways (chelate vs bridge, *syn* vs *anti* conformation when bridging) depending on the length and rigidity of the spacer group, so there is potential for many structural types in silver diphosphine complexes.⁴ Many of the binuclear structures shown in Chart 2 (in this chart, the group PP is a diphosphine with unspecified spacer group) are known. For example, the complex $[\text{Ag}_2(\mu\text{-O}_2\text{CCF}_3)_2(\mu\text{-bis}(\text{diphenylphosphino})\text{methane})]$ adopts the structure A.^{4f} Structure C is found with the diphosphine ligand 1,2-bis[(diphenylphosphino)methyl]benzene,^{4a} while structure D is found with the ligands 1,5-bis(diphenylphosphino)pentane and 1,6-bis(diphenylphosphino)hexane.^{4b,h} Structures F and G are known with the diphosphines 1,1'-bis(diphenylphosphino)ferrocene or bis(diphenylphosphino)acetylene.^{4i,5} However, the isomeric polymeric or network structures B, E, and H are now reported for the first time.⁴⁻⁶ The polymeric complexes are very sparingly soluble, probably with fragmentation to smaller units. Characterization therefore relies primarily on X-ray structure determinations though spectroscopic and analytical data were also obtained.

Results and Discussion

Complexes with AgPO_2 or AgPO_3 Coordination and the Effect of the Diphosphine Ligand. The complexes $[\text{Ag}_2(\mu\text{-O}_2\text{CCF}_3)_2(\mu\text{-cis-Ph}_2\text{PCH=CHPPH}_2)]$ [1; structure A, Chart 2, PP = *cis*- $\text{Ph}_2\text{PCH=CHPPH}_2$, X = CF_3CO_2] and $[\{\text{Ag}_2(\mu\text{-O}_2\text{CCF}_3)_2(\mu\text{-trans-Ph}_2\text{PCH=CHPPH}_2)\}_x]$ [2; structure B, Chart 2, PP = *trans*- $\text{Ph}_2\text{PCH=CHPPH}_2$, X = CF_3CO_2] were prepared simply from the corresponding silver salt and diphosphine ligand in the required ratio, and were isolated as colorless crystalline solids. The structures are shown in Figures 1 and 2, while selected bond lengths and angles are listed in Tables 1 and 2.

The structure of complex 1 (Figure 1) is that of a dimer of binuclear silver(I) complexes of structure A (Chart 2). Formation of each binuclear unit occurs by coordination of the silver atoms by one phosphorus atom from the bridging diphosphine ligand and by two oxygen atoms from the bridging bidentate trifluoroacetate groups as shown in Figure 1a. The distance $\text{Ag}(1)\text{-Ag}(2) = 2.8757(3)$ Å between the two silver centers is indicative

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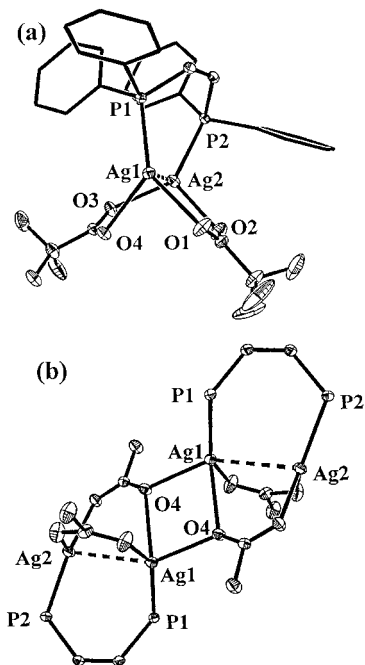


Figure 1. The structure of complex 1: (a) an individual disilver unit, with thermal ellipsoids for phenyl group carbons omitted for clarity and (b) the “dimer of dimers” structure, with phenyl groups and fluorine atoms omitted for clarity. Thermal ellipsoids are shown at 30% probability.

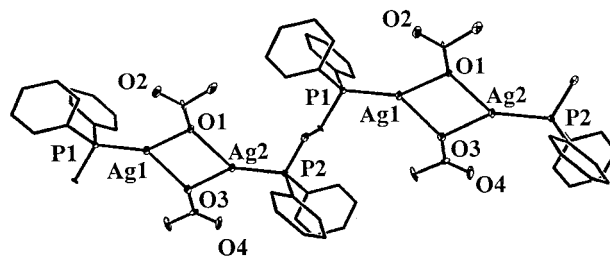


Figure 2. A view of the polymeric chain structure of complex 2. Thermal ellipsoids are not shown for phenyl carbons, and fluorine atoms of the disordered trifluoroacetate ligands are omitted for clarity. Thermal ellipsoids are shown at 30% probability.

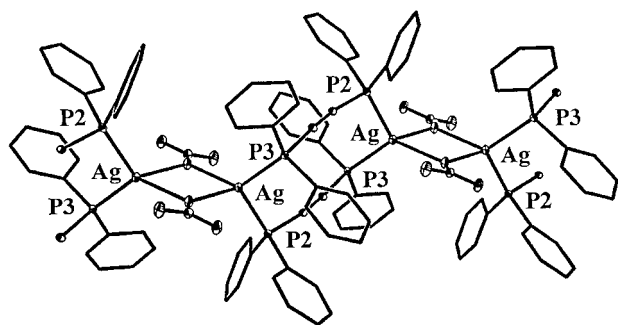
Table 1. Selected Bond Lengths (Å) and Angles (deg) for Complex 1

Ag(1)–O(4)	2.479(2)	P(1)–Ag(1)–O(1)	142.29(7)
Ag(1)–O(4A)	2.411(2)	P(1)–Ag(1)–O(4A)	119.83(6)
Ag(1)–O(1)	2.258(2)	P(1)–Ag(1)–O(4)	125.39(5)
Ag(2)–O(2)	2.329(2)	P(2)–Ag(2)–O(2)	115.52(7)
Ag(2)–O(3)	2.242(2)	P(2)–Ag(2)–O(3)	134.71(6)
Ag(1)–P(1)	2.3597(7)	O(4A)–Ag(1)–O(4)	79.58(6)
Ag(2)–P(2)	2.3587(7)	O(1)–Ag(1)–O(4)	81.72(8)
Ag(1)–Ag(2)	2.8757(3)	O(3)–Ag(2)–O(2)	109.68(9)
		Ag(1A)–O(4)–Ag(1)	100.42(6)

of a weak attractive interaction. The structure of this unit is similar to that of $[\text{Ag}_2(\mu\text{-O}_2\text{CCF}_3)_2(\mu\text{-dppm})]$, dppm = $\text{Ph}_2\text{PCH}_2\text{PPh}_2$, which has a similar value of $\text{Ag}\cdots\text{Ag} = 2.8892(9)$ Å.^{4f} The diphosphine bridges the pair of silver(I) centers and adopts the *syn* conformation, and this is a key feature that allows formation of the binuclear unit (Figure 1a). The “dimer of dimers” is formed by additional bridging of the oxygen atom O(4) of a trifluoroacetate ligand to a silver atom Ag(1A) of a neighboring dimer and the complementary bridging $\text{Ag}(1)\text{-O}(4\text{A})$, as shown in Figure 1b. The overall result is that Ag(1) has AgPO_3 coordination (distorted tetrahedral) while Ag(2) has AgPO_2 coordination (distorted trigonal planar). The distances

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complex 2

Ag(1)–O(1)	2.292(10)	P(1)–Ag(1)–O(1)	149.4(3)
Ag(2)–O(3)	2.281(9)	P(1)–Ag(1)–O(3)	137.8(2)
Ag(2)–O(1)	2.433(10)	P(2)–Ag(2)–O(1)	137.8(2)
Ag(1)–O(3)	2.402(9)	P(2)–Ag(2)–O(3)	150.1(2)
Ag(1)–P(1)	2.362(4)	O(1)–Ag(1)–O(3)	72.2(3)
Ag(2)–P(2)	2.364(4)	O(1)–Ag(2)–O(3)	71.8(3)
		Ag(1)–O(1)–Ag(2)	107.3(4)
		Ag(1)–O(3)–Ag(2)	108.7(4)

**Figure 3.** A view of the polymeric chain structure of complex 3. Thermal ellipsoids are not shown for phenyl carbons for clarity. Thermal ellipsoids are shown at 30% probability.

Ag(1)–O(4) and Ag(1)–O(4A) are 2.479(2) and 2.411(2) Å, respectively; they are longer than the other Ag–O bonds present in this structure (see Table 1). The Ag–P bond distances are Ag(1)–P(1) = 2.3597(7) Å and Ag(2)–P(2) = 2.3587(7) Å, which are not significantly different despite the different coordination numbers of Ag(1) and Ag(2).

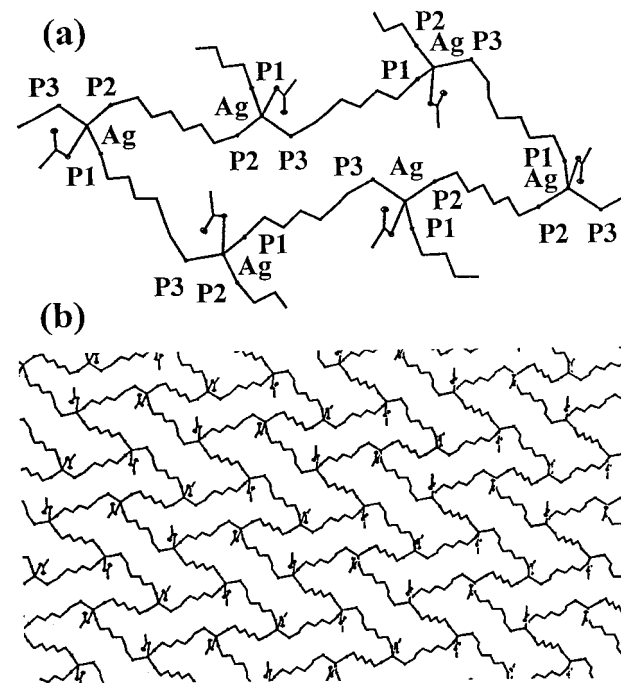
As seen in Figure 2, the complex $[\{Ag_2(\mu-O_2CCF_3)_2(\mu-trans-Ph_2PCH=CHPh_2)\}_x]$, **2**, forms a polymeric chain structure in the solid state. The major difference in comparison to **1** is that the diphosphine ligand *trans*-Ph₂PCH=CHPh₂ adopts the anti conformation in bridging between silver(I) centers and this favors polymer rather than ring formation. The chains are continued through bridging of the trifluoroacetate ligands, which bridge as $\mu-\eta^1$ ligands (Figure 2) rather than the $\mu-\eta^2$ bridging mode observed in **1** (Figure 1). All silver(I) centers in complex **2** are three-coordinate with distorted trigonal planar AgPO₂ coordination. Clearly, the different structures of **1** and **2** arise as a result of the different geometries and conformations of the diphosphine ligands *cis*- or *trans*-Ph₂PCH=CHPh₂, respectively. Complex **2** is the first known example of structure **B** (Chart 2).

It is noteworthy in the structures of both **1** and **2** that the trifluoroacetate anion bridges between silver atoms either through one or two oxygen donors, rather than chelating through both oxygen donors. An important factor in this respect is the relatively low coordination numbers of 3 and 4 involved, with natural trigonal or tetrahedral bond angles, respectively, such that the small OAgO bond angle in a chelate complex is relatively unfavorable compared to metal centers having higher coordination numbers.

A Polymeric Complex with AgP₂O₂ Coordination. The complex $[\{Ag_2(\mu-NO_3)_2(\mu-Ph_2PC\equiv CPh_2)_2\}_x]$, **3**, was prepared simply by reaction of silver nitrate with the diphosphine ligand in the required ratio. The structure of complex **3** is shown in Figure 3 and selected bond parameters are given in Table 3. It is the first known example of the polymeric structure **E** (Chart 2, X = NO₃, PP = Ph₂PC≡CPh₂). In complex **3** each silver-

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Complex 3

Ag(1)–O(1)	2.323(3)	O(1)–Ag(1)–P(2)	123.42(9)
Ag(1)–O(1A)	2.443(3)	O(1)–Ag(1)–P(3)	123.18(9)
Ag(1)–P(2)	2.458(1)	O(1A)–Ag(1)–P(2)	118.68(9)
Ag(1)–P(3)	2.462(1)	O(1A)–Ag(1)–P(3)	109.93(8)
		O(1)–Ag(1)–O(1A)	68.1(1)
		Ag(1)–O(1)–Ag(1A)	111.9(1)
		P(2)–Ag(1)–P(3)	107.32(4)

**Figure 4.** Views of the structure of complex 4: (a) a single giant ring and (b) the puckered sheet network structure. The phenyl substituents on phosphorus and the fluorine atoms of the trifluoroacetate ligands are omitted for clarity. Thermal ellipsoids are shown at 30% probability.**Table 4.** Selected Bond Lengths (Å) and Angles (deg) for Complex 4

Ag(1)–O(1)	2.464(2)	P(1)–Ag(1)–O(1)	84.19(5)
Ag(1)–P(1)	2.5089(7)	P(2)–Ag(1)–O(1)	111.91(5)
Ag(1)–P(2)	2.4371(7)	P(3)–Ag(1)–O(1)	108.50(5)
Ag(1)–P(3)	2.4813(7)	P(2)–Ag(1)–P(1)	124.83(2)
		P(2)–Ag(1)–P(3)	116.55(2)
		P(3)–Ag(1)–P(1)	105.77(2)

(I) center is four-coordinate with distorted tetrahedral AgP₂O₂ coordination. The diphosphines bridge between silver(I) centers to give 10-membered Ag₂(PCCP)₂ rings that are connected by bridging nitrate groups. The nitrate groups bridge through a single oxygen donor, similar to the trifluoroacetate bridges in the polymeric complex **2** (Figure 2). In both **2** and **3**, the alternate structures **A** and **C** or **D**, respectively (Chart 2), are disfavored by the geometrical constraints of the diphosphine ligands and so the self-assembly naturally gives the observed polymeric forms **B** or **E**. Attempts were made to crystallize the corresponding trifluoroacetate complex so as to study the anion effect on the self-assembly, but without success. The silver(I) centers in **3** are more sterically hindered than in **2**, and it is possible that the low steric effects of the nitrate anion are important in allowing the structure to form.

A Puckered Sheet Structure with AgP₃O Coordination. The reaction of silver(I) trifluoroacetate with an excess of the

Table 5. Crystal Data and Structure Refinements for Complexes **1**, **2**, **3**, and **4**

	1	2	3·2CH₂Cl₂	4
formula	C ₃₀ H ₂₂ Ag ₂ F ₆ O ₄ P ₂	C ₃₀ H ₂₂ Ag ₂ F ₆ O ₄ P ₂	C ₅₄ H ₄₄ Ag ₂ Cl ₄ N ₂ O ₆ P ₄	C ₄₇ H ₄₈ AgF ₃ O ₂ P ₃
fw	838.16	838.16	1298.33	902.63
<i>T</i> (K)	200(2)	200(2)	150(2)	150(2)
cryst syst	monoclinic	triclinic	triclinic	monoclinic
space group	<i>P</i> 2(1)/ <i>n</i>	<i>P</i> 1	<i>P</i> $\bar{1}$	<i>P</i> 2(1)/ <i>n</i>
<i>a</i> (Å)	13.2240(3)	8.4040(4)	10.5392(7)	12.4871(3)
<i>b</i> (Å)	10.7446(3)	10.1275(6)	11.7291(7)	18.5027(4)
<i>c</i> (Å)	21.7756(6)	10.4449(6)	12.1754(10)	19.7472(3)
α (deg)	90	114.040(2)	110.701(3)	90
β (deg)	93.8560(10)	97.505(3)	98.828(3)	107.3960(10)
γ (deg)	90	104.681(3)	96.685(4)	90
<i>V</i> (Å ³)	3087.02(14)	757.35(7)	1367.30(17)	4353.81(16)
<i>Z</i>	4	1	1	4
μ (mm ⁻¹)	1.443	1.471	1.079	0.623
<i>F</i> (000)	1648	412	652	1860
θ range (deg)	2.58–30.02	2.60 to 27.49	2.85 to 27.54	2.57 to 30.05
no. of reflns coll./ind.	16808/8986	4882/4882	9233/6274	23962/12725
Goof	0.926	1.095	1.105	0.734
<i>R</i> [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0354 <i>wR</i> ₂ = 0.0823	<i>R</i> ₁ = 0.0295 <i>wR</i> ₂ = 0.0698	<i>R</i> ₁ = 0.0525 <i>wR</i> ₂ = 0.1486	<i>R</i> ₁ = 0.0414 <i>wR</i> ₂ = 0.1124
<i>R</i> (all data)	<i>R</i> ₁ = 0.0651 <i>wR</i> ₂ = 0.0893	<i>R</i> ₁ = 0.0369 <i>wR</i> ₂ = 0.0724	<i>R</i> ₁ = 0.0722 <i>wR</i> ₂ = 0.1578	<i>R</i> ₁ = 0.0770 <i>wR</i> ₂ = 0.1306

flexible, long-chain diphosphine ligand 1,6-bis(diphenylphosphino)hexane gave the complex $[\{\text{Ag}(\text{O}_2\text{CCF}_3)(\mu\text{-Ph}_2\text{P}(\text{CH}_2)_6\text{-PPh}_2)_{1.5}\}_x]$ [**4**; structure **H**, Chart 2, PP = Ph₂P(CH₂)₆PPh₂, X = CF₃CO₂], whose remarkable structure is shown in Figure 4, with selected bond parameters in Table 4.

In complex **4** each silver(I) center is four-coordinate with distorted tetrahedral AgP₃O coordination. A given silver atom is connected to three others by bridging diphosphine ligands, and the trifluoroacetate ligands are terminally coordinated (Figure 4a). The presence of monodentate trifluoroacetate, compared to the bridging forms seen in complexes **1** and **2**, is expected since the silver(I) centers have the 18-electron configuration with AgP₃O coordination. All silver atoms are crystallographically equivalent and each is a node in three giant 54-membered [AgPC₆P]₆ rings, one of which is illustrated in Figure 4a. The angles around the Ag center are distorted from tetrahedral geometry, with the P–Ag–P angles ranging from 105.77(2) to 124.83(2)°. Each giant ring in complex **4** adopts an extended chair conformation, with each ring edge trans-fused to an adjacent ring. The resulting extended structure, illustrated in Figure 4b, is a clear example of the puckered sheet structure [Chart 1c, M = Ag, X = CF₃CO₂, E = diphosphine]. It is likely that the preference for the anti conformation of a diphosphine ligand Ph₂P(CH₂)_{*n*}PPh₂ when *n* is an even integer is a factor in favoring the extended structure rather than the isomeric forms such as **F** and **G** (Chart 2), though such flexible long-chain ligands are also capable of adopting the syn conformation.^{1,4} The puckered sheet structure has been observed in copper(I) chemistry in the complex cation $[\{\text{Cu}(\mu\text{-NC}_4\text{H}_4\text{N})_{1.5}(\text{MeCN})\}_x]^{x+}$, with rigid bridging pyrazine ligands, and there is one precedent in silver(I) chemistry using tripyrazolylborate ligands.^{3,7} Another analogue is the complex $[\{\text{Ag}_2(\mu\text{-NO}_3)_2(\mu\text{-phenazine})\}_x]$, which has a 3-dimensional network structure comprised of sheets connected by nitrate bridges. Within each sheet, there are distorted hexagons of silver(I) atoms with edges bridged by either phenazine or nitrate ions.^{3,8} In gold chemistry a related

complex $[\{\text{Au}(\mu\text{-Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2)_{1.5}\}_x]^{x+}$ forms a honeycomb sheet structure (Chart 1) containing fused 42-membered [Au₆(μ-PP)₆] rings; since gold(I) prefers a lower coordination number compared to silver(I), the anions are not coordinated in this case.⁹ There appear to be no significant intersheet secondary bonding interactions in complex **4** and so it might be expected to easily accommodate intercalated guests, but none are present in the solid-state structure.

In summary, it has been possible to design polymers incorporating silver(I) centers with AgP, AgP₂, and AgP₃ coordination arising from bridging diphosphine ligands by considering the rigidity, bite distance, and conformational preference of the diphosphine ligands. The use of the “node + spacer” concept in the synthesis of a silver(I) coordination polymer having the important puckered sheet structure is reported. Finally, it is noted that the polymer or network structures **B**, **E**, and **H** (Chart 2) are related to the binuclear structures **A**, **C**, **D**, **F**, and **G** by formal ring-opening polymerization. Conversion of **A** to **B** or **D** to **E** requires conversion of intradimer to interdimer Ag₂(μ-X) links and is expected to be favorable if the relatively close Ag⋯Ag separation that is necessary in structures **A** and **D** causes strain in the Ag₂(μ-PP) unit. The structure of complex **1** (Figure 1b) is particularly interesting since it contains *both* types of Ag₂(μ-X) links (Figures 1a and 2), and so could be regarded as an intermediate between the binuclear and polymeric forms. It also highlights the importance of the anion in the self-assembly process. Conversion of **C** to **E** or **F** to **H** requires opening of chelating Ag(PP) to bridging Ag₂(μ-PP) units and will be favored when the chelate is strained, while conversion of **G** to **H** requires double ring-opening polymerization and will be favored when the diphosphine has a preference for the anti rather than syn conformation.^{5,9} Self-assembly is a complex process and it is difficult to eliminate other factors that might play a role in determining selectivity. The only case in which other bonding forces might be significant is in complex **4**, for which intralayer phenyl–phenyl face-to-face π-stacking is present (centroids separated by less than 4 Å) and may serve to stabilize the large

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rings. No significant interchain or interlayer secondary bonding interactions were identified. The principles outlined above can clearly be applied to the design and synthesis of other coordination polymers and networks with the convenient diphosphine ligands used in the present work. Many silver(I) phosphine complexes show emissive properties in the solid state^{1,3,4} but those described above do not, and this may be a result of the polymeric structures.

Experimental Section

Solution ¹H and ³¹P NMR spectra were recorded on a Varian Inova 400 MHz spectrometer and chemical shifts are reported relative to TMS or 85% H₃PO₄(aq). ³¹P CP-MAS solid-state NMR spectra were collected on a Varian Infinity Plus WB 9.4 T spectrometer, with a ³¹P operating frequency of 161.72 MHz, and using a ramp and tppm decoupling at a spinning rate of 15 kHz, with zirconium oxide rotors. ³¹P CP-MAS chemical shifts were referenced to NH₄H₂PO₄ at 0.81 ppm (wrt H₃PO₄). Syntheses were carried out at room temperature and crystals were grown at 4 °C.

$[\{\text{Ag}_2(\mu\text{-O}_2\text{CCF}_3)_2(\mu\text{-cis-Ph}_2\text{PCH=CHPh}_2)\}_x]$, **1**. A mixture of *cis*-1,2-bis(diphenylphosphino)ethylene (0.071 g, 0.179 mmol) and silver trifluoroacetate (0.079 g, 0.358 mmol) in THF (10 mL) was allowed to stir for 2 h. Pentane was then added dropwise, to yield the product as a white precipitate. Yield: 0.11 g, 73%. Crystals were obtained from a CH₂Cl₂ solution layered with pentane. NMR in CD₂Cl₂: $\delta^1(\text{H})$ 7.56 [m, 10H, Ph]; 7.44 [m, 10H, Ph]; 7.06 [t, $J_{\text{obs}}(\text{PH}) = 18$ Hz, 2H, CH=CH]. $\delta^{31}(\text{P})$ 1.9 (broad).

$[\{\text{Ag}_2(\mu\text{-O}_2\text{CCF}_3)_2(\mu\text{-trans-Ph}_2\text{PCH=CHPh}_2)\}_x]$, **2**. **2** was prepared similarly from *trans*-1,2-bis(diphenylphosphino)ethylene (0.060 g, 0.151 mmol) with silver trifluoroacetate (0.067 g, 0.303 mmol) in THF (10 mL). Yield: 0.10 g (79%). Crystals were obtained from a CH₂Cl₂ solution layered with pentane. NMR in CD₂Cl₂/CD₃OD: $\delta^1(\text{H})$ 7.40 [m, 20H, Ph]; 7.02 [t, $J_{\text{obs}}(\text{PH}) = 18$ Hz, 2H, CH=CH]. $\delta^{31}(\text{P})$ (CP-MAS solid state) 8.5 [broad].

$[\{\text{Ag}_2(\mu\text{-NO}_3)_2(\mu\text{-Ph}_2\text{PC}\equiv\text{CPh}_2)_2\}_x]$, **3**. This complex was prepared in a similar fashion from bis(diphenylphosphino)acetylene (0.143 g, 0.363 mmol) and silver nitrate (0.063 g, 0.371 mmol) in THF (10 mL). Yield: 0.18 g (86%). Crystals were obtained from a CH₂Cl₂

solution layered with pentane. NMR in CD₂Cl₂/CD₃OD: $\delta^1(\text{H})$ 7.39 [m, broad, 40H, Ph]. $\delta^{31}(\text{P})$ (CP-MAS solid state) -21.5 (broad).

$[\{\text{Ag}(\text{O}_2\text{CCF}_3)(\text{Ph}_2\text{P}(\text{CH}_2)_6\text{PPh}_2)_{1.5}\}_x]$, **4**. 1,6-Bis(diphenylphosphino)hexane (0.211 g, 0.464 mmol) was added to a solution of silver trifluoroacetate (0.68 g, 0.310 mmol) in THF (10 mL). After the mixture was stirred for 2 h, a white precipitate of was collected by filtration, and washed with THF, ether, and pentane. Yield: 0.20 g (70%). Crystals were obtained from a CH₂Cl₂ solution layered with pentane. NMR in CD₂Cl₂/CD₃OD: $\delta^1(\text{H})$ 7.34 [m, 12H, *o*-H Ph]; 7.18 [m, 18H, *m,p*-H Ph]; 2.16 [m, 6H, CH₂-P]; 1.33 [m, 12H, CH₂CH₂-P]. $\delta^{31}(\text{P})$ (CP-MAS solid state) -1.5 (broad).

X-ray Structure Determinations. Data were collected on a Nonius Kappa-CCD diffractometer with use of COLLECT (Nonius, 1998) software. The unit cell parameters were calculated and refined from the full data set. Crystal cell refinement and data reduction was carried out with the Nonius DENZO package. The data were scaled by using SCALEPACK (Nonius, 1998) and no other absorption corrections were applied. The SHELXTL 5.1 (Sheldrick, G. M., Madison, WI) program package was used to solve the structure by direct methods, followed by refinements with successive difference Fouriers. The hydrogen atoms were calculated geometrically, riding on their respective carbon atoms. For complex **2**, all non-hydrogen atoms were refined anisotropically except for C5 and the F atoms, which were restrained so that their U_{ij} component approximates isotropic behavior (ISOR). The phenyl rings were constrained to be regular hexagons (AFIX 66). There was disorder in the positions of the fluorine atoms of the CF₃ group and two sets of fluorine atoms were refined to 71/29% occupation. For complexes **1**, **3**, and **4**, all non-hydrogen atoms were refined with anisotropic thermal parameters.

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Supporting Information Available: Tables of X-ray data for complexes **1–4** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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