Ring-Opening Polymerisation of Silver–Diphosphine [M_2L_3] Coordination Cages To Give [M_2L_3]$_\infty$ Coordination Polymers

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Abstract: [M_2L_3] coordination cages and linear [M_2L_3]$_\infty$ polymers of the rigid, bridging diphosphines bis(diphenylphosphino)acetylene (dppa) and *trans*-1,2-bis(diphenylphosphino)ethylene (dppet) with silver(I) salts have been investigated in the solution and solid states. Unlike flexible diphosphines, 1:1 dppa/AgX mixtures do not selectively form discrete [Ag_2(diphos)$_2$(X)$_2$] macrocycles; instead dynamic mixtures of one-, two- and three-coordinate complexes are formed. However, 3:2 dppa/AgX ratios (X = SbF_6, BF_4, O_3SCF_3 or NO_3) do lead selectively to new [M_2L_3] triply bridged cage complexes [Ag_2(dppa)$_3$(X)$_2$] **1a–d** (X = SbF_6 **a**, BF_4 **b**, O_3SCF_3 **c**, NO_3 **d**), which do not exhibit Ag–P bond dissociation at room temperature on the NMR time scale (121 MHz). Complexes **1a–d** were characterised by X-ray crystallography and were found to have small internal cavities, helical conformations and multiple intramolecular aromatic interactions. The nucleophilicity of the anion subtly influences the cage shape: Increasing nucleophilicity from SbF_6 (**1a**) through BF_4 (**1b**) and O_3SCF_3 (**1c**) to NO_3 (**1d**) increases the pyramidal distortion at the AgP_3 centres, stretching the cage framework (with Ag⋯Ag distances increasing from 5.48 in **1a** to 6.21 Å in **1d**) and giving thinner internal cavities. Crystal packing strongly affected the size of the helical twist angle, and no correlation between this parameter and the Ag–Ag distance was observed. When crystalline **1c** was stored in its supernatant for 16 weeks, conversion occured to the isostoichiometric [M_2L_3]$_\infty$ coordination polymer [Ag(dppa)$_2$Ag(dppa)(O_3SCF_3)$_2$]$_\infty$ (**1c′**). X-ray crystallography revealed a structure with ten-membered Ag_2(dppa)$_2$ rings linked into infinite one-dimensional chains by a third dppa unit. The clear structural relationship between this polymer and the precursor cage **1c** suggests a novel example of ring-opening polymerisation. With dppet, evidence for discrete [M_2L_3] cages was also found in solution, although ^{31}P NMR spectroscopy suggested some Ag–P bond dissociation. On crystallisation, only the corresponding ring-opened polymeric structures [M_2L_3]$_\infty$ could be obtained. This may be because the greater steric bulk of dppet versus dppa destabilises the cage and favours the ring-opening polymerisation.

Keywords: crystal engineering · phosphanes · ring-opening polymerization · silver

Introduction

Two current themes in synthetic coordination chemistry are those of coordination cages[1] and coordination polymers.[2] Most often, nitrogen-donor bridging ligands have been used in this work and relatively little use has been made of phosphines.[3] We have been investigating complexes of silver ions with bridging multidentate phosphines in the hope of discovering novel types of coordination cages or polymeric structures.[3a,b] Due to the general tendency of silver–monophosphine complexes to dissociate in solution,[4] we were initally interested in cases in which certain multisilver multidentate phosphine structures appear to form selectively and maintain their integrity in solution (Figure 1).[3a,b, 5] For instance there are several examples in which flexible oligomethylene-backboned diphosphines and silver(I) ions adopt dinuclear macrocyclic structures, several of which have been characterised in the solid state, and some ^{31}P NMR data also reported for their solutions.[5a] In addition to the inherent stability of unstrained rings, we postulated that a stabilising factor in this type of structure was the ability of anions to bridge between the metal cations.

In order to gain more information on this aspect, we investigated the use of the rigid bridging diphosphines bis(diphenylphosphinoacetylene) (dppa) and *trans*-1,2-bis(diphenylphosphino)ethylene (dppet; Figure 2). Due to their rigid backbones, the orientations of their lone pairs are restricted, so that these ligands cannot point inwards and set up the metals for anion bridging. They could therefore be expected to produce different products to those of the extensively studied flexible diphosphines. In a preliminary communication[3b] we reported that this is indeed the case. In

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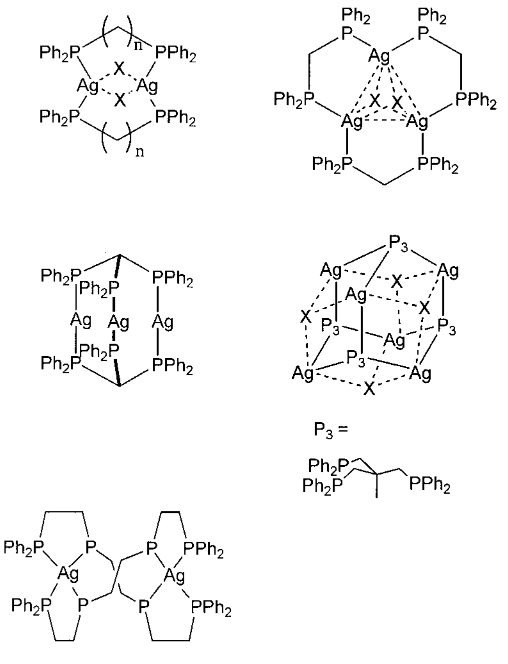

P = PPh

Figure 1. Examples of ring, cage and helical structures that can assemble from silver ions and multidentate phosphines[3a, 5] (X = anion).

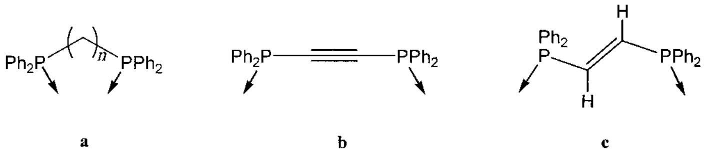

Figure 2. The different orientations of lone pairs of flexible diphosphines in macrocyclic disilver complexes **a**, and the rigid diphosphine ligands dppa **b** and dppet **c**.

particular we described the selective formation of triply bridged dinuclear cage complexes [$Ag_2(dppa)_3(X)_2$] **1a–d** (X = SbF_6 **a**, BF_4 **b**, O_3SCF_3 **c**, NO_3 **d**), including a brief discussion of the crystal structure of complex **1b**. Here we give a fuller account of these studies, including X-ray crystal structures of each complex, which reveals a "cage-stretching" influence of the more nucleophilic anions. We further report the slow conversion of one such cage into a one-dimensional chain coordination polymer **1c′**. There is a clear relationship between the structure of this polymer and that of the precursor cage **1c**; this suggests that the polymer is formed from the cage by a ring-opening polymerisation. Though ring-opening polymerisation is common in p-block rings and cages,[6] to our knowledge it has not been described previously for coordination cages. Parallel studies with *trans*-1,2-bis(diphenylphosphino)ethylene (dppet) are also described; these suggest that with this ligand the analogous triply bridged cages are destabilised by transanular steric repulsion between the *trans* ethylene groups. Consistent with the postulated ring-opening polymerisation, on crystallisation only linear $[M_2L_3]_\infty$ polymeric products were obtained with this ligand.

Results

Bis(diphenylphosphino)acetylene (dppa): We have previously communicated our studies of the complexation of silver salts by dppa, including the synthesis of [$Ag_2(dppa)_3(BF_4)_2$], here denoted **1b**. The related complexes [$Ag_2(dppa)_3(X)_2$] (X = SbF_6, **1a**; X = O_3SCF_3, **1c**; X = NO_3, **1d**), for which ^{31}P NMR data were reported, were prepared similarly. All compounds were obtained as crystalline solids in greater than 70% yield, and on redissolution, their ^{31}P NMR spectra were identical to those observed when they were prepared in situ. The complexes were also found to be indefinitely stable in common organic solvents under ambient conditions. ^1H NMR spectra ($CDCl_3$ or $CDCl_3/CD_3NO_2$) for each complex showed three signals due to the chemically distinct aromatic nuclei, indicating that on the NMR time scale the aromatic groups are equivalent. The twisted or "helical" conformations of the complexes observed in the solid state (see below) are therefore either not adopted in solution, or undergo rapid flipping between enantiomeric forms on the NMR time scale. Variable-temperature ^1H NMR spectroscopy, however, gave no further information on this point, since there was no significant change in the ^1H NMR spectrum of complex **1b** on cooling to $-80\,^\circ C$ (500 MHz). The ^1H NMR spectra were generally sharp, except for the complexes with oxoanions **1c** and **1d**, in which signals due to the *ortho* protons were broadened. This is most likely associated with C–H···O hydrogen bonding with the anion, as observed in the solid state of complex **1d** (see below).

X-ray crystal structures of [$Ag_2(dppa)_3X_2$] complexes: X-ray crystal structure determinations were carried out on all four complexes **1a–d** (X = SbF_6 **a**, BF_4 **b**, O_3SCF_3 **c**, NO_3 **d**). The X-ray structure of **1b** has been reported and discussed briefly before, but in order to make structural comparisons within the series it is included in the discussions here. For each complex, crystals were obtained from chloroform/nitromethane (**1a** and **1c**) or chloroform/acetonitrile/nitromethane (**1b** and **1d**) solutions by layering with diethyl ether. Bond lengths and angles were unexceptional unless otherwise stated. All complexes have the same overall connectivity, with the two silver centres triply bridged by dppa, and all complexes have helical conformations, that is, the dppa ligands are all canted in the same rotational sense with respect to the Ag···Ag axis (Figure 3). However, the increasing anion nucleophilicity in the series from **1a** to **1d** has resulted in certain structural trends.

*[$Ag_2(dppa)_3(SbF_6)_2$] · 0.5 CH_3NO_2 (**1a**)*: Four independent complexes occur in the unit cell. A representative molecule is shown in Figure 3 (top left). There is approximate trigonal geometry at the silver centres, but with slight pyramidal distortion (average distance of Ag from P_3 mean planes is 0.48 Å). Although the SbF_6 anions are disordered, they do appear to be weakly associated with the cations, with F···Ag distances in the range 2.5–2.8 Å and F···H distances as short as 2.4 Å. The P-CC-P backbones bow outwards from the centre of the cage, with the average P-C-C angles occurring in the range 168.3–173.5°. This slight strain appears to result

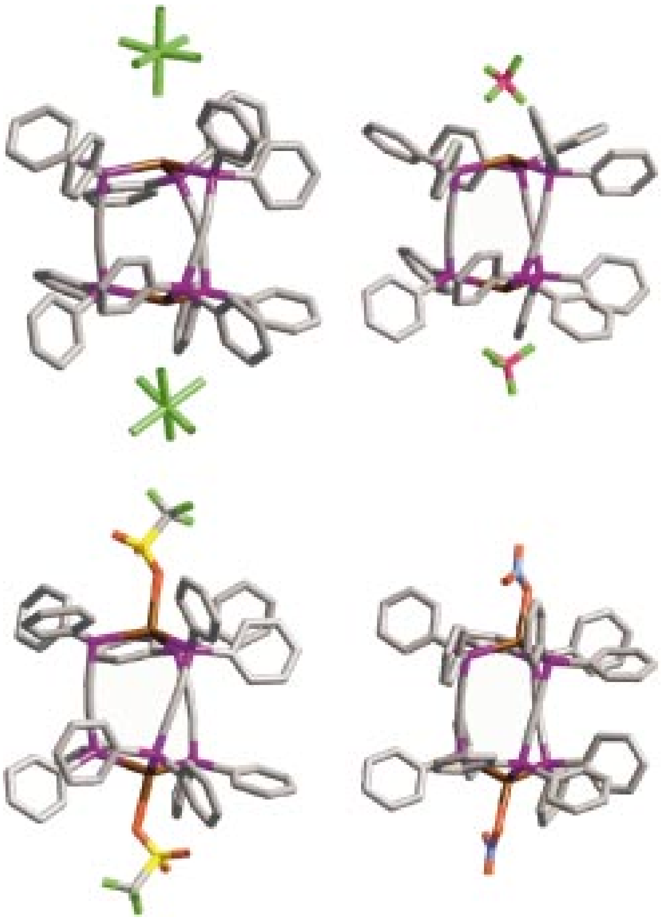

Figure 3. Crystal structures of triply bridged complexes $[Ag_2(dppa)_3(X)_2]$ {X = SbF_6 **1a** (top left); BF_4 **1b** (top right); O_3SCF_3 **1c** (bottom left); NO_3 **1d** (bottom right)} showing the cage elongation with increasing anion nucleophilicity. H atoms are omitted for clarity.

from the mismatch between the distorted tetrahedral geometry at phosphorus and the requirement for pseudo-cofacial coordination of the two silver centres in the cage, and is also partially alleviated by the pyramidal distortion at silver. Overall, the average helical twist is 33.0° for the four cations, about their Ag ··· Ag axes, taken as the average of the three Ag-P-P-Ag torsion angles for each complex. The spread of values for the same complex (see Table 1) indicates how important crystal packing is in determining the degree of helicity. A small void exists at the centre of the cage (average dimensions: Ag ··· Ag distance 5.46 Å, average C≡C centroid to molecular centroid 2.57 Å for the four cations). Possibly significant in conferring the unusual solution state stability of these complexes (see also the discussion below) are a number of arene–arene interactions. Specifically, for each complex there are between 18 and 22 C ··· C contacts indicated by C ··· C distances between 3.5 and 3.8 Å.

*$[Ag_2(dppa)_3(BF_4)_2]\cdot 0.5\,CHCl_3\cdot 1.5\,CH_3NO_2$ (**1b**)*: The molecular structure of this compound is shown in Figure 3 (top right). There is slightly stronger anion–cation interaction than in complex **1a**, with shorter contacts from fluorine to the silver(I) centres and to some *ortho* hydrogen atoms. Intramolecular contacts shorter than the sum of the van der Waals radii (2.67 Å) between fluorine and hydrogen are F11–H62A 2.593, F21–H12B 2.589 and F22–H36B 2.507 Å. To the Ag centres, contacts shorter than the combined van der Waals radii (3.19 Å) are F21–Ag1 2.933(9), F22–Ag1 2.751(7), F11–Ag2 2.861(9) and F12–Ag2 2.656(9) Å. The BF_4 anions are each disordered over two sites with occupancies of 65% and 60% for the major component of each anion, for which the above contact distances are given. As a consequence of the stronger anion coordination, there is greater pyramidal distortion at the silver centres than in complex **1a** (the average distance of Ag1 and Ag2 from their P_3 mean planes is 0.54 Å). Consequently the cage framework is slightly "stretched" relative to complex **1a** as evidenced by the larger Ag ··· Ag distance of 5.66 Å. Further consequences of this stretching are seen in the less distorted diphosphine bridges (P-C≡C angles lying in the range 171.3(4) to 175.1(4)°) and thinner central void (a typical C≡C centroid to molecular centroid distance is 2.48 Å). The twist of complex **1b** is also correspondingly less pronounced than that of **1a**, being about 27°, about the Ag ··· Ag axis. In common with complex **1a**, there are multiple (16) intramolecular aromatic contacts of both stacking and C–H ··· π types between the 12 phenyl groups in the range 3.5–3.8 Å (C–C distance).

*$[Ag_2(dppa)_3(O_3SCF_3)_2]\cdot 0.5\,CH_3NO_2$ (**1c**)*: The molecular structure is shown in Figure 3 (bottom left). The unit cell contains three unique complexes, two of which are located about inversion centres, and four unique anions. Both the anions and the phenyl groups of the cations are disordered and have been modelled as having two sites. The large atomic displacement parameters associated with the anions indicate a higher degree of disorder, but further modelling of this has proved impossible. However, the triflate anions do appear to coordinate to Ag^I more strongly than the BF_4^- ions in complex **1b**, with Ag–O distances of between 2.43 and 2.56 Å. There is pronounced pyramidal geometry at the AgP_3 coordination centres—the average distance of the silver centres from their P_3 planes is 0.62 Å. The diphosphine backbones are less strained, being close to linear (with P-C≡C angles now lying in the range 172–176°). The cage framework is also correspondingly further elongated than in **1b**, with an average Ag ··· Ag distance of 5.88 Å and an average C≡C centroid to molecular centroid distance of 2.50 Å. Overall, **1c** has the most pronounced helical twist of all the complexes, with an average value of 35.3°.

*$[Ag_2(dppa)_3(NO_3)_2]\cdot CH_3NO_2$ (**1d**)*: The molecular structure is shown in Figure 3 (bottom right). With nitrate having the strongest coordinating ability of the anions used here (the Ag–O distances are 2.390 and 2.398 Å) the structural trends observed for complexes **1a–c** are concluded in complex **1d**. In particular, it has the longest Ag ··· Ag distance (6.21 Å), the straightest P-CC-P backbones (the average of the P-C-C angles is 174.7°) and the narrowest central void (the average C≡C centroid to molecular centroid distance is 2.389 Å). The helical twist, for which there seems to be no clear trend within the four complexes, is 28.6°. The nitrate anions are monodentate, but each anion uses a second oxygen atom in making short contacts to phenyl *ortho* hydrogens. Both of these

Table 1. Comparison of significant distances and angles for compounds **1a–d, 1c′**, **2a·CH$_3$NO$_2$** and **2a**.

Compound	Ag···Ag distance [Å]	Ag distance from P$_3$ mean plane [Å]	Ag···Ag centroid to C≡C centroid distance [Å]	Twist torsion angles Ag-P-P-Ag [°]
1a	5.47	0.45	2.56	42.7
		0.48	2.57	28.7
			2.60	29.4
	5.41	0.48	2.59	45.4
		0.47	2.60	36.6
			2.57	36.3
	5.53	0.53	2.54	38.7
		0.49	2.57	27.7
			2.58	24.5
	5.50	0.50	2.50	33.2
		0.46	2.63	22.7
			2.59	30.2
1b	5.66	0.55	2.49	27.1
		0.54	2.55	2.55
			25.6	28.8
1c	5.89	0.68	2.37	33.9
			2.54	33.8
			2.54	46.9
	5.88	0.49	2.53	25.1
			2.53	25.1
			2.46	46.5
	5.87	0.64	2.45	35.6
		0.67	2.47	41.5
			2.58	29.2
1d	6.21	0.80	2.38	22.0
		0.85	2.38	37.0
			2.40	36.8
1c′	7.00	0.58	2.14	30.6
		0.58	2.14	30.6
2a·CH$_3$NO$_2$	6.74	0.39	1.40	33.9
		0.29	2.33	111.7
2a	6.58	0.44	1.82[a]	45.3
		0.44	1.82[a]	45.3

[a] Closest contact across the rings is between C2 and C2′ (symmetry code $= -1-x, 1-y, 2-z$).

interactions are bifurcated with distances to H atoms of the most strongly canted dppa ligand being slightly the shorter in each pair (2.57 and 2.48 Å). Lists of the structural paramerters discussed are collected in Table 1.

Although the disorder associated with the anions in **1a–1c** (and also cations in **1c**) makes it difficult to draw firm conclusions on the hydrogen bonding to the *ortho* hydrogens of the phenyl rings, we note that in certain of these cages one of the dppa ligands is markedly more canted with respect to the Ag···Ag vector than the other two (see Table 1). It may be that this canting positions the *ortho* hydrogens of the phenyl rings on these ligands sufficiently close to form C-H···O hydrogen bonds with the uncoordinated oxygen atoms of the anions (cf. H···O 2.4–2.6 Å).

*The ring-opened coordination polymer [Ag(dppa)$_2$Ag(dppa)-(O$_3$SCF$_3$)$_2$]$_\infty$ (**1c′**)*: When a crystalline sample of the triflate cage complex **1c**, prepared as above, was sealed in its supernatant, over a period of 16 weeks new crystals of a different morphology grew at the meniscus. This material was found to be insoluble in all common organic solvents. Its structure was, however, determined by single-crystal X-ray crystallography to be a coordination polymer [Ag(dppa)$_2$-Ag(dppa)(O$_3$SCF$_3$)$_2$]$_\infty$ (Figure 4, top), which is isostoichiometric with the cage **1c** (i.e., the repeat unit is [M$_2$L$_3$]). The structure consists of ten-membered Ag$_2$(dppa)$_2$ rings, with distorted tetrahedral P$_3$AgOTf silver(I) centres, which are linked into one-dimensional chains by a third *exo*-cyclic bridging diphos. The propagation of the chains is in the crystallographic 001 direction. The Ag···Ag distances are 7.0 Å across the ring and 8.3 Å across the single dppa bridge. The triflate anion is monodentate with an Ag···O distance of 2.48 Å, and the P-CC-P backbones are close to linear with an average P-C-C angle of 176°. There are also several close contacts between the aromatic groups. In particular there are 26 intrachain C···C distances of 3.5–3.8 Å per monomer repeat unit. We have not yet studied in detail the possibility of similar polymerisations for the other cage complexes **1a**, **b** and **d**.

***trans*-1,2-Bis(diphenylphosphino)ethylene (dppet)**: To assess how general the formation of triply bridged [M$_2$L$_3$] complexes is to other rigid diphosphines, we also investigated the ligand *trans*-1,2-bis(diphenylphosphino)ethylene (dppet). At 3:2 ligand-to-metal ratios under similar conditions to those described above ^{31}P NMR spectra were somewhat broadened at room temperature relative to those of dppa. However, at −60°C sharp spectra were obtained. These were second-order spectra (presumably due to significant through-backbone three-bond P–P coupling), but could be satisfactorily simulated by using the following coupling constants for the AgSbF$_6$ complex (Hz): $^1J(^{109}\mathrm{Ag},^{31}\mathrm{P}) = 331$, $^2J(^{31}\mathrm{P},^{31}\mathrm{P}) = -100$, $^3J(^{31}\mathrm{P},^{31}\mathrm{P}) = 36$, $^4J(^{109}\mathrm{Ag},^{31}\mathrm{P}) = -0.4$. Again, the one-bond silver–phosphorus coupling strongly indicates AgP$_3$ coordination, and it seems likely that in solution an analogous triply-bridged dinuclear cage structure [Ag$_2$(dppet)$_3$(SbF$_6$)$_2$] (**2a**) is formed.

X-ray crystal structures of dppet complexes: On crystallisation, however, the structure as determined by X-ray crystallography was not that of a cage, but in fact a coordination polymer {[Ag(dppet)$_2$Ag(dppet)](SbF$_6$)$_2$·CH$_3$NO$_2$}$_\infty$ denoted **2a′·CH$_3$NO$_2$** (Figure 4, middle). Interestingly, the connectivity of polymer **2a′·CH$_3$NO$_2$** is directly analogous to that formed by dppa in **1c′**. In particular, ten-membered Ag$_2$-(dppet)$_2$ rings are linked into polymeric chains by the third bridging dppet ligand. The chain propagates in the crystallographic 001 direction. The SbF$_6$ anions also occupy similar

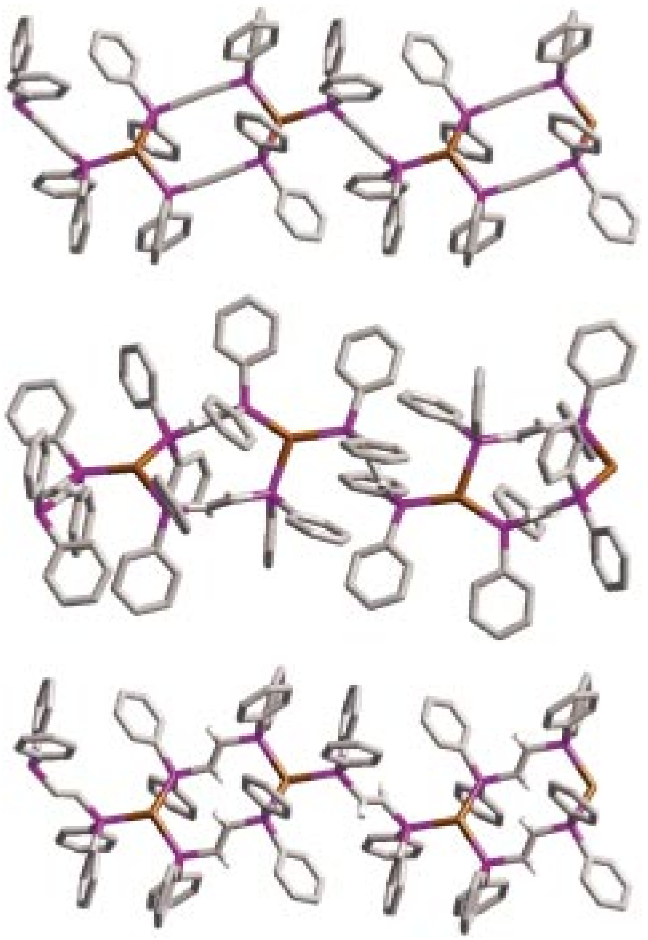

Figure 4. Crystal structures of the ring-opened coordination polymers $[Ag(dppa)_2\ Ag(dppa)(O_3SCF_3)_2]$ (**1c′**; top), $[Ag(dppet)_2Ag(dppet)(SbF_6)_2]\cdot CH_3NO_2$ (**2a′·CH$_3$NO$_2$**; middle) and $[Ag(dppet)_2Ag(dppet)(SbF_6)_2]$ (**2a′**; bottom). Anions, solvents of crystallisation and H atoms are omitted for clarity.

positions to those taken by triflate anions of the dppa polymer **1c′**, but are only very weakly associated with the silver(I) centres (the closest Ag–F distances are 2.83 and 2.78 Å). There are 18 intrachain C···C contacts of 3.5–3.8 Å per monomer repeat unit. A second crystal structure determination of crystals taken from the meniscus of the solvent revealed the same polymeric chain, but in an unsolvated form, denoted **2a′**. Its structure is illutrated in Figure 4 (bottom). The chain propagates in the crystallographic 011 direction, and there is one weak interaction between each silver ion and anion (Ag···F = 2.99 Å). Here there are 32 C···C contacts between 3.5 and 3.8 Å per monomer repeat unit.

Discussion

We have discussed previously the interaction between dppa and silver ions, and the selective formation of triply bridged complexes, as compared to the doubly bridged complexes characterised for flexible diphosphines.[3b] The stability of the triply bridged complexes is presumably to some degree inherent in their cage connectivity; however, the numerous intramolecular arene–arene interactions, which are apparent from the X-ray crystal structure determinations, may also have an important effect. Although individually weak,[7] in significant numbers they could influence equilibrium contants in solutions. It may further be significant that large numbers of aromatic contacts were observed in the unexpected and stable silver–triphosphine (triphos) cage complexes $[Ag_6(triphos)_4(anion)_4]^{2+}$.[3a] However, very few of the interactions observed correspond closely to the archetypal edge-to-face or offset face-to-face geometries that have been identified as energy minima for two interacting benzene rings. This is presumably due to the geometric contraints inherent in the structures themselves, the presence of additional intermolecular interactions in the crystals, interactions between rings and anions, and because most of the rings engage in more than one close contact. Despite the existence of these multiple contacts, we could identify no clearly repeating symmetrical structural motifs, of the "embrace" type which have been characterised by Dance and co-workers[7] for triarylphosphine and related compounds.

It is interesting to compare the behaviour of dppa with that of 1,1′-bis(diphenylphosphino)ferrocene (dppf) and bis(diphenylphosphino)methane (dppm). For dppf, two $[Ag_2L_3]$ complexes, $[Ag_2(\eta^2\text{-dppf})_2(\mu\text{-dppf})(X)_2]$ ($X = HCO_3$[8] or NO_3[9]), have been reported. They were characterised by X-ray crystallography and found to have the structure shown in Figure 5a, with one bridging dppf and two chelating. ^{31}P NMR spectroscopy suggested that this was also the major species present in solution. For dppm, $[Ag_2L_3]$ complexes with SbF_6[10] and OTf[11] counter ions have been investigated in solution by ^{31}P NMR spectroscopy. Both complexes were found to exist as the triply bridged "manxane" structure in Figure 5b; this structure was inert to Ag–P bond dissociation on the NMR timescale at low temperatures. This structure has also been characterised in the solid state.[12] At higher temperatures an "end-over-end" fluxional process was identified for the dppm ligands, and an intermediate complex $[Ag_2(\mu\text{-dppm})_2(\text{dppm-}P,P')]^{2+}$ was proposed, as shown in Figure 5c, with two bridging dppm ligands and one chelating to give a transiently four-coordinate silver ion. The different abilities of dppf, dppm and dppa to chelate accounts for the observed differences in their coordination behaviours. Dppf can easily form unstrained chelates, whereas the strain in the four-membered dppm chelate only allows it to form tran-

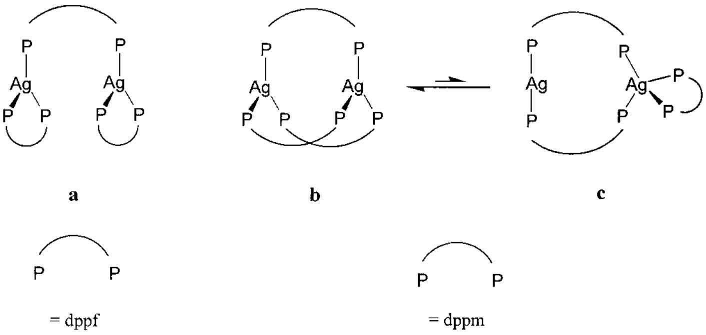

Figure 5. Coordination behaviours of $[Ag_2L_3]^{2+}$ complexes where L = dppf or dppm.

siently. Dppa cannot chelate and so forms only the triply bridging structure in which no end-over-end fluxional process is observed.

Previously, some other related triply bridged $[M_2L_3]$ complexes, in which L = rigid bridging diphosphine, have been characterised in the solid state. These are the hexa-coordinate dimolybdenum complex $[Mo(CO)_3(\mu\text{-dppa})_3Mo(CO)_3]$,[13] and the butyltelluro copper complexes $[Cu(TeBu)(\mu\text{-dppa})_3Cu(TeBu)]$ and $[Cu(TeBu)(\mu\text{-}Ph_2P\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}PPh_2)_3Cu(TeBu)]$.[14] Also the one-dimensional diphosphine 2,9-bis(diphenylphosphino)-1,8-naphthyridine (dppn) has been used to prepare the trisilver complex $[Ag_2(\mu\text{-dppn})_3Ag](PF_6)_3$, which was characterised in the solid state and contains two terminal AgP_3 silver centres and an internally coordinated AgN_4 centre.[15] Two further related $[Ag_2L_3]$ complexes $[Ag_2\{3,6\text{-bis(diphenylphosphino)pyridazine}\}_3(NO_3)_2]$ and $[Ag_2\{2,6\text{-bis(diphenylphosphino)pyridine}\}_3(ClO_4)_2]$ were recently reported by Mak and co-workers[16] and have been structurally characterised in the solid state. In solution, no coupling between phosphorus and silver was observed by ^{31}P NMR spectroscopy, indicating Ag–P bond dissociation in solution on the NMR timescale.

Ring-opening polymerisation: The transformation of cage **1c** into polymer **1c′** under the conditions described presumably occurs because of an equilibrium between the solution and crystalline states of the discrete cage **1c** and the slow but irreversible crystallisation of its insoluble polymeric form **1c′**. It seems likely that the insolubility of the polymer would lead to its rapid crystallisation once formed, and, therefore, the rate-determining factor is likely to be the ring-opening polymerisation reaction itself, rather than the crystallisation. Coordination polymers have received a great deal of interest recently,[2] due to their potential for highly complex and novel topologies, as well as their ability to support nanoscale cavities; these now represent an important branch of crystal engineering. Despite this, to our knowledge nothing has been reported of the mechanisms by which coordination polymers might form. This is probably partly because NMR spectroscopy is not normally useful for determining the identity of complex mixtures of species present in solution when nitrogen-donor ligands are used. Polymer **1c′** is therefore notable in that the clear relation of its structure to that of the precursor species observed in solution, that is, cage **1c**, suggests a ring-opening polymerisation mechanism. It would appear that cages **1a – d** do undergo some Ag–P bond dissociation, although it is not sufficiently significant to register in the NMR spectra, which can allow the ring-opening process. Considering the crystal structures of complexes **1a – d**, it seems likely that changing the diphosphine from dppa to the *trans*-ethylene-backboned dppet could destabilise such a cage due to transannular steric repulsion between the hydrogen atoms of the *trans*-CH=CH bridges. This is expected to favour the formation of a ring-opened polymer, and is consistent with the isolation of only the ring-opened polymeric complexes **2a′ · CH_3NO_2** and **2a′** when this ligand was used. Although ring-opening polymerisation is well known in main-group inorganic chemistry,[6a] and it has also been applied to the preparation of some transition-metal-containing polymers, most notably polyferrocenes,[6b] we are unaware of any previous reports of ring-opening of coordination cages leading to coordination polymers.

Conclusion

In contrast to flexible-backboned diphosphines, the rigid bridging ligand dppa does not lead to the selective formation of disilver macrocycles, but it does form triply bridged dinuclear complexes selectively at the appropriate metal-to-ligand ratio, and these complexes do not undergo Ag–P bond dissociation on the NMR timescale. Under crystallisation conditions a competing product is the isostoichiometric coordination polymer $[M_2L_3]_\infty$. The clear structural relationship between the discrete cages and this coordination polymer suggest that dissociation of an Ag–P bond in the cage leads to a ring-opening polymerisation. The formation of this polymer rather than discrete cages appears to be favoured by both prolonged standing, which involves spontaneous recrystallisation, and steric destabilisation of the cage through inter-ligand repulsion, as supported by parallel studies with dppet.

Experimental Section

General considerations: dppa and silver salts were purchased from Aldrich and used as supplied. No particular precautions were taken with regard to solvent purification. NMR spectra were recorded on Bruker AM 300 MHz or AM 500 MHz spectrometers, ^1H spectra were referenced to the protio residue in the solvent, ^{31}P spectra to external 85 % H_3PO_4 (aq) ($\delta = 0$), ^{19}F spectra to $CFCl_3$ ($\delta = 0$).

$[Ag_2(dppa)_3(SbF_6)_2]$ (1a): A solution of dppa (95 mg, 0.24 mmol) in $CHCl_3$ (8 mL) was added to a stirred solution of $AgSbF_6$ (55 mg, 0.16 mmol) in acetonitrile/nitromethane (2 mL). Layering with diethyl ether produced colourless crystals after several days (113 mg, 71 %). Elemental analysis calcd (%) for **1a** · $CHCl_3$: C 47.64, H 3.06; found C 47.75, H 3.06; ^{31}P NMR (121 MHz, $CDCl_3$, 25 °C, 85 % H_3PO_4): $\delta = -18.0$ ($^1J(^{31}P,^{109}Ag) = 360$ Hz); ^1H NMR (300 MHz, [D_3]nitromethane, 25 °C, TMS): $\delta = 7.50$ (m, 36 H; H_{ortho}, H_{para}), 7.27 (t, $^3J(H,H) = 7.6$ Hz, 24 H; H_{meta}).

$[Ag_2(dppa)_3(BF_4)_2]$ (1b): Preparation was similar to that for **1a**, but with $AgBF_4$ (86 mg, 0.44 mmol) in acetonitrile/nitromethane (8 mL) and dppa (263 mg, 0.66 mmol) in $CHCl_3$ (10 mL). Layering with diethyl ether gave colourless prisms (343 mg, 91 %). Elemental analysis calcd (%) for **1b** · 0.5 $CHCl_3$ · CH_3NO_2: C 56.34, H 3.75, N 0.83; found C 56.80, H 3.82, N 0.92; ^{31}P NMR (121 MHz, [D_1]chloroform 25 °C, 85 % H_3PO_4): $\delta = -19.4$ ($^1J(^{31}P,^{109}Ag) = 377$ Hz); ^1H NMR (300 MHz, [D_1]chloroform, 25 °C, TMS): $\delta = 7.54$ (m, 24 H; H_{ortho}), 7.32 (t, $^3J(H,H) = 7.5$ Hz, 12 H; H_{para}), 7.12 (t, $^3J(H,H) = 7.5$ Hz, 24 H; H_{meta}).

$[Ag_2(dppa)_3(O_3SCF_3)_2]$ (1c): Preparation was similar to that for **1a**, but with AgO_3SCF_3 (30 mg, 0.12 mmol) in nitromethane (2 mL) and dppa (70 mg, 0.18 mmol) in $CHCl_3$ (3 mL). Layering with diethyl ether gave colourless prisms (76 mg, 71 %). Elemental analysis calcd (%) for **1c** · $CHCl_3$: C 53.5, H 3.4; found C 53.7, H 3.6 %; ^{31}P NMR (121 MHz, [D_1]chloroform, 25 °C, 85 % H_3PO_4): $\delta = -19.8$ ($^1J(^{31}P,^{109}Ag) = 352$ Hz); ^1H NMR (300 MHz, [D_3]nitromethane/[D_1]chloroform/[D_3]acetonitrile, 25 °C, TMS): $\delta = 7.51$ (d, $^3J(H,H) = 7$ Hz, 24 H; H_{ortho}), 7.32 (t, $^3J(H,H) = 7$ Hz, 12 H; H_{para}), 7.13 (t, $^3J(H,H) = 7$ Hz, 24 H; H_{meta}).

$[Ag_2(dppa)_3(NO_3)_2]$ (1d): Preparation was similar to that for **1a**, but with $AgNO_3$ (78 mg, 0.46 mmol) in nitromethane/acetonitrile (3 mL) and dppa (272 mg, 0.69 mmol) in $CHCl_3$ (3 mL). Layering with diethyl ether gave colourless prisms (363 mg, 99 %). Elemental analysis calcd (%) for **1d** · CH_3NO_2: C 59.85, H 3.98, N 2.65; found C 59.74, H 3.63, N 1.31; ^{31}P NMR (121 MHz, [D_1]chloroform, 25 °C, 85 % H_3PO_4): $\delta = -23.7$, ($^1J(^{31}P,^{109}Ag) = 336$ Hz); ^1H NMR (300 MHz, [D_1]chloroform, 25 °C, TMS): $\delta = 7.5$, (br s, 24 H; H_{ortho}), 7.27 (t, $^3J(H,H) = 7.5$ Hz, 12 H; H_{para}), 7.06 (t, $^3J(H,H) = 7.5$ Hz, 24 H; H_{meta}).

$[Ag(dppa)_2\ Ag(dppa)(O_3SCF_3)_2]_{<M\&>}$ (1c′): A crystalline sample of complex **1c** prepared as above was sealed in its supernatant at ambient temperature for 16 weeks. Fresh crystals were obtained from the meniscus. Elemental analysis calcd (%) for **1c′** $\cdot$ $CH_3NO_2 \cdot CHCl_3$: C 52.4, H 3.4 found C 52.5, H 3.3 %.

$[Ag(dppet)_2\ Ag(dppet)(SbF_6)]_{<M\&>}$ (2a′): Preparation was similar to that for **1a**, but with $AgSbF_6$ (160.8 mg, 0.468 mmol) in nitromethane/acetonitrile (2 mL) and dppet (280 mg, 0.704 mmol) in $CHCl_3$ (6 mL). Layering with diethyl ether produced colourless crystals (358 mg, 81 %). Elemental analysis calcd (%) for **2a′**: C 49.9, H 3.5 found C 49.5, H 3.3.

X-ray crystallography: Data for all complexes were collected on a Bruker AXS SMART diffractometer with $Mo_{K\alpha}$ radiation. The crystals' stability was monitored and there were no significant variations (1%). Cell parameters were determined from 400–600 accurately centred reflections. Data were collected at approximately 120 K in a dinitrogen stream, and Lorentz and polarisation corrections were applied. An empirical absorption correction was applied by using SADABS.[17] The anions in **1a**, **1c** and **1c′** were disordered and were modelled as having two sites. In **1c** examination of the atomic displacement parameters showed the cations to be disordered and these have been modelled as having two sites with 57(1)% for the major position. The structures were solved by direct methods and all non-hydrogen atoms, except those exhibiting disorder, were refined with anisotropic atomic displacement parameters. The atoms of disordered cations and anions were refined isotropically. Hydrogen atom positions were added at idealised positions and a riding model was used for subsequent refinement. The function minimised for $wR2$ was $\Sigma[w(|F_o|^2 - |F_c|^2)]$ with reflection weights $w^{-1} = [\sigma^2|F_o|^2 + (g_1P)^2 + g_2P]$, in which $P = [\max|F_o|^2 + 2|F_c|^2]/3$ for all F^2. The function minimised for $R1$ was $\Sigma[w(|F_o| - |F_c|)]$. The SMART, SAINT and SHELXTL packages[18] were used for data collection, reduction, structure solution and refinement.

Crystal data for 1a: $M = 1900.84$, monoclinic, space group $P21/c$, $a = 21.570(2)$, $b = 34.022(4)$, $c = 43.031(4)$ Å, $\beta = 92.691(2)°$, $V = 31545(6)$ Å^{-3}, $Z = 16$, $F(000) = 15008$, $\rho_{calcd} = 1.601$ g cm^{-3}, $\mu = 1.361$ mm^{-1}, crystal size $0.48 \times 0.44 \times 0.36$ mm, max/min transmision 0.928/0.623. A total of 307 550 reflections were measured for the angle range $1.5 < 2\theta < 25$, and 55 568 independent reflections were used in the refinement for 3593 parameters. The final parameters were $wR2 = 0.3267$ and $R1 = 0.1083$ $[I > 2\sigma(I)]$.

Crystal data for 1c: $M = 1711.98$, orthorhombic, space group $Pccn$, $a = 21.234(3)$, $b = 35.401(4)$, $c = 41.173(5)$ Å, $V = 30949(6)$ Å^{-3}, $Z = 16$, $F(000) = 13860$, $\rho_{calcd} = 1.470$ g cm^{-3}, $\mu = 0.750$ mm^{-1}, crystal size $0.58 \times 0.38 \times 0.26$ mm, max/min transmision 0.927/0.705. A total of 294 493 reflections were measured for the angle range $2 < 2\theta < 50$, and 27 269 independent reflections were used in the refinement for 1576 parameters and 1242 restraints. The final parameters were $wR2 = 0.3369$ and $R1 = 0.1052$ $[I > 2\sigma(I)]$.

Crystal data for 1c′: $M = 1696.96$, triclinic, space group $P\bar{1}$, $a = 11.4687(7)$, $b = 11.8218(8)$, $c = 15.021(1)$ Å, $\alpha = 90.162(1)°$, $\beta = 107.342(1)°$, $\gamma = 109.153(1)°$, $V = 1824.9(2)$ Å^{-3}, $Z = 1$, $F(000) = 858$, $\rho_{calcd} = 1.544$ g cm^{-3}, $\mu = 0.795$ mm^{-1}, crystal size $0.32 \times 0.24 \times 0.12$ mm, max/min transmision 1.000/0.780. A total of 21 340 reflections were measured for the angle range $2.8 < 2\theta < 58$, and 8236 independent reflections were used in the refinement for 575 parameters. The final parameters were $wR2 = 0.1146$ and $R1 = 0.0490$ $[I > 2\sigma(I)]$.

Crystal data for 1d: $M = 1583.88$, monoclinic, space group $P2_1/c$, $a = 17.465(5)$, $b = 22.440(5)$, $c = 18.264(4)$ Å, $\beta = 91.19(2)°$, $V = 7156(3)$ Å^{-3}, $Z = 4$, $F(000) = 3224$, $\rho_{calcd} = 1.470$ g cm^{-3}, $\mu = 0.740$ mm^{-1}, crystal size $0.36 \times 0.28 \times 0.25$ mm, max/min transmision 1.000/0.865. A total of 68 312 reflections were measured for the angle range $2.3 < 2\theta < 58$, and 16 524 independent reflections were used in the refinement for 884 parameters. The final parameters were $wR2 = 0.1314$ and $R1 = 0.0466$ $[I > 2\sigma(I)]$.

Crystal data for 2a′ $\cdot$ CH_3NO_2: $M = 1937.41$, triclinic, space group $P\bar{1}$, $a = 13.498(4)$, $b = 14.399(4)$, $c = 22.399(6)$ Å, $\alpha = 87.071\ (5)°$, $\beta = 89.106\ (5)°$, $\gamma = 62.939\ (4)°$, $V = 3872(2)$ Å^{-3}, $Z = 2$, $F(000) = 1920$, $\rho_{calcd} = 1.662$ g cm^{-3}, $\mu = 1.388$ mm^{-1}, crystal size $0.39 \times 0.20 \times 0.14$, max/min transmision 1.000/0.534. A total of 30 957 reflections were measured for the angle range $1.8 < 2\theta < 50$, and 13 222 independent reflections were used in the refinement for 938 parameters. The final parameters were $wR2 = 0.2061$ and $R1 = 0.0672$ $[I > 2\sigma(I)]$.

Crystal data for 2a′: $M = 1876.36$, triclinic, space group $P\bar{1}$, $a = 11.6025(17)$, $b = 11.7849(17)$, $c = 14.655(2)$ Å, $\alpha = 90.615(3)°$, $\beta = 106.597(3)°$, $\gamma = 106.781(3)°$, $V = 1825.1(5)$ Å^{-3}, $Z = 1$, $F(000) = 928$, $\rho_{calcd} = 1.707$ g cm^{-3}, $\mu = 1.467$ mm^{-1} crystal size $0.26 \times 0.24 \times 0.21$ mm, max/min transmision 0.928/0.646. A total of 20 131 reflections were measured for the angle range $2.9 < 2\theta < 53$, and 7487 independent reflections were used in the refinement for 451 parameters. The final parameters were $wR2 = 0.1773$ and $R1 = 0.0616$ $[I > 2\sigma(I)]$.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-153566, CCDC-153567, CCDC-153568, CCDC-153569, CCDC-153570, CCDC-153571, WAWQEQ. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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